Engineering Thermodynamics - Concepts and Laws
An Informal Presentation

By:

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Preface

"Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time, you know you don’t understand it, but by that time you are so used to it, it doesn’t bother you anymore." Arnold Sommerfeld

The quote often attributed to Arnold Sommerfeld—that thermodynamics is a subject one never truly understands—reflects a historical view of the field. I respectfully disagree with this perspective, if it is extended to the context of engineering applications of thermodynamics. Thermodynamics is a branch of science that has inspired humanity’s intellect since ancient times, following the discovery of fire and its manipulation by subsequent generations. Yet, from the time of Aristotle, as the first biologist, and the work of several other Greek mathematicians, progress had come to an impasse during the rise of scholastic establishments that practiced and developed only religiously sanctioned concepts. However, after the Middle Ages, thanks to breakthroughs during the Renaissance era, a new branch of science was born. Indeed, the mechanics of particle motion were well developed by scientists such as Descartes, Newton, and Leibniz during the 16th to 17th centuries and it was mathematically formalized by Lagrange and Hamilton, becoming an established subject, in the context of Newtonian mechanics, with no major controversies. Nevertheless, the subject of heat and its relation to motion was not yet clear up to the 1840s.

The foundation of thermodynamics was laid in the 18th century, driven by engineers inspired by the spirit of the Industrial Revolution—itself part of a smooth transition from the Middle Ages to the Renaissance. Humanity had started to question natural phenomena and seek explanations for them. The theory of heat and how it could be used to build prime movers was formulated within a scientific framework during the 19th century, thanks to the contributions of several scientists (to be mentioned later). The initial motivation was intellectual inquiry: understanding the behavior of substances such as gases, and their relationship to work and heat. The Industrial Revolution provided the second major incentive, as steel consumption surged. The use of steel in railroads, bridges, and machinery required more coal to be extracted from mines, where underground water beds posed a serious obstacle. Engines were needed to drain water from coal mines. Thus, the material necessity of understanding nature was actively present, providing a genuine economic motivation.

The most notable scientist to mention in this short preface is Francis Bacon—a philosopher who insisted on a rigorous methodology, which he called the scientific method. He explained that research should follow certain conditions to prevent misconceptions and false conclusions arising from personal taste or a priori beliefs of the researcher. Important figures in natural science and engineering to mention include Boyle, Gay-Lussac, Avogadro, Savery, Newcomen, Watt, Mayer, Joule, Carnot, Kelvin, Clausius, and Boltzmann. Their contributions will be discussed in the text where appropriate.

In the first half of the 20th century, the literature on thermodynamics was in disarray, with no standard presentation of the subject. The need for a textbook to teach this new scientific discipline had already been felt in the late 19th century. Maxwell and Planck wrote their books by integrating the results of previous researchers during the transition from the 19th to the 20th century. After World War I, Fermi wrote his textbook, and after World War II, Sommerfeld wrote his. In the 1960s, Keenan and Hatsopoulos at MIT presented the laws of thermodynamics within the framework of Carathéodory's definition of heat. Carathéodory had formulated the laws of thermodynamics in a novel way to avoid defining heat as the foundation of the second law. Although Carathéodory's axiomatic formulation is mathematically elegant, these notes adopt the more conventional approach based on heat engines and Kelvin-Causius statements because it tends to develop physical intuition more directly. The conventional method of Kelvin and Clausius from the 1840s and 1850s, was plausibly inspired by Carnot's thought experiments in the 1820s and focuses on the characteristics of heat engines.

The pedagogical approach to teaching thermodynamics after World War II has progressed profoundly, thanks to the excellent textbooks published since the 1960s, making the subject far more accessible to undergraduate engineering students. Today, these books are cited as primary reference textbooks. To name just a few among many, we can introduce the textbooks by Zemansky and Dittman (who were physicists) and by Van Wylen and co-authors (who came from a mechanical engineering department). Zemansky had written his textbook in 1937, which was later completed and updated by Dittman.

This note is not intended as a companion to such established textbooks. It is not a substitute. You will find few worked examples, exercises, or detailed figures here; for those, the reader is directed to the primary textbooks. The first author's teaching experience has shown that students often consider thermodynamics undergraduate course as a frustrating puzzle game of manipulating steam tables which not only cast shadows on the concepts, but gives a feeling that the concepts are far from being understood by students at their undergraduate level.

It is our hope that these notes will provide the conceptual depth that inspires a more profound and intuitive engagement with thermodynamics. We have intentionally omitted the presentation of phase change. However, after studying this note, readers who are student should turn to read established textbooks to fully understand and solve practical engineering problems, such as analyzing power plants and refrigeration systems.

In this note, efforts have been made to present the concepts of thermodynamics in a logically consistent manner, ensuring that no circularity occurs in the reasoning.

The authors are aware that the presentation of thermodynamics in this note does not follow an orthodox method, and some parts may appear dense or irrelevant at first glance. Nevertheless, this is the nature of an informal presentation. Indeed, this is offered with no claim to perfection or completeness.

The structure of these notes is as follows:

The first chapter presents the fundamental concepts. This chapter should not be dismissed as mere review or philosophical preamble; it constitutes the essential foundation of thermodynamics. I urge you to pause and reflect on each concept and definition, critically engaging with the material and even considering alternative formulations.

Chapter 1 establishes a critical foundation for subsequent material by rigorously defining the thermodynamics system and detailing the treatment of its properties under equilibrium conditions.

Building upon this foundation, Chapters 2 and 3 provide a detailed elaboration of the concepts of work and heat, the two fundamental modes of energy transfer.

The core laws of thermodynamics are introduced beginning in Chapter 4. This chapter covers the Zeroth Law and the principle of thermometry. In Chapter 5, based on the First law of thermodynamics, a new system property—internal energy—is derived, utilizing concepts established in the preceding chapters. Moreover, another form of energy—enthalpy—arises when applying the first law of thermodynamics to open systems. Consequently, a separate section is devoted to this topic.

Chapter 6 explains the pivotal distinction between reversible and irreversible processes. This sets the stage to introduce the Second Law of Thermodynamics explained in chapters 6 to 8.

Chapter 9 reflects the authors' personal understanding of entropy. It should be read with caution, as its contents may be controversial.

Exergy—defined as the available work or the available energy to do work with respect to a dead state—is intentionally not covered in this note. First of all, Exergy is not itself a fundamental law; rather, it is a derived concept from the first and second laws. Second, applying the exergy concept requires an understanding of optimization in energy systems under specific constraints such as cost, sustainability, and other factors. Consequently, a dedicated field known as exergoeconomics formally studies the application of exergy.

This note focuses on the basic concepts and laws of thermodynamics, with applications primarily in the domains of engineering majors such as mechanical and chemical engineering.

Finally, to ensure a clear and paced presentation, key historical developments that contributed to the unified understanding of thermodynamic laws are included in the appendices. A thorough review of this supplementary material is highly recommended for a deeper and more complete mastery of the subject.

Note that each chapter builds upon the preceding material and readers with moderate exposition to Thermodynamics are encouraged to revisit earlier chapters whenever difficulties arise.

Formal references have been intentionally omitted, as this document is not a formal textbook.

Finally, the reader may find the tone of the manuscript rather philosophical, yet its purpose is to insist on the logical arguments required to explain or prove the concepts. Logic, of course, is a branch of philosophy. Moreover, the style of the manuscript resembles that of an oral lecture. This is, of course, a deliberate choice by the authors.

The authors acknowledge that this note may contain inaccuracies or address controversial issues, and welcome feedback and error notifications.

Tehran, Iran

July 2026

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Chapter 1: Introduction

Wisdom can be learned by three methods. Reflection, the noblest, Imitation, the easiest, and Experience, the bitterest.

Confucius

Based on the first author's experience there is a misunderstanding regarding the domain and strength of validity of statements accepted and established in science. Hence, it is important to clarify, for example, what is a theory and a law and how they are formulated. Another important point is that thermodynamics is a branch of empirical science; the reader or learner should not consider it similar to analytic logic and mathematics, where, upon well accepted axioms, several theorems can be proved rigorously and universally accepted. Therefore, we should not, even unintentionally, look for a mathematical proof of "laws" derived from a step-by-step logical path. We have to realize that natural sciences are grounded in experiment, while mathematics rests on clear, self-evident axioms that yield formal, rigorous proofs. In what follows, certain important scientific terms are explained; these would be useful for understanding the principles and foundations of Thermodynamics.

a) Hierarchy of Scientific Knowledge:

According to Kant, one of the most distinguished philosopher of the 18th century, some of our knowledge such as the concepts of time and space are innate and are not inferred from experiment. Psychologists today believe that even infants have numerical sensitivity and understand that objects around them can be single or numerous.

Science, in the broadest sense, refers to any systematic knowledge or practice. Fields of science are commonly classified along two major lines:

Natural sciences which study natural phenomena including biological life and social sciences which study human behavior and societies. They are both called empirical science which emphasizes that the knowledge must be based on observable phenomena and capable of being experimented for its validity by other researchers working under the same conditions.

In contrast, mathematics is classified as formal science, which uses a priori axioms that are intuitively evident rather than empirical methods. The formal sciences also include statistics and logic.

Hypothesis: A tentative, testable explanation for an observed phenomenon. It is an initial proposal that requires validation through experimentation and is not yet supported by significant evidence.

Postulate (or Axiom): A fundamental statement that is accepted as true and evident without proof within a specific theory. Postulates form the foundational assumptions upon which a theory is built (e.g., the postulates of kinetic theory of ideal gas or axioms of Euclidean geometry). They are justified by the fact that theories based on them yield predictions that agree with experiment (see appendix A for examples).

Theory: A comprehensive, well-substantiated explanation of some aspect of the natural world that is acquired through the scientific method, based on first principles, and repeatedly tested and confirmed through observation and experimentation. A good theory is predictive and falsifiable—it makes specific claims that could be proven wrong by empirical evidence. Theories are the highest form of scientific knowledge. Yet, many philosophers of science would argue that laws and theories are different kinds of knowledge, not hierarchical. A theory explains why; a law describes what.

Law: A concise, verbal or mathematical statement that describes a consistent and universal relationship between observable phenomena under a prescribed set of conditions (e.g., Newton's Laws of Motion, the Ideal Gas Law). Laws are typically inductive, based on a vast body of empirical evidence, and are considered to be true within their domain of validity. Like theories, they are falsifiable.

See appendix A for the principle of falsification.

Induction: How do we get from empirical observations to scientific theories?

According to empiricists, all of our information comes from observation. Inductivism is based on observation—this is the foundation-stone of inductive approaches. According to what we might call "naïve inductivism," science starts with observation, this observation provides a secure base on which scientific knowledge is supported, and scientific knowledge is derived from observation using induction (inductive inferences). Rationalists, on the other hand, are not inclined to observation—some knowledge (about the world) can come from pure reason alone. In contrast, according to empiricists, our knowledge is justified by our experience (observation, data, experiment). The objectivity and rationality of science is taken to rest on the role experience plays in choosing between hypotheses and in justifying those hypotheses. Empirical observations in the context of science, are explained by hypotheses of a general kind. These hypotheses apply to all of a class of events or phenomena, only a sample of which have or will ever be observed.

See appendix B for more discussion.

b) Concepts and definitions

Definitions:

System: A finite, identifiable quantity of matter (a closed system) or a specific region in space (an open system or control volume) upon which attention is focused for thermodynamic analysis.

System Boundary: The real or imaginary surface that separates the system from its surroundings (everything external to the system). The boundary may be fixed or movable, and it may be rigid or flexible. By definition, the boundary has zero thickness and thus contains no mass.

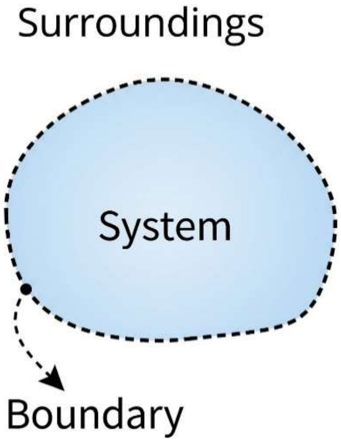


Figure 1-1: The schematic presentation of a thermodynamic system.

Types of Systems:

Systems are classified based on the interactions of mass and energy across their boundaries:

Closed System (Control Mass): A system of fixed mass where no mass can cross its boundary. Nevertheless, energy (in the form of heat or work) can cross the boundary.

Open System (Control Volume): A system where both mass and energy can cross its boundary.

Adiabatic System: A system whose boundary is impermeable to heat transfer. An adiabatic system can be either open or closed. The defining characteristic is that no heat is transferred, regardless of mass transfer.

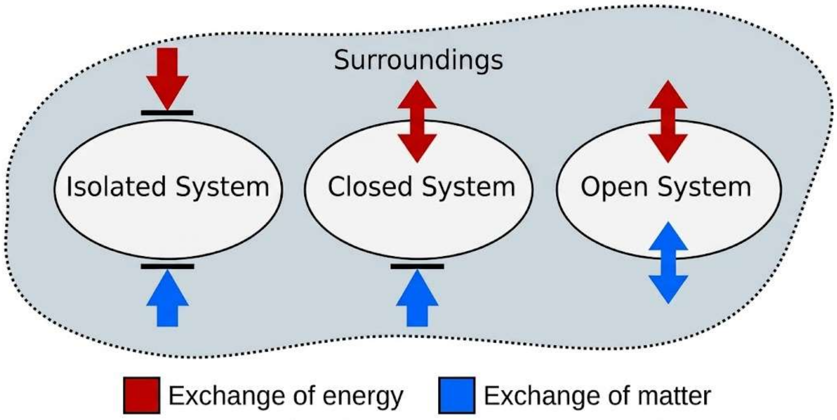


Figure 1-2: Conceptual presentation of different thermodynamic systems.

c) Fundamental Concepts:

Work: We are well familiar from high school physics about the work defined in mechanics. So, we consider it as a fundamental concept. In thermodynamics, work is an interaction between a system and its surroundings whereby energy is transferred by means of a force acting through a displacement. For a simple mechanical case, this is calculated as $W = \int F \cdot ds$. In Figure 1-3, a gas is compressed within a piston-cylinder device. The system is defined as the gas inside the cylinder. This is a closed system, as no mass is transferred across the system boundary during compression. However, the system can exchange heat and work with its surroundings. The work done on the gas is proportional to the applied force and the resulting decrease in volume, which is itself proportional to the piston's displacement.

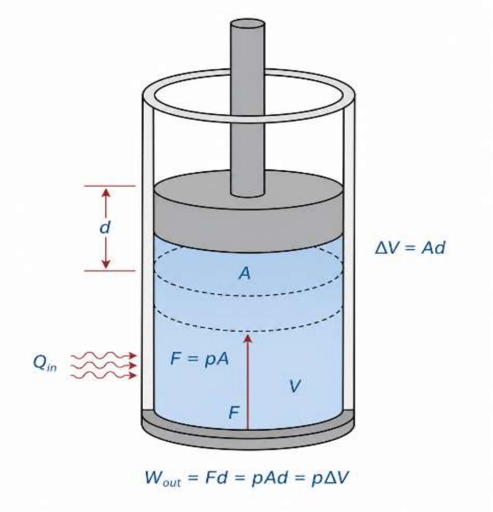


Figure 1-3: A closed system under compression.

Power is the time rate of doing work. Power as $P = \frac{\delta W}{dt}$ and is measured in Watts (J/s). A large amount of work done over a long-time interval can result in the same average power as a small amount of work done over a proportionally shorter time interval.

d) System State and Properties

A thermodynamic system possesses a unique condition at a given instant, called its state. The state is the complete description of the system's condition, defined by the values of all its macroscopic, measurable characteristics, known as properties.

A thermodynamic property is any measurable or calculable characteristic that defines the state of a system. The values of these properties depend only on the current state, not on the system's history. However, the definition may seem abstract because it is a general definition of any conceivable property. To be more concrete pressure and temperature are measurable properties of but the device does not care about the past events that the systems (gas or liquid) have undergone.

Most properties, like pressure (with a manometer), temperature (with a thermometer), and volume (with a ruler), are directly measurable. However, some fundamental properties, most notably entropy, are not directly measured in a simple instrument. Instead, they are calculated from other measurable properties.

Remark: Mass is a property of a system, but it is not considered a thermodynamics state property. Thermodynamic properties are quantities whose values change when the thermodynamic state changes. In a closed system, the mass remains constant during any change of state, so it does not help distinguish one thermodynamic state from another.

Properties are classified into two fundamental categories:

Intensive Properties: These are properties that are independent of the mass (or extent) of the system. They are local in nature and can vary from point to point within a system until equilibrium is reached. Examples: Pressure (P), Temperature (T), Density (ρ), Specific Volume (v).

Extensive Properties: These are properties whose values depend on the size or extent of the system. They are additive in nature; the value for the whole system is the sum of the values for its parts. Examples: Total Volume (V), Mass (m), Internal Energy (U), Enthalpy (H), Entropy (S).

Any extensive property can be made intensive by expressing it per unit mass. These are called specific properties (e.g., specific volume $v = \frac{V}{m}$, specific internal energy $u = \frac{U}{m}$).

Intensive properties are usually denoted with lowercase letters, while extensive properties are shown with capital letters.

The State Postulate: A fundamental principle of thermodynamics, the state postulate (as formalized by Gibbs), establishes that the state of a simple, compressible system (simple means we ignore surface, magnetic, and electrical effects) is completely specified by at least two independent, intensive properties. Recall the ideal gas law from introductory physics course. The term "ideal" (historically sometimes called "perfect" for gases that could not be liquified by the pre 20th century technology and were considered to be only in a gaseous phase) refers to a theoretical model that accurately describes the behavior of real gases under conditions of low pressure and high temperature. This model is particularly effective for gases like hydrogen and oxygen at ambient conditions, which liquefy at very low temperatures. The foundation of this model rests on experimental observations from the 17th to 19th centuries. Therefore, according to the ideal gas relation ($PV = n\overline{R}T$), if two independent properties among pressure (P), volume (V), and temperature (T) are specified, the third property is uniquely determined for n moles of a gas. $\overline{R}$ is the universal gas constant. These observations and the mathematical relation are consistent with the state postulate.

Remark: A "simple, compressible substance" is one where the only significant energy modes are translational, rotational, vibrational and intermolecular forces (e.g., not magnetic or electrical). This postulate implies that all other intensive properties—such as internal energy (u), enthalpy (h), and entropy (s)—are functions of the two chosen independent properties.

See appendix C for the microscopic derivation of ideal gas law and appendix D for macroscopic derivation.

We can visualize the state of a substance as a point on a multi-dimensional surface. For example, if we imagine a property Z (which could be internal energy, enthalpy, entropy, properties to be explained later), it can be described as a function of two independent variables, X and Y (which could be pressure and temperature, or any other pair of independent properties):

$$Z = f(X, Y) \tag{1-1}$$

This is why we use two-property diagrams (like P-v, T-v, or P-T diagrams) in thermodynamics. Fixing any two properties determines not only the state but also the values of all other unknown properties for that state.

Thermodynamics Equilibrium: In classical thermodynamics, the study of systems is primarily confined to those in a state of equilibrium. A closed system (control mass) is in thermodynamic equilibrium when its intensive properties—such as pressure and temperature, —are uniform throughout the entire system and do not change over time.

This uniformity is a necessary condition. For instance, if a pressure difference existed within a closed system, one could conceptually insert a device to exploit this gradient and extract work. A defining characteristic of a closed system in equilibrium is that it cannot spontaneously produce work or facilitate a net transfer of heat within itself; all such driving forces are balanced.

The state a simple compressible substance is defined by two independent intensive properties. Therefore, if pressure and temperature are uniform and constant (implying equilibrium), all other properties such as internal energy or entropy are fixed values.

Remark:

1. For a control volume (open system) especially during unsteady variations in system properties, mass accumulation or depletion occurs. This does not invalidate the state postulate. It means the state postulate applies to the material inside the control volume at a given instant at a small region (called local uniformity and equilibrium stability) where the properties can be considered uniform within it. However, mass accumulation influences the energy balance (via momentum and energy transfer)-another property of the system- which influences the distribution of pressure and temperature.
2. Near melting (e.g., ice near 0°C), a solid behaves more like a compressible substance. There, the pressure-volume-temperature relationships are behaved in a manner that the state postulate can apply approximately. But, the elastic behavior, latent heat, and phase interface effects make it more complex than gases or liquids.
3. The state postulate holds exactly for compressible fluids — gases, vapors, and liquids — because pressure, temperature, and volume are strongly interrelated. But solids, being nearly incompressible and structurally complex, do not follow the same rules. We often need more than two properties to fully define their state — especially if stress or strain plays a role.

A process: A thermodynamic process is defined as a change in the state of a system from an initial equilibrium state to a final equilibrium state. Crucially, while the system must be in a state of thermodynamic equilibrium at both the start and end points, it is not necessarily in equilibrium during the process itself.

Quasi-equilibrium (or quasi-static) process: It is an idealized, infinitely slow process in which the system undergoes a continuous sequence of infinitesimal changes. At every instant during this process, the system deviates only negligibly from an internal state of thermodynamic equilibrium. In other word, the process is indeed a sequence of equilibrium states.

Because the system's properties (like pressure and temperature) are uniform and well-defined at every point along the way, a quasi-equilibrium process can be represented as a continuous path on a thermodynamic diagram (e.g., P-v, or P-T) as depicted in Figure 1-4.

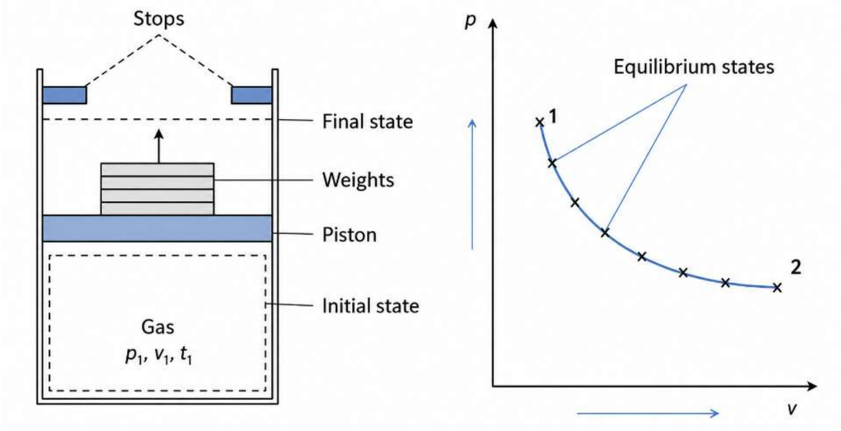


Figure 1-4: The slow expansion of a gas by removing small weights and its path in P-v coordinates.

In contrast, for a non-equilibrium process (e.g., a rapid compression or expansion), the system's properties are not uniform internally. Consequently, the intermediate states do not have unique, well-defined values for the system as a whole, and the process cannot be depicted as a meaningful path on such a diagram.

Although an arbitrary process can be conceptually represented on a diagram (e.g., as a zigzag path), real-world processes are often not only in strict quasi-equilibrium but arbitrary curved or zigzag processes cannot be envisaged practically. Nevertheless, they can be effectively modeled using a single or several idealized processes defined by specific relationships between intensive properties.

For the special case of an ideal gas, which is governed by a well-defined equation of state, several standard processes are employed for this purpose. These include isothermal (constant temperature), isochoric (constant volume), isobaric (constant pressure), and adiabatic (no heat transfer) processes. A more general and widely used approximation is the polytropic process, defined by the relation PV^n=constant (see figure 1-5).

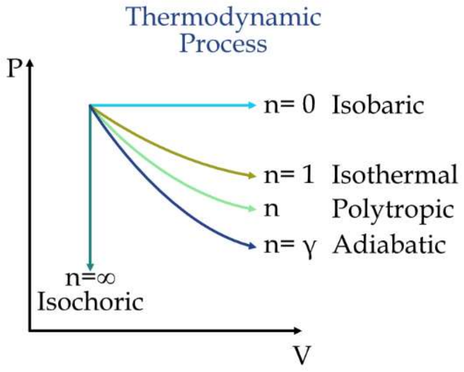


Figure 1-5: The path and slope of different processes of an ideal gas.

Thermodynamic cycle: A thermodynamic cycle is defined as a series of processes through which a system undergoes changes and ultimately returns to its initial state. Because the system's final state is identical to its initial state, the net change in any and all of its properties—both intensive and extensive—is zero for the entire cycle. It is important to note that this definition considers only the state of the system itself; changes in the state of the surroundings are explicitly excluded. This principle is essential for analyzing cyclic devices such as heat engines and refrigerators.

Chapter 2: Work in Thermodynamic Systems

Having established the definitions of a thermodynamic process and equilibrium, we can now analyze mechanical energy transfer via work. In mechanics, work is defined as a force acting through a distance. This definition extends directly to thermodynamics, where it is often applied to the boundary of a system (see Figure).

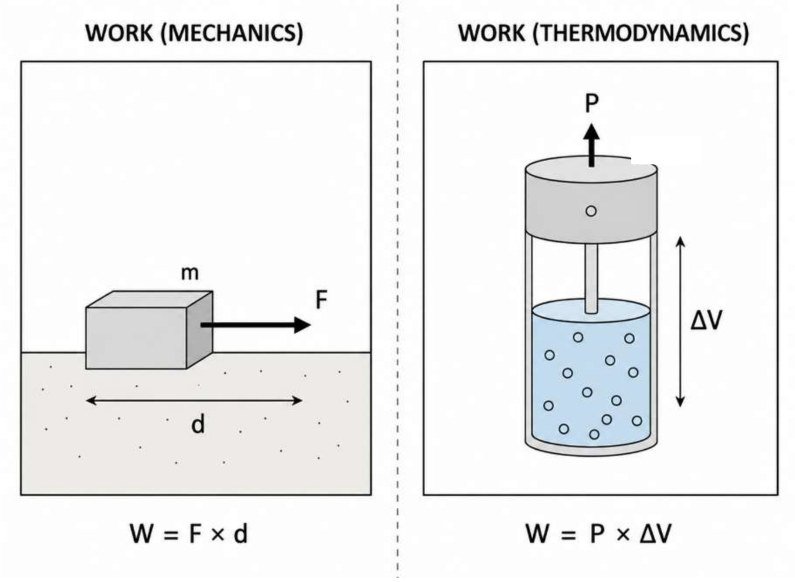


Figure 2.1 Comparison of work in solid mechanics and thermodynamics.

By convention, in thermodynamics (see figure 2-2):

Work done by the system (e.g., an expanding gas pushing a piston) is positive.

Work done on the system (e.g., a piston compressing a gas) is negative.

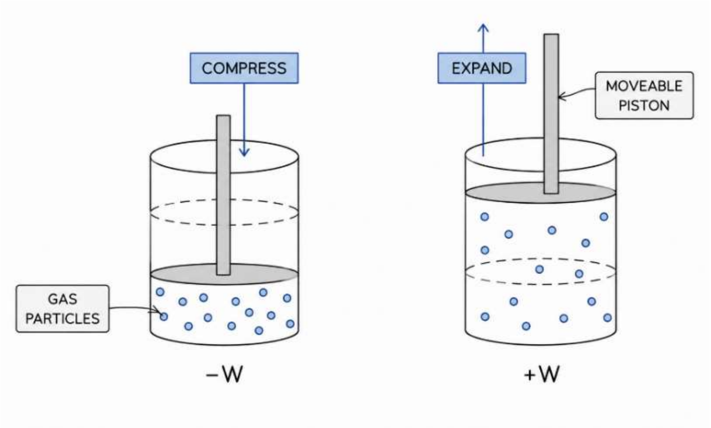


Figure 2-2: Sign convention of work.

For a closed system assumed simple compressible, the most common work mode is boundary work, or PdV work, associated with the expansion or compression of a fluid as derived in the following section.

2.1 Work Calculation in a Piston-Cylinder Device

The piston-cylinder arrangement is a classic example for calculating boundary work. The force exerted by the gas is due to its pressure acting on the piston face ($F = P \cdot A$). If the piston moves a differential distance dx, the differential work done is:

$$\delta W = F \cdot dx = (PA) \cdot dx \tag{2-1}$$

Noting that the change in volume is $dV = A\,dx$, the equation becomes:

$$\delta W = PdV \tag{2-2}$$

Therefore, the total work transfer during a process from state 1 to state 2 is the integral of this expression:

$$W = \int_1^2 \delta W = \int_1^2 PdV \tag{2-3}$$

This integral's value depends on the path of the process, defined by the relationship between pressure and volume $\left(P = f(V)\right)$. The area under the process path on a P-V diagram (Figure 2-3) represents the magnitude of the work transfer.

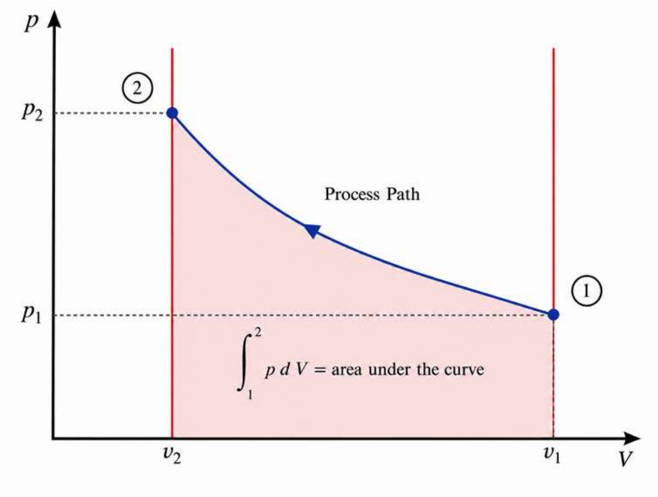


Figure 2-1: The path of process and the work calculated by integration.

2.2 Work for Different Idealized Processes

a) Isobaric Process (Constant Pressure, $\Delta P = 0$)

Since pressure is constant, it can be taken out of the integral.

$$W = \int_1^2 PdV = P\int_1^2 dV = P(V_2 - V_1) \tag{2-4}$$

Example: Heating a gas in a cylinder with a free-floating piston held down by a constant weight.

a) Isochoric Process (Constant Volume, $dV = 0$)

There is no change in volume, so the piston does not move.

$$W = \int_1^2 PdV = 0 \tag{2-5}$$

Example: Heating a gas in a sealed, rigid container (no boundary work is done).

b) Isothermal Process (Constant Temperature, ΔT = 0)

For an ideal gas, the equation of state ($PV = mRT$) implies that $P = \frac{mRT}{V}$. Since T is constant, the work integral becomes:

$$W = \int_1^2 PdV = \int_1^2 \frac{mRT}{V}dV = mRT\int_1^2 \frac{1}{V}dV = \mathrm{mRT}\ln\left(\frac{V_2}{V_1}\right) \tag{2-6}$$

Example: A slow expansion/compression that allows heat transfer to maintain a constant temperature.

c) Adiabatic Process (No Heat Transfer, $Q = 0$)

For a quasi-equilibrium adiabatic process involving an ideal gas, the relationship $PV^\kappa = constant$ holds, where $\kappa = \frac{c_p}{c_v}$ (the specific heat ratio). The relation will be developed in chapter 7. The work is calculated from the integral:

$$W = \int_1^2 PdV = \int_1^2 constant\ V^{-\kappa}\, dV \tag{2-7}$$

Solving this integral gives:

$$W = \frac{P_2V_2 - P_1V_1}{1-\kappa} \tag{2-8}$$

d) Polytropic Process (A General Case)

A polytropic process follows the relationship $PV^{\mathrm{n}} = constant$, where n is the polytropic index. The work calculation is identical in form to the adiabatic case:

$$W = \int_1^2 PdV = \int_1^2 constant\ V^{-n}\, dV = \frac{P_2V_2 - P_1V_1}{1-n} \quad (for\ n \neq 1) \tag{2-9}$$

To demonstrate that work is path-dependent, consider air as an ideal gas with mass of $1\, kg$ and gas constant R=0.287.

The initial state (State 1) is defined as $\mathrm{P_1} = 100\mathrm{kPa},\ \mathrm{V_1} = 1\,\mathrm{m}^3$, and temperature is calculated as:

$$T1 = \frac{P_1V_1}{mR} = \frac{100 \times 1}{1 \times 0.287} \approx 348.43\, K$$

(State 2) is defined as $\mathrm{P_2} = 200\,\mathrm{kPa},\ \mathrm{V_2} = 0.5\,\mathrm{m}^3$, and temperature is:

$$T2 = \frac{P_2V_2}{mR} = \frac{200 \times 0.5}{1 \times 0.287} \approx 348.43\, K$$

Thus, state 1 and state 2 have the same temperature but different pressure and volume.

Now consider two different paths between state 1 to state 2:

Path 1: Isothermal Process

Since temperature is constant, the work done for an ideal gas is given by:

$$W_{1-2} = \mathrm{mRT} \ln\left(\frac{V_2}{V_1}\right)$$

Using $mRT = P_1V_1 = 100\, kJ\ (approximately)$ and $\frac{V_2}{V_1} = 0.5$:

$$W_{1-2} = 100 \times \ln(0.5) \approx 100 \times (-0.693147) = -69.3147\, kJ$$

This represents work done on the gas during compression.

Path 2: Isobaric Process Followed by Isochoric Process

Isobaric process (constant pressure P_1) from State 1 to an intermediate state with volume $V_{int} = V_2 = 0.5\, m^3$.

The intermediate state has $\mathrm{P_{int}} = \mathrm{P_1} = 100\,\mathrm{kPa}$, $\mathrm{V_{int}} = 0.5\,\mathrm{m}^3$, and temperature is:

$$\mathrm{T_{int}} = \frac{\mathrm{P_{int}V_{int}}}{\mathrm{mR}} = \frac{100 \times 0.5}{1 \times 0.287} \approx 174.22$$

Work done in the isobaric process:

$$W'_{1-2a} = P_1(V_{int} - V_1) = 100 \times (0.5 - 1) = 100 \times (-0.5) = -50\,kJ$$

Isochoric process (constant volume) from the intermediate state to State 2. Since volume is constant, no work is done:

$$W'_{1-2b} = 0$$

Total work for Path 2:

$$W'_{1-2} = W'_{1-2a} + W'_{1-2b} = -50\,kJ$$

Since $W_{1-2} \neq W'_{1-2}$, this shows that the work performed depends on the path taken, even though the initial and final states are the same in terms of thermodynamic properties (pressure, volume, and temperature are fixed for State 1 and State 2). This path dependence is a key characteristic of work in thermodynamics depicted in Figure 2-4.

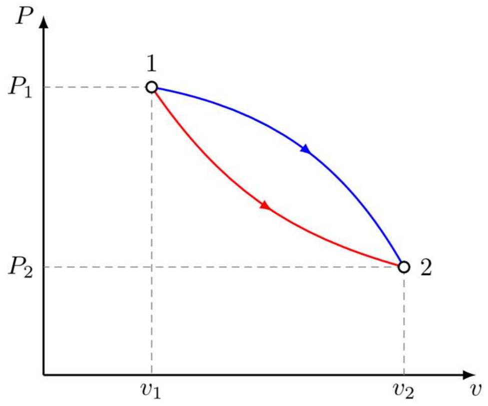


Figure 2-2: The work done in path dependent as the area under the curves of two different paths are not equal.

A useful analogy is traveling between two cities:

The cities are like states (State 1: (P_1, V_1, T_1), State 2: (P_2, V_2, T_2)).

The path we take (a direct flight, a scenic route, a mountain trail) is the process. The amount of gasoline we use or the money we spend on the trip is like work (W) or heat (Q). It depends entirely on the path we choose.

We have already calculated that the work done depends on the path taken between the same two states. Since heat is also a form of energy transfer (to be proved later in chapter 4), it is logical to conclude that it, too, must be path-dependent.

2.3 The Case of Free Expansion

Free expansion is a classic example that perfectly illustrates a non-quasi-equilibrium process where the standard work calculation ($W = \int P\, dV$) fails, and yet we can easily determine that no work is done.

An ideal gas is confined by a partition in one half of a rigid, insulated container. The other half is a vacuum (see Figure 2-5). The partition is ruptured. The gas rapidly and uncontrollably expands to fill the entire container.

No Work is Done ($W = 0$): The expansion is against a vacuum $P_{ext} = 0$. Since there is no opposing pressure, the gas does not push against any force to expand. The container is rigid, so no boundary is moved.

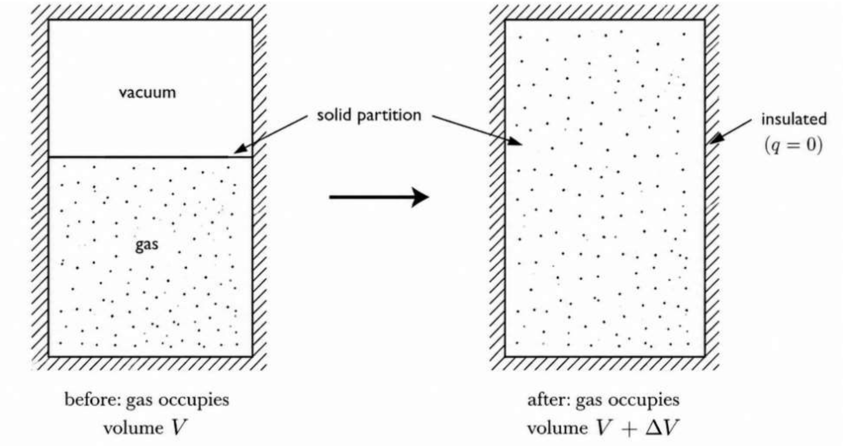


Figure 2-3: Free expansion of a gas where no work is done by the gas

Therefore, the gas does not exert a force through a distance to transfer energy to its surroundings. No work interaction occurs.

Why it's Non-Quasi-Equilibrium: The process is extremely rapid and violent. The gas is not in a well-defined state of pressure and volume during the expansion. The pressure is non-uniform and impossible to measure. Therefore, the integral $\int P\, dV$ is meaningless for the system during the process, as P is not defined and unique value all over the gas.

2.4 Calculating Work for Non-Quasi-Equilibrium Processes

When a process is so fast that the system's properties are not uniform (non-quasi-equilibrium), we cannot use the system's pressure to calculate work ($W = \int P_{system}\, dV$ is invalid).

However, we can always calculate work by examining the surroundings.

Work is mechanical energy transferred across the system boundary. The work done by the system on the surroundings must be equal to the work done on the surroundings by the system (with a sign change).

If we cannot define the state of the system during the process, we can often define the state of the surroundings very well using the following method:

$$W = \int F_{surr} \cdot dx \tag{2-10}$$

or, for a simple piston,

$$W = \int P_{ext} dV \tag{2-11}$$

where P_{ext} is the external pressure that the surroundings exert on the system (e.g., atmospheric pressure plus any pressure from a weight on the piston).

2.5 Rapid Expansion Against Constant Pressure

Imagine a gas in a cylinder with a piston held down by a constant weight (representing a constant external pressure, P_{ext}). The piston is released and the gas expands rapidly (non-quasi-equilibrium) to a new volume.

We cannot use $W = \int P_{gas}\, dV$ because p_{gas} is not uniform or definable during the rapid expansion. We can use $W = \int P_{ext}\, dV$. Since P_{ext} is constant (fixed by the weight and atmosphere), the work done by the system is simply:

$$W = P_{ext} \Delta V \tag{2-12}$$

This is the work done by the system on the surroundings (the weight and atmosphere) as it lifts them.

This approach reinforces a key insight in thermodynamics. For energy accounting, if the state of the system is ambiguous, we can often find a definitive answer by carefully defining and analyzing the surroundings.

An interlude is now required (see the next chapter) to acknowledge heat as a path-dependent mechanism of energy transfer, a concept that will be formally defined subsequently. Heat Q and work W are not properties of a system, but they are as energy in transit between a system and its surroundings. They describe processes or actions, not the state of the system.

Problem Setup

- Piston mass = m, area = A, vertical orientation.
- No friction, no atmospheric pressure, no extra weight – the only resisting force is gravity on the piston.
- Gas expands, pushing piston upward from x_1 to x_2.
- **Given:** Piston velocity $v = 0$ at x_1 and again at x_2.

From Newton's second law (instantaneous) we write:

Forces on the piston (upward positive):

$$P_{\text{gas}}(t) \cdot A - mg = m\frac{dv}{dt} \tag{2-13}$$

From the Work-energy theorem from x_1 to x_2, multiply both sides by $dx = v\,dt$ and integrate:

$$\int_{x_1}^{x_2} P_{\text{gas}}\, A\, dx - \int_{x_1}^{x_2} mg\, dx = \int_{x_1}^{x_2} m\frac{dv}{dt}\, dx \tag{2-14}$$

The leftmost term is the work done by the gas, W_{gas}.

The second term is $-mg(x_2 - x_1) = -mg\Delta x$.

The right side:

$$\int m\frac{dv}{dt}dx = \int mv\, dv = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2 \tag{2-15}$$

Applying the at rest conditions:

Given $v_1 = 0$ and $v_2 = 0$, the right side is zero. Therefore:

$$W_{\text{gas}} - mg\Delta x = 0 \rightarrow W_{\text{gas}} = mg\Delta x \tag{2-16}$$

Physical interpretation

- $mg\Delta x$ is exactly the increase in gravitational potential energy of the piston.
- Because the piston started and ended at rest, no net work was done to change its kinetic energy. All the work done by the gas went into raising the piston against gravity.

Remark: In a typical thermodynamics "piston-cylinder" problem with a quasi-equilibrium process, we assume the piston moves so slowly that its kinetic energy is negligible at every instant, and it is at rest initially and finally. Under that assumption:

$$W_{\text{gas}} = \int P_{\text{gas}} dV = \int (mg/A)\,(A\,dx) = mg\Delta x$$

The gas pressure is just enough to balance the piston's weight (plus any other external forces) at all times.

Chapter 3: The Concept of Heat and Heat Capacity

3.1 Historical Context

Prior to the 19th century, heat was misunderstood and thought to be an invisible, weightless fluid called Caloric. This theory proposed that objects contained caloric fluid, and temperature change was caused by its flow from a hotter substance to a colder one. It is interesting that Fourier's conduction theory for solids is based on the flow of free electrons in metal. However, there is no accumulation of electrons in the metal and they merely transfer heat from the hot end to the cold end. Thus, it is conceptually different from the caloric theory.

Benjamin Thomson (Count Rumford) in 1805 performed several experiments in which heat is produced by friction. In his text-book of 1829, Biot associated the heat liberated in Rumford's experiment with the separation of the surface particles of the metal. This calorie, he said, must have been present between the particles of bronze which were separated in the boring process.

According to both the critics and the advocates of the theory, if caloric were material, then it ought to have mass and weight. The absence of weigh of caloric was an important problem for the caloric theory. It was not proven by any experiment that the weight of bodies in increased by heating.

It should be mentioned that caloric was distinguished from heat in the sense that the latter was the observable effect of the transportation of caloric from a hot body to a cold one.

In 1799 Davy showed that ice melts by friction without the using of a heating agent. In 1840s Mayer announced that he had raised the temperature of water from 12 to 13 degrees Celsius by agitating it. Mayer rejected the supposition of the Calorists' that the production of frictional heat is caused by the decrease in volume, because water may be heated by shaking whereupon its volume increases.

The modern understanding of heat as a form of energy transfer can be developed through a simple thought experiment.

Imagine placing 1 kg of water in a closed system over a stove heated by burning charcoal. We allow the system to reach a steady state, meaning the water temperature stabilizes and no longer changes with time. At this point, the rate of heat input from the burning charcoal equals the rate of heat loss to the surroundings. Now, we increase the fire by adding more charcoal. The system eventually reaches a new, higher steady-state temperature. We repeat this process, each time adding more fuel and recording the new equilibrium temperature.

If we plot the total amount of charcoal burned (representing the total energy input) against the resulting steady-state water temperature, we would observe an approximately linear relationship (see figure 3-1).

3.2 Defining Heat Capacity

The slope of this line, which is the ratio of the change in charcoal amount (Δ[charcoal]) to the change in temperature (ΔT), is a constant for the water. Let's call this constant **C**.

$$C = \frac{\Delta[Charcoal]}{\Delta T} \tag{3-1}$$

In essence, (c) represents the amount of charcoal (and thus, the energy released by its combustion) required to raise the temperature of 1 kg of water by 1 degree Celsius.

If we now replace the water with any other substance and repeat the experiment, we would find a different slope for each one. This demonstrates that different substances require different amounts of energy input to achieve the same temperature increase.

This property is called Heat Capacity. To make this a universal concept independent of the fuel type, we replace the arbitrary "charcoal" unit with a standard unit of energy, the joule (J) or the calorie (Cal), where 1 calorie is historically defined as the energy needed to raise the temperature of 1 gram of water by 1°C.

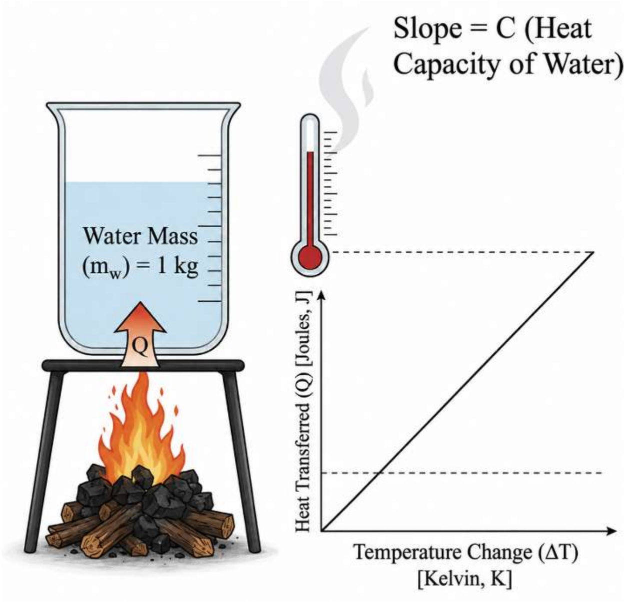


Figure 3-1: Variation of temperature vs heat

Therefore, the specific heat capacity (c) of a substance is formally defined as the amount of heat (Q) that must be transferred to raise the temperature of a unit mass (m) of the substance by one degree Celsius (or Kelvin).

The formula is:

$$Q = m \cdot c \cdot \Delta T \tag{3-2}$$

A table of specific heat capacities allows us to predict the energy required for heating or cooling any substance, which is a fundamental calculation in thermodynamics.

3.3 The Mechanical Equivalent of Heat and the Unity of Energy

Historically, the units for heat (the calorie) were separate from the units for mechanical energy (the joule). This supported the mistaken idea that heat was a unique substance ("caloric") rather than a form of energy as discussed in section 3.2.

The key to unifying these concepts was to demonstrate that mechanical work could produce a measurable heating effect. James Prescott Joule famously established this connection through a series of meticulous experiments around 1840s.

3.4 Joule's Experiment: A Conceptual Overview

Joule's most famous apparatus involved a paddle wheel immersed in an insulated container of water (see figure 3-2). The paddles were connected by a pulley to a descending weight.

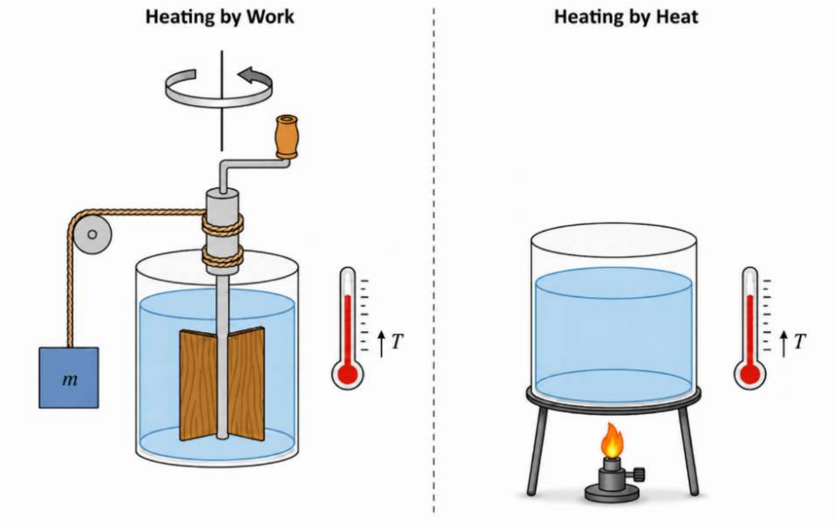


Figure 3-2: Joule experiment depicted conceptually

As the weight fell, it did work by turning the paddle wheel against the viscous friction of the water. This work was transferred as energy to the water, agitating its molecules.

Joule observed that the temperature of the water increased precisely in proportion to the work done by the falling weight. He carefully measured the following values:

The work input (W), calculated from the loss of gravitational potential energy of the weight is expressed as:

$$W = m \cdot g \cdot h \tag{3-3}$$

The heat input (Q), calculated from the temperature rise of the water

$$Q = m_{water} \cdot c_{water} \cdot \Delta T \tag{3-4}$$

Through repeated experiments, Joule found a consistent proportionality constant between work and heat. He determined that expending approximately 4.184 joules of mechanical work was equivalent to raising the temperature of 1 gram of water by 1 °C (i.e., transferring 1 calorie of heat). This constant is now known as the mechanical equivalent of heat (its modern defined value is 4.184 J/Cal).

3.5 The Nature of Heat and Work

Joule's experiment proved conclusively that:

Heat is a form of energy: The unit of heat, the calorie, is not a unique substance but is fundamentally equivalent to the unit of mechanical work, the joule (1 Cal = 4.184 J).

Work and Heat are both energy transfers. They are not properties of a system itself, but rather the two fundamental mechanisms by which energy is transferred across the boundary of a system. Work is energy transfer due to a force acting through a distance (e.g., a rising or falling weight). Heat is energy transfer driven solely by a temperature difference.

This discovery was a cornerstone in the development of the First Law of Thermodynamics, which formalizes the principle of conservation of energy, with heat and work as the two recognized forms of energy transfer (see chapter 5).

In 1850s, Thomson introduced the general term "energy" for that which Helmholtz and Mayer had called "Kraft." This term (energy) had already been used by Young (1800s) in place of vis viva, that indeed, had been implicitly employed by Galileo and Newton in the framework of mechanics of motion. Finally, in 1850s, Rankine divided energy into "potential" and "actual," and this terminology was soon adopted by Thomson and others in the context of thermodynamics- new branch of science.

At this stage, the interested reader is encouraged to read Appendix E.

There, you will discover that the concept of kinetic energy was not immediately accepted and that the historical tension between the conservation of momentum and *vis viva* (kinetic energy) was only resolved in the mid-18th century

Chapter 4: The Zeroth Law of Thermodynamics

Although named after the establishment of the first and second laws, the Zeroth Law is the fundamental principle that justifies the concept of temperature and its measurement. It states:

If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

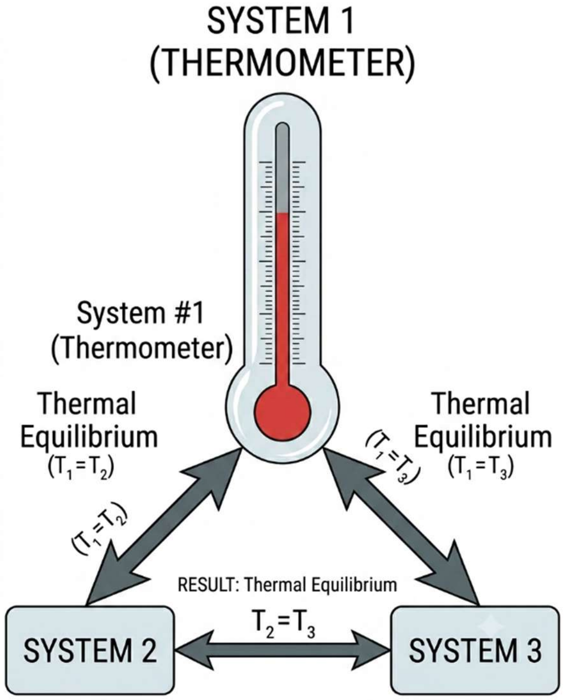


Figure 4-1: Experimental manifestation of the zeroth law

A common experimental manifestation of this law is when a thermometer (the "third system") shows the same reading when brought into contact with two different objects (see Figure 4-1). The Zeroth Law implies that these two objects must then be at the same temperature. It is crucial to note that this law is a foundational experimental observation, not a logical deduction from other principles or premises.

4.1 Thermometry

Thermometry is the application of the Zeroth Law to measure temperature. Numerous methods exist, typically based on measuring a thermometric property (e.g., volume of a liquid, electrical resistance, pressure of a gas) that changes predictably with the thermal state of a system.

A key challenge in thermometry is that different types of thermometers (e.g., mercury-glass, alcohol-based, gas, electrical) rely on different physical properties. These properties may not scale identically with temperature. Consequently, while all thermometers can be calibrated to agree perfectly at fixed reference points (such as the triple point or the freezing and boiling points of water), their readings may not coincide exactly at intermediate temperatures. For many practical purposes, these differences are negligible, but they highlight the need for a standardized temperature scale that is independent of any particular thermometric substance.

4.2 A Brief Review of Temperature Scales and the Concept of Absolute Zero

In the 18th century, scientists systematically studied the thermal expansion of materials. A key observation was that metals, such as iron or brass, expand predictably when heated. This property provided one of the first reliable methods for measuring temperature.

If one plots the length of a metal rod against its temperature on the Celsius scale, the relationship is approximately linear over a wide range. Crucially, when this straight line is extrapolated backward to the point where the theoretical length of the rod would be zero, it intersects the temperature axis at approximately -273 °C (see Figure 4-2).

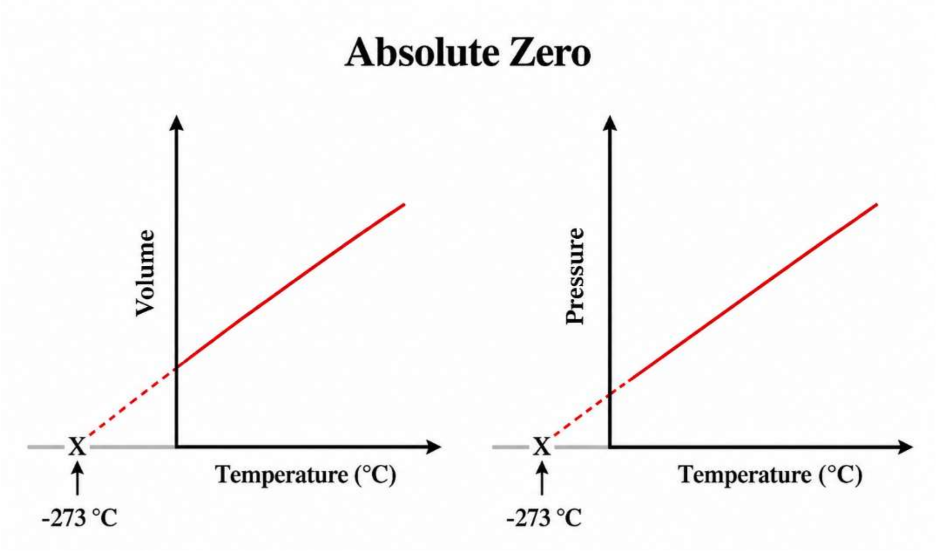


Figure 4-2: Conceptual presentation of finding absolute zero

This remarkable result was consistent across different gases and solids, leading scientists like Lord Kelvin to a profound inference. This temperature, -273.15 °C, represents a fundamental lower limit to temperature, now known as absolute zero. At this point, the thermal motion of atoms and molecules reaches its minimum possible energy.

4.3 The Problem with the Celsius and Fahrenheit Scales

The zero points on the Celsius (0 °C) and Fahrenheit (0 °F) scales are arbitrary. They were chosen for human convenience (the freezing point of water and a brine solution, respectively). Because zero is placed arbitrarily, the numbers are relative.

Is 20 °C twice as hot as 10 °C? If we convert these to Fahrenheit, we get 68 °F and 50 °F. 68 is not twice 50. This is a clear contradiction. Since the calculation gives a different answer depending on the scale, the idea of one temperature being "twice" another is meaningless on these relative scales.

4.4 The Special Meaning of Zero in the Kelvin Scale

The Kelvin scale is different. Its zero-point, 0 K (Absolute Zero), is not arbitrary. It is a fundamental, universal limit based on the physics of matter.

Zero degrees Kelvin is the theoretical point where particles (atoms, molecules) have the minimum possible thermal energy. They have essentially stopped moving (a quantum mechanical concept called zero-point energy means they aren't completely stationary, but for thermodynamics, this is the baseline). At any temperature above 0 K particles have kinetic energy (energy of motion). The temperature of a substance (in Kelvin) is directly proportional to the average kinetic energy of its particles (see Figure 4-3). This relationship is given by the kinetic theory of gases as expressed below (see appendix C):

$$\text{Average Kinetic Energy per Particle} = \frac{3}{2}\mathrm{k_B T}$$

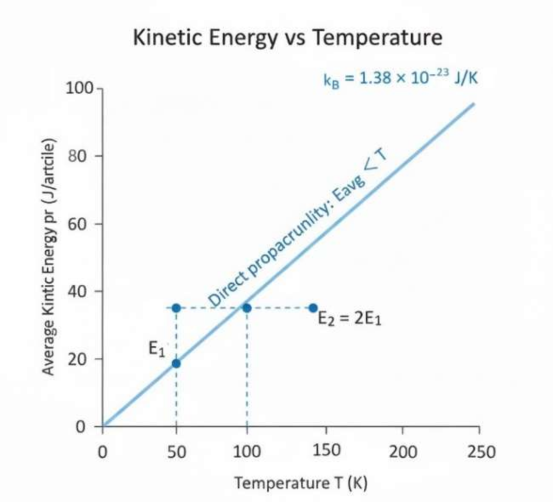


Figure 4-3: Variation of Kinetic energy vs absolute temperature

where k_B is Boltzmann's constant (a fundamental number of nature) and T is the temperature in Kelvin (K).

So, what does "100 K is twice as hot as 50 K" *really* mean? It means the average thermal energy of the particles at 100 K is twice the average thermal energy of the particles at 50 K.

At $50\ K$:

$$\text{Average KE } = \frac{3}{2}\mathrm{K_B}(50)$$

At $100\ K$:

$$\text{Average KE } = \frac{3}{2}\mathrm{K_B}(100)$$

The average kinetic energy has doubled.

So, we need a device that measures the temperature not depending on the properties of the medium substance and consistent with absolute scale of temperature which is called constant volume gas thermometer.

See appendix G where Constant Volume Gas Thermometer is explained which measures the temperature independent of the property of a given substance.

Chapter 5: The First Law of Thermodynamics

The First Law of Thermodynamics is fundamentally a statement of the conservation of energy principle as it applies to thermodynamic systems. It asserts that energy cannot be created or destroyed; it can only change forms or be transferred between a system and its surroundings.

The discovery of the conservation of mechanical energy was fundamentally rooted in experiment—though it later gained theoretical grounding. The same is true for the conservation of mechanical energy of a particle. See appendix E. Thus, note that neither the conservation of mass nor energy are conceived from philosphically argument that something cannot appear from nothing.

5.1 A Thought Experiment: Analyzing a Power Plant Cycle

Consider a simplified model of a power plant operating on a thermodynamic cycle (see Figure 5-1). The working fluid (e.g., $\frac{liquid\ water}{steam}$) circulates through four key devices:

Boiler: Heat transfer (Q_{in}) *to* the fluid from a high-temperature source.

Turbine: The high-pressure high temperature fluid expands, producing work output (W_{out}).

Condenser: Heat transfer (Q_{out}) *from* the fluid to a low-temperature sink.

Pump: Work input (W_{in}) is required to compress the fluid back to a high pressure.

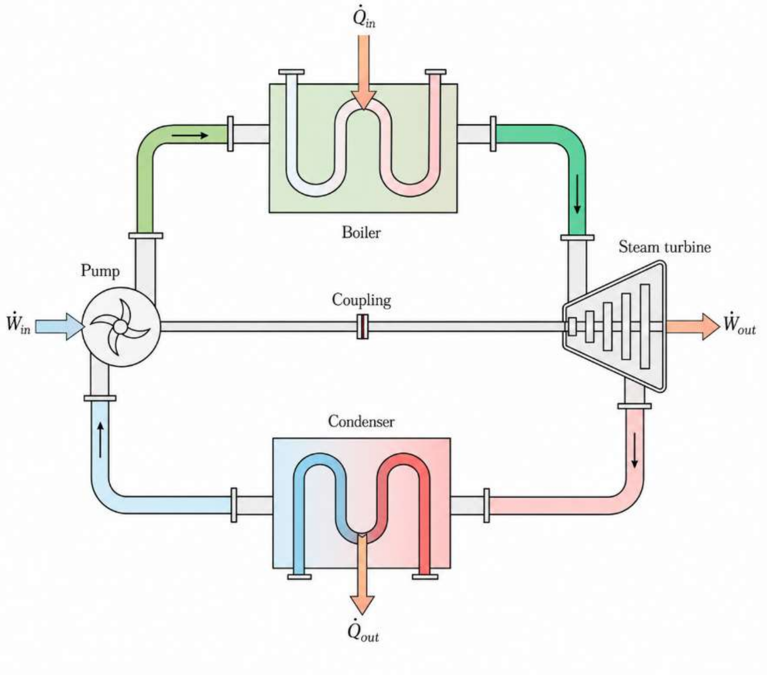


Figure 5-1: A simple schematic of a power plant's thermodynamic cycle

The system is defined as the working fluid itself as it completes a full cycle, returning to its initial state. We can meticulously measure all energy interactions across the system boundary for one complete cycle:

The net heat transfer to the fluid is the algebraic sum:

$$Q_{net} = Q_{in} - |Q_{out}| \tag{5-1}$$

The network transfer from the fluid is the algebraic sum:

$$W_{net} = |W_{out}| - W_{in} \tag{5-2}$$

(The convention is positive for heat added to the system and work done by the system.)

A profound realization emerges from this accounting: the net heat transfer is exactly equal to the network transfer for the cycle.

$$Q_{net} = W_{net} \; or \oint \delta Q = \oint \delta W \tag{5-3}$$

This result is a direct consequence of the First Law. Since the fluid returns to its initial state, its total internal energy (a state property) is unchanged (see section 5.4). Therefore, the net energy added to the system must equal the net energy that leaves it. The energy entering as heat (Q_{in}) must exit in two ways, as work output (W_{out}) and as wasted heat rejected (Q_{out}). The pump work (W_{in}) being a necessary energy input to complete the cycle.

This balance confirms that energy is not consumed but merely converted from one form (heat) to another (work) within the constraints of the First Law.

5.2 First Law: Conservation of Energy

The first law of thermodynamics is grounded in experiment, as we discussed. It states that energy cannot be created or destroyed; it can only be transformed between different forms, such as heat and work. This law is empirical and testable — it comes from observable, measurable phenomena. It's easy to demonstrate experimentally and is supported by a wealth of practical evidence.

The first law does not imply any metaphysical concept, like "energy is eternal" or "energy is a mystical force"; it simply says that in isolated systems, energy remains constant. The first law is conservation-based and requires no philosophical interpretation beyond what is observed.

5.3 Demonstrating that (Q - W) is a property: The Path to Internal Energy

The First Law of Thermodynamics not only asserts energy conservation but also leads us to the definition of a fundamental thermodynamic property.

The path dependence of Heat and Work is iterated in this step.

Consider a closed system undergoing a process from an initial state (1) to a final state (2).

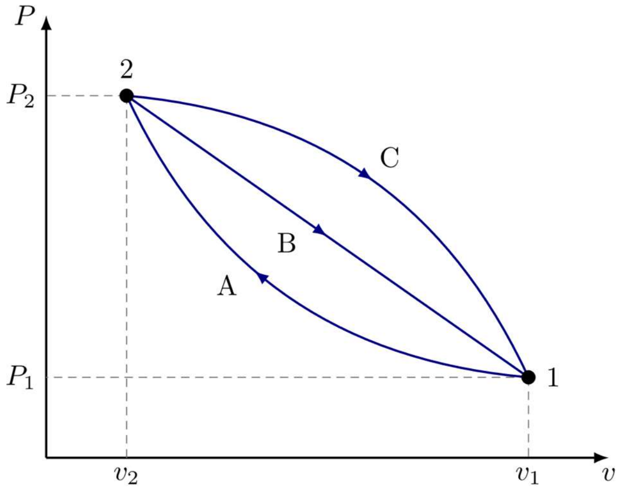


Figure 5-2: Thermodynamic paths (A, B, C) between states 1 and 2 on a P-v diagram.

We can envision many different paths (Process A, B, C, etc.) to achieve this change (see Figure 5-2).

Process A might be slow and isothermal. Process B might be rapid and adiabatic. Process C might involve a complex series of steps.

For each of these paths, the amounts of heat transfer (Q) and work transfer (W) will be different. A single value of Q or W cannot be associated solely with states 1 and 2; their values depend entirely on the path taken. We say that the differentials of heat and work are inexact differentials, denoted by δQ and δW.

Internal Energy-The Definition of another Thermodynamic Property

In thermodynamics, any quantity whose value depends solely on the state of the system (e.g., pressure, temperature, volume) and not on its history is called a state property or a point function.

Consider a system that undergoes a cycle in which it changes from state 1 to state 2 by process *A* and returns from state 2 to state 1 by process *B.* This cycle is shown in Fig. on a pressure versus another intensive property. Here we used the specific volume. Another cycle can be defined by processes A and C.

From the first law of thermodynamics,

$$\oint (\delta Q - \delta W) = 0 \tag{5-4}$$

For the cycle following path $1 \rightarrow A \rightarrow 2 \rightarrow B \rightarrow 1$, the first law gives:

$$\int_{1-A-2-B-1}(\delta Q-\delta W)=0 \tag{5-5}$$

Or

$$\int_{1,A}^{2}(\delta Q-\delta W)\;+\;\int_{2,B}^{1}(\delta Q-\delta W)=0 \tag{5-6}$$

which can be rewritten as

$$\int_{1,A}^{2}(\delta Q-\delta W)=-\int_{2,B}^{1}(\delta Q-\delta W) \tag{5-7}$$

Or

$$\int_{1,A}^{2}(\delta Q-\delta W)=\int_{1,B}^{2}(\delta Q-\delta W)\,\text{(i)} \tag{5-8}$$

Similarly, for the cycle following path $1 \to A \to 2 \to C \to 1$, the first law yields

$$\int_{1-A-2-C-1}(\delta Q-\delta W)=0 \tag{5-9}$$

Or

$$\int_{1,A}^{2}(\delta Q-\delta W)\;+\;\int_{2,C}^{1}(\delta Q-\delta W)=0 \tag{5-10}$$

Or

$$\int_{1,A}^{2}(\delta Q-\delta W)=-\int_{2,C}^{1}(\delta Q-\delta W) \tag{5-11}$$

Or

$$\int_{1,A}^{2}(\delta Q-\delta W)=\int_{1,C}^{2}(\delta Q-\delta W)\,\text{(ii)} \tag{5-12}$$

From equations (i) and (ii) it is clear that

$$\int_{1,A}^{2}(\delta Q-\delta W)=\int_{1,B}^{2}(\delta Q-\delta W)=\int_{1,C}^{2}(\delta Q-\delta W) \tag{5-13}$$

which shows that $(\delta Q - \delta W)$ is a property (the change in internal energy dU), because it is independent of the path followed between states 1 and 2.

Now, let's explain the above abstract proof by the following example. We perform a series of experiments where we measure the net heat transfer (Q) and the network transfer (W) for various paths connecting the same two states (1 and 2).

Table 5-1: Demonstration of path independence for the quantity (Q - W) across different processes connecting two fixed states.

Process	Heat Transfer (Q)	Work Transfer (W)	Quantity $(Q - W)$
Path A	50 kJ	20 kJ	30 kJ
Path B	35 Kj	5 Kj	30 kJ
Path C	40 kJ	10 kJ	30 kJ

Since $(Q - W)$ is path-independent, its value for an infinitesimal process is an exact differential. We have therefore discovered a new thermodynamic property explained its properties as follows.

5.4 Defining Internal Energy

The units of Q and W are both joules (energy). Therefore, the quantity $(Q - W)$ also has dimensions of energy. This newly identified state property represents the net energy added to the system that was not used to do work. It must therefore be energy stored within the system itself. In other words, the net energy lost by the system could be the difference between heat and work transfer of the system.

The first law is a statement of energy conservation. It tells us that a system can exchange energy with its surroundings by the transmission of heat and by the performance of work. The net energy exchanged is then equal to the change in the total mechanical energy of the molecules of the system (i.e., the system's internal energy). Thus, if a system is isolated, its internal energy must remain constant.

Notice that in deducing the internal energy, we did not assume that the transitions were quasi-static. This is because the first law is not subject to such a restriction. It describes transitions between equilibrium states but is not concerned with the intermediate states. The system does not have to pass through only equilibrium states. For example, if a gas in a steel container at a well-defined temperature and pressure is made to explode by means of a spark, some of the gas may condense, different gas molecules may combine to form new compounds, and there may be all sorts of turbulence in the container—but eventually, the system will settle down to a new equilibrium state. This system is clearly not in equilibrium during its transition; however, its behavior is still governed by the first law because the process starts and ends with the system in equilibrium states. As internal energy is a property so the system has energy at each thermodynamic equilibrium state, however we cannot assign work and heat for a state of the system. Heat and work are not the property of the system. They can only be presented as a value by measurement or calculated by finding the area under the curve of P-v diagram. So, we can write:

$$\Delta U(1 \rightarrow 2) = U_2 - U_1 = Q - W \tag{5-14}$$

This is the canonical form of the First Law of Thermodynamics for a Closed System. For an infinitesimal process, it is written as:

$$dU = \delta Q - \delta W \tag{5-15}$$

where, dU is an exact differential (because U is a state property). δQ and δW are inexact differentials (because they are path-dependent transients, not properties).

In summary, the path independence of $(Q - W)$ for a given state change is the experimental evidence that allows us to define the internal energy U as a fundamental property of a system. It accounts for all energy stored at the microscopic level, such as kinetic and potential energy of molecules.

5.5 The Total Energy of a System

While the First Law led us to generalize the internal energy (U), this is not the only form of energy a system can possess. The total energy (E) of a system is the sum of its macroscopic and microscopic energy contributions:

$$E = U + KE + PE \tag{5-16}$$

Internal Energy (U): This is the energy associated with the microscopic or internal state of the system. It includes:

Kinetic energy of molecules (translational, rotational, vibrational motion).

Potential energy of molecules (due to intermolecular forces like bonding and attraction).

Chemical energy and other forms of energy at the atomic and subatomic level.

Kinetic Energy (KE): This is the energy associated with the macroscopic motion of the system as a whole. It is given by $KE = \frac{1}{2}mV^2$, where m is the system's mass and V is the velocity of its center of mass relative to some external reference frame.

Potential Energy (PE): This is the energy associated with the macroscopic position of the system in an external force field, such as gravity. It is given by $PE = mgz$, where g is gravitational acceleration and z is the elevation of the system's center of mass relative to a chosen reference plane.

See Appendix E for a historical review of the concept of mechanical energy.

In this appendix you will find the tension between 18th century scientists regarding the principle of conservation of momentum and energy and the nature of energy called *vis viva* in 18th century.

5.6 The General Form of the First Law

The First Law of Thermodynamics, which states that energy cannot be created or destroyed, applies to the total energy of the system. The most general form of the First Law for a closed system can be written as:

$$\Delta E = Q - W \tag{5-17}$$

This can be expanded to show all the energy forms:

$$\Delta U + \Delta KE + \Delta PE = Q - W \tag{5-18}$$

where, ΔE is the change in the total energy of the system, is the net heat transfer to the system and W is the net work done by the system (this includes all forms of work, such as boundary work PdV, shaft work, etc.).

Remarks: A Common Simplification

In many thermodynamic analyses, especially those involving stationary equipment like power plants, compressors, or closed tanks, the system has no change in its macroscopic kinetic or potential energy ($\Delta KE = 0$, $\Delta PE = 0$). This is an excellent approximation.

For these stationary closed systems, the change in total energy is solely a change in internal energy:

$$\Delta E = \Delta U \tag{5-19}$$

Thus, the First Law simplifies to its most familiar form:

$$\Delta U = Q - W \tag{5-20}$$

This simplification powerfully connects the microscopic world (internal energy) to the macroscopic energy transfers we can measure (heat and work), reinforcing that the First Law governs the conservation of all energy, in all its forms.

5.7 The Microscopic View of Internal Energy

The internal energy (U) of a substance is the sum of all the microscopic kinetic and potential energies of its molecules. The type of motion molecules can depend on their atomic structure (monatomic, diatomic, polyatomic), which directly determines their internal energy and, consequently, their specific heat at constant volume.

The Equipartition Theorem for an ideal gas provides the key link. It states that each quadratic "degree of freedom" of a molecule contributes an average of $\frac{1}{2}K_B T$ of energy per molecule, or $\frac{1}{2}\overline{R}T$ per mole, where $\overline{R}$ is the universal gas constant, T is the absolute temperature and K_B is Boltzmann constant.

A "degree of freedom" is an independent way a molecule can store energy (e.g., moving along the x-axis, spinning around the y-axis, (see figure 5-2)).

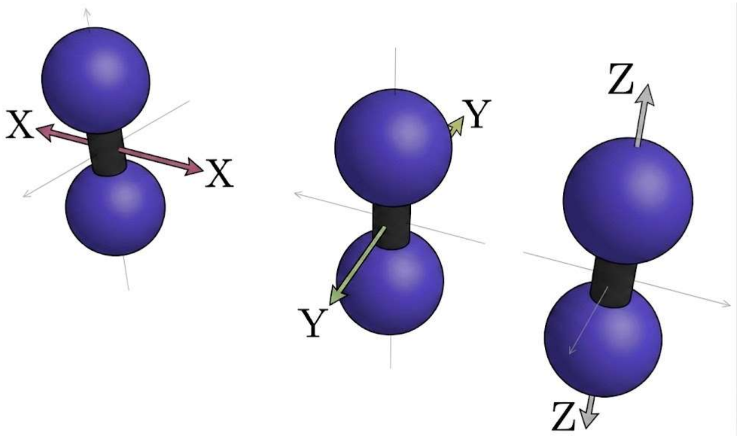


Figure 5-2: The rotational degrees of freedom of a diatomic gas.

The key is that the energy must be a quadratic term in the equations of motion (e.g., proportional to the square of a velocity). Indeed, the equipartition theorem links the kinetic energy of molecules to temperature. In other words, according to this theory, energy—a fundamental concept in Newtonian mechanics—is taken as primitive, while temperature is a derived property. Thus, what we measure with a thermometer is ultimately a consequence of energy transfer driven by a temperature difference between the thermometer and its medium. According to statistical thermodynamics, a temperature difference directly corresponds to a difference in the average molecular kinetic energy per degree of freedom. The thermometer exchanges energy with the medium until thermal equilibrium is reached, at which point no net energy transfer occurs and their average molecular kinetic energies are equal. The thermometer then reports a numerical value (temperature) based on a chosen scale, and that value is proportional to the common average kinetic energy.

The proof of the equipartition theorem rests fundamentally on statistical mechanics, pioneered by Boltzmann, who expressed the probability of a given molecular velocity using an exponential function that includes temperature. A full derivation of this theorem is beyond the scope of this note. Nevertheless, statistical mechanics is useful for explaining why a gas behaves as an ideal gas. However, the empirical ideal gas equation of state merely describes the rules that such a gas obeys.

Facing a pedagogical dilemma, we have added an appendix to this manuscript that briefly discusses the cornerstone of deriving equipartition theorem from statistical thermodynamics (see appendix F).

The most common types of kinetic energy of molecules are:

Translational: Energy from moving through space are kinetic energies ½mv_x^2, ½mv_y^2, ½mv_z^2.

Rotational: Energy from spinning is the kinetic energy: ½$I\omega^2$ (where the symbol I denotes the moment of inertia, ω is angular velocity).

Vibrational: Energy from atoms oscillating relative to each other. This has two quadratic components consisting of kinetic energy of vibration and potential energy of vibration expressed as ½kx^2 (like a spring).

5.8 Definition of specific heat at constant volume

By definition, c_v, the specific heat at constant volume is the energy required to raise the temperature of a unit mass by one degree at constant volume. For a constant volume process, no work is done ($W = 0$), so from the First Law, $\Delta U = Q$. Therefore:

$$c_v = \left(\frac{1}{n}\right)\left(\frac{\partial U}{\partial T}\right)_v \quad (for\ a\ mole,\ n = 1)$$

5.9 Internal Energy of Monatomic Gas (e.g., He, Ar, Ne)

Molecular Structure: A single atom. Think of it as a point mass or a tiny sphere.

Degrees of Freedom are:

Translation only. It can move independently in three perpendicular directions (x, y, z).

It has no rotational energy (the moment of inertia around its center is negligible).

It has no vibrational energy (a single atom cannot vibrate).

Total Degrees of Freedom: 3 (all translational).

Internal Energy (per mole):

$$U = 3 \times \frac{1}{2} RT = \frac{3}{2} \overline{R}T \tag{5-21}$$

Therefore:

$$c_v = \left(\frac{1}{n}\right)\left(\frac{\partial U}{\partial T}\right)_v \ (for\ a\ mole,\ n = 1) \tag{5-22}$$

For a monatomic gas:

$$c_v = \frac{d}{dT}\left[\frac{3}{2}\overline{\mathrm{R}}\mathrm{T}\right] = \frac{3}{2}\overline{R} \tag{5-23}$$

- $\overline{R} \approx 8.314\, J/mol \cdot K$
- Therefore, $\mathrm{c_v} \approx 12.47\, \mathrm{J/mol} \cdot K$

This value is constant and matches experimental results for noble gases almost perfectly.

5.10 Internal Energy of Diatomic Gas (e.g., N_2, O_2, H_2)

Molecular Structure: Two atoms rigidly connected (like a dumbbell, see figure 5-2).

Degrees of Freedom are:

Translation: 3 (x, y, z motion of the center of mass).

Rotation: 2. It can rotate about two independent axes perpendicular to the line joining the two atoms. Rotation *along* the line joining the atoms has negligible moment of inertia.

Vibration: At room temperature, the vibrational mode is "frozen out"—molecules are typically in their ground vibrational state and require significant energy to excite. It does not contribute to c_v.

Total Degrees of Freedom: 5 (3 trans + 2 rot).

Internal Energy (per mole) is thus found as:

$$U = 3 \times \frac{1}{2}\overline{R}T + 2 \times \frac{1}{2}\overline{R}T = \frac{5}{2}\overline{R}T \tag{5-24}$$

Specific Heat at Constant Volume **(c_v)** can be expressed as:

$$c_v = \frac{d}{dT}\left(\frac{5}{2}\overline{R}T\right) = \frac{5}{2}\overline{R} \approx 20.8\, J/mol \cdot K$$

This value holds very well for common diatomic gases like N_2 and O_2 at room temperature.

Remark: As temperature increases significantly (e.g., >1000 K for O_2), the vibrational mode becomes active. Vibration has *two* quadratic energy terms: one for kinetic energy. Atoms move in their equilibrium state toward each other or move farther) and one for potential energy (spring effect). Therefore, it contributes 1 RT (not $\frac{1}{2}$) to the internal energy per mole.

At very high temperatures, a diatomic gas has 7 degrees of freedom (3 trans + 2 rot + 2 vib), leading to:

$$U = \frac{7}{2}\overline{R}T \text{ and } c_v = \frac{7}{2}\overline{R} \approx 29.1 J/mol \cdot K$$

5.11 Internal Energy of Polyatomic Gas (e.g. H_2O, CH_4)

Molecular Structure: Three or more atoms.

Degrees of Freedom are:

Translation: 3.

Rotation: 3. A non-linear molecule can rotate about all three perpendicular axes (x, y, z).

Vibration: Multiple vibrational modes, which are frozen out at low temperatures.

Total Degrees of Freedom (at Room Temperature): 6 (3 trans + 3 rot).

Internal Energy (per mole):

$$U = 3 \times \frac{1}{2}\overline{R}T + 3 \times \frac{1}{2}\overline{R}T = 3\overline{R}T \tag{5-25}$$

Specific Heat at Constant Volume (c_v) is expressed as:

$$c_v = \frac{d}{\mathrm{dT}}\left(3\overline{R}T\right) = 3\overline{R} \tag{5-26}$$

As with diatomic gases, vibrational modes become active at high temperatures, causing c_v to rise above 3R.

Remarks:

a) CO_2 is a linear molecule (O=C=O), and that determines its rotational behavior. A linear molecule has 2 rotational degrees of freedom. Rotation around the molecular axis doesn't count because it produces essentially no change in energy (the moment of inertia is negligible). So, for CO_2: Number of rotational degrees of freedom = 2. These correspond to rotation about axes perpendicular to the molecular axis.

b) Diatomic molecule has 1 vibrational degree of freedom. There's only one way for two atoms to vibrate relative to each other: They move back and forth along the bond (stretching and compressing it like a spring). Subtle but important point is that 1 vibrational mode actually contains 2 energy contributions: Kinetic energy (atoms moving) and Potential energy (bond stretching like a spring). So, in thermodynamics that single vibrational mode can contribute 2 degrees of freedom worth of energy when fully active.

c) Intermolecular forces affect the heat capacity of diatomic and polyatomic gases. For a diatomic gas like Oxygen or Nitrogen (not assuming Ideal gas case) when intermolecular forces are included attractive and repulsive forces between molecules become important. In other words, part of the energy supplied, goes into changing intermolecular potential energy, not just kinetic energy. So, to raise the temperature by the same amount, we may need more energy. In real conditions heat capacity can deviate from the ideal gas value. Usually, this effect is stronger at high pressure and also stronger at low temperature.

d) If heat capacity is low, it means a small amount of heat causes a large increase in temperature. Temperature is proportional to the average kinetic energy of molecules. For a monoatomic gas if temperature rises a lot, the average molecular speed increases. Low heat capacity means a small amount of heat produces a large increase in temperature and thus a large increase in average molecular kinetic energy. If heat capacity is low the system has fewer active degrees of freedom, so the energy added is distributed among fewer modes. For example, for the monoatomic gas, lower energy goes only into translation and faster increase in speed. For the case of diatomic gas higher energy spreads into rotation (and maybe vibration) leading to a slower increase in speed and therefore lower increase in temperature.

5.12 Joule's Experiment: The physical evidence for dependence of internal energy of an ideal gas

In the 1840s, James Joule conducted a simple but profound experiment to investigate the dependence of a gas's internal energy U on its volume V and temperature T.

Two copper vessels were connected by a valve and placed in a water bath. One vessel was filled with a gas at high pressure; the other was evacuated.

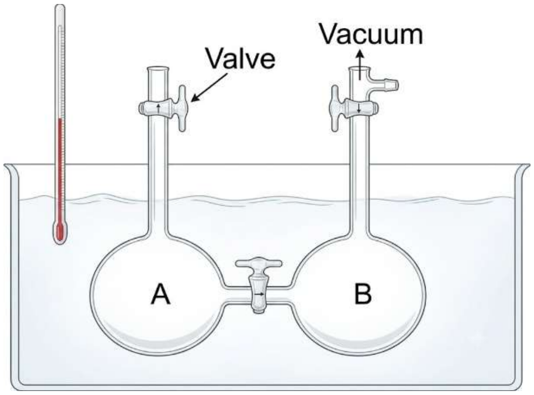


Figure 5-3: Free expansion of ideal gas.

As depicted in figure 5-3, the valve was opened, allowing the gas to undergo a free expansion into the vacuum. As established, this is a rapid, non-quasi-equilibrium process where no work is done ($W = 0$). The entire apparatus was insulated, so no heat was transferred ($Q = 0$).

Joule observed no change in the temperature of the water bath.

We can conclude from the First Law the following:

Since $\Delta U = Q - W = 0 - 0 = 0$ and the volume changed ($\Delta V > 0$) , but the temperature did not change ($\Delta T = 0$), it follows that:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{5-27}$$

Therefore, the internal energy of a gas does not change with volume at constant temperature. Therefore, for a given gas, internal energy must be a function of temperature only:

$$U = U(T) \tag{5-28}$$

This is Joule's Law. It holds very well for ideal gases and is a good approximation for real gases at low pressures.

The state postulate states that for a simple, compressible substance, the state is fixed by two independent, intensive properties (e.g., T and V, or P and T).

Gibbs state postulate says that U can be a function of two properties: $U = U(T, V)$.

Joule's experiment (and the ideal gas model) tells us that for a specific substance (an ideal gas), this function simplifies to $U = U(T)$. This is not a violation of the state postulate. It is a specific result for a specific model. The postulate defines the maximum number of properties needed to fix the state. For an ideal gas, it turns out that only one property T is needed to determine U, because changes in V (at constant T) have no effect on U. The state postulate is still used to define the state itself (we still need P and T to fix the state), but the internal energy has a special, simplified dependence.

Remark: It should be mentioned that the absence of heat transfer from the system to the water bath or from the water bath to the system (gas), in Joule experiment, does not hold for the expansion of a liquid water at low pressure as it may evaporate which needs latent heat to vaporize. Consequently, heat is transferred from the water bath and the water temperature drops. Thus, our intuition that expansion of a gas does not need necessarily any heat transfer to the surrounding is not valid. Repeating the experiment with a gas at high pressure so that intermolecular forces are important would show that indeed the temperature of water bath changes.

See appendix H titled, The Mathematical Link: The Maxwell Relations & The Ideal Gas for more discussion about the ideal gas behavior

5.13 The Practical Engineering Perspective: Constant Specific Heats

In reality, for both ideal and real gases, the specific heats are functions of temperature. As temperature increases, more vibrational modes are excited, which increases the specific heat. This means the simple formulas $U = c_v T$ are not exact if c_v are truly constant; the correct calculation requires integration:

$$\Delta u = U_2 - U_1 = \int_{T_2}^{T_1} C_v(T) dT \tag{5-29}$$

However, for a vast number of engineering applications, this complexity is intentionally avoided in the initial design phase.

Here's the standard practical approach:

Engineers often assume constant specific heats, typically using their values at or near room temperature (300K / 27°C). This is known as the cold-air-standard or room-temperature assumption. It dramatically simplifies calculations. The equations become linear and algebraic ($e.g., \ \Delta U = m \times c_v, \ avg \times \Delta T$), allowing for quick, closed-form solutions.

The primary goal of initial design is to understand the trends and relationships between parameters (e.g., how compression ratio affects efficiency in an engine cycle) rather than to predict an exact efficiency value down to the decimal. A constant specific heat model preserves these trends with remarkable fidelity. For many applications where the temperature range is not excessively wide (e.g., from -50°C to 100°C), the variation in c_v is small enough that the error introduced by assuming a constant value is acceptable for a first-pass design.

After the initial design is complete and the key parameters (pressures, temperatures, mass flow rates) are established, a more accurate analysis is performed. This is when the temperature dependence is introduced. Using formulas for the function $c_v(T)$ and performing the necessary integrals the calculations become less approximate.

For common gases like air, pre-computed Gas Tables (or Ideal Gas Property Tables) are used. These tables list the values of internal energy u, enthalpy h, and other properties as functions of temperature, effectively building the integral of the specific heat into the tabulated value. Using these tables is the standard, accurate method for final calculations.

5.14 Enthalpy: Definition of a Property Independent of Process

Enthalpy, denoted as H, is simply a defined thermodynamic property. It is a combination of other state properties:

$$H \equiv U + PV \tag{5-30}$$

where, U is the internal energy (a state property), P is the pressure (a state property) and V is the volume (a state property).

Because U, P, and V are all state properties, their combination $(U + PV)$ must also be a state property. This means the enthalpy of a system, like internal energy or temperature, has a unique value at a given state and its change between two states depends only on the initial and final states, not on the path taken.

Note that the new property is not deduced from the first principles of the first law. It is just a definition with useful applications.

The utility of this specific combination $(U + PV)$ becomes apparent in the analysis of certain systems, but its definition does not depend on them. The two most common applications are:

a) **Flow Processes (Open Systems):** The term PV represents flow work—the work required to push a volume of fluid into or out of a control volume against a pressure P. Thus, enthalpy H can be interpreted as the total energy content of a fluid parcel, comprising its internal energy U plus the energy required to make room for it in a flow environment (PV). This is why enthalpy is the central energy property in the First Law for open systems (see section 5.13).

b) **Constant-Pressure Processes:** For a closed system undergoing a constant-pressure process, the heat transfer Q is equal to the change in enthalpy ΔH. This is a consequence of the definition and the First Law, not the reason for it. For this process as pressure is constant we can derive:

$$Q = \Delta U + P\Delta V = \Delta(U + PV) = \Delta H \tag{5-31}$$

his makes H a convenient "heat function" for this specific, but very common, type of process.

Remark: The property exists and is well-defined for any system at any state, regardless of the process it is undergoing.

5.15 Defining Specific Heat at Constant Pressure (c_p)

The specific heat at constant pressure, C_p, is defined as the amount of energy transfer as heat required to raise the temperature of a unit mass of a substance by one degree, while the pressure is maintained constant.

By the definition of specific heat at constant pressure:

$$c_p \equiv \frac{1}{m}\left(\frac{\partial Q}{\partial T}\right)_P \tag{5-32}$$

Substituting our result $\delta Q = dH$:

$$c_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_P \tag{5-33}$$

For a per-unit-mass analysis (using specific enthalpy, $h = \frac{H}{m}$), this becomes:

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P \tag{5-34}$$

The specific heat at constant pressure is the partial derivative of specific enthalpy with respect to temperature, while pressure is held constant.

5.16 The Ideal Gas Simplification for *C_P*

For an ideal gas, enthalpy $H = H(T)$ and the internal energy U=U(T) depend only on temperature.

The enthalpy H is defined as:

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P \tag{5-35}$$

The ideal gas law states:

$$PV = n\overline{R}T \tag{5-36}$$

For a unit mass (specific quantities), we use lowercase letters:

$$h = u + Pv \tag{5-37}$$

and the ideal gas law becomes:

$$Pv = RT \tag{5-38}$$

where R is now the specific gas constant (i.e., the universal gas constant divided by the molar mass).

To express enthalpy in terms of temperature we substitute the ideal gas law into the definition of specific enthalpy:

$$h = u + Pv = u + RT \tag{5-39}$$

Since u depends only on T, it follows that h also depends only on T.

Therefore, the partial derivative becomes a total derivative:

$$c_p = \frac{dh}{dT} \tag{5-31}$$

This leads to the simple and very useful formulas for calculating changes in specific enthalpy for an ideal gas:

$$\mathit{\Delta} h = h_2 - h_1 = \int_{T_2}^{T_1} c_p\,(T)dT \tag{5-41}$$

And if c_p is assumed constant over the temperature range:

$$\mathit{\Delta} h = c_p \mathit{\Delta} T \tag{5-42}$$

5.17 Relations between Constant Volume and constant Pressure Specific Heats of an ideal Gas

By definition, the specific heat at constant volume is:

$$C_v = \left(\frac{\partial u}{\partial T}\right)_V \tag{5-32}$$

For an ideal gas, $u = u(T)$, so this becomes a total derivative:

$$C_v = \left(\frac{du}{dT}\right) \tag{5-44}$$

The specific heat at constant pressure is:

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p \tag{5-33}$$

Again, since $h = h(T)$, this simplifies to:

$$C_p = \left(\frac{dh}{dT}\right) \tag{5-34}$$

Substituting into the differentiated equation follows:

$$C_p = C_v + R \tag{5-47}$$

Rearranging gives:

$$C_p - C_v = R \tag{5-35}$$

This result holds for any temperature, as R is a constant and the derivation relied only on the properties of an ideal gas.

The adiabatic index is defined as:

$$\gamma = \frac{c_p}{c_v} \tag{5-49}$$

Remark: While the difference between the specific heats for an ideal gas is always equal to the gas constant R, it is not true that their ratio, known as γ the adiabatic index, is constant.

The ratio γ is temperature-dependent. The reason is fundamental and stems from the microscopic view of internal energy as explained in the following:

As previously discussed, the constant-volume specific heat c_v is a measure of how many ways a molecule can store energy. At low temperatures, only translational and rotational modes are active. As temperature increases, vibrational modes begin to contribute.

c_p is always greater than c_v, since $c_p = c_v + R$. So, if c_v increases with temperature, c_p must also increase by the same absolute amount (R is constant).

However, adding a fixed value R to an increasingly number (c_v) causes the ratio $\frac{c_p}{c_v}$ to decrease.

Example: Imagine at a low temperature, $c_v = \frac{5}{2}\,\overline{R}$ for a diatomic gas.

Then $c_p = \frac{5}{2}\overline{R} + \overline{R} = \frac{7}{2}\overline{R}$

The ratio is $\gamma = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 7/5 = 1.4$

At a very high temperature, vibrational modes activate, and c_v might become $(\frac{7}{2}\overline{R})$.

Then $c_p = \frac{7}{2}\overline{R} + \overline{R} = \frac{9}{2}\overline{R}$

The new ratio is $\gamma = \frac{\frac{9}{2}R}{\frac{7}{2}R} = 9/7 \approx 1.284$

As the internal energy increases, a greater fraction of the energy added at constant volume goes into increasing U (raising c_v), leaving a smaller relative difference between c_p and c_v. Thus, the ratio γ approaches 1.0 as temperature approaches infinity, though it never quite reaches it.

5.18 The First Law for a Control Volume (open system)

For any closed system (a fixed quantity of mass), the First Law is:

$$\Delta E = Q - W \tag{5-50}$$

where E is the total energy ($E = U + KE + PE$), Q is the heat transfer to the system, and W is the work done *by* the system.

For a differential process:

$$dE = \delta Q - \delta W \tag{5-36}$$

Consider an open system called also as control volume (CV) with mass flowing in through inlet i and out through outlet e (see figure 5-4).

At time t, the system is the mass contained within the CV (dashed line). At time $t + dt$ a small amount of mass dm_i has entered the CV and a small amount of mass dm_e has left the CV. The system boundary has moved.

The work done by the system, δW, now includes two types:

Shaft Work (W_{sh}): The work done by the machine (e.g., by a turbine rotor or on a compressor blade).

Flow Work (W_{flow}): The work required to push mass into and out of the CV. This is the work done on the system at the inlet and by the system at the outlet.

Applying the First Law to the moving closed system we can proceed as follows:

The change in energy of the closed system, dE, is the change between the two states:

$$dE = E_{CV}(t + dt) + dE_e - E_{CV}(t) - dE_i \tag{5-52}$$

where:

$E_{CV}(t)$ is the energy inside the CV at time t.

$dE_i = e_i dm_i$ is the energy of the mass that entered.

$dE_e = e_e dm_e$ is the energy of the mass that exited.

$E_{CV}(t + dt)$ is the energy inside the CV at time $t + dt$.

So,

$$dE = [E_{CV}(t + dt) - E_{CV}(t)] + [e_e dm_e - e_i dm_i] \tag{5-37}$$

The heat transfer is δQ and the work done is $\delta W = \delta W_{sh} + \delta W_{flow}$.

The flow work is the work done to move mass across the boundary. The work done on the system to push dm_i into the CV is $P_i v_i dm_i$. The work done by the system to push dm_e out is $P_e v_e dm_e$. Therefore, the net flow work done by the system is:

$$\delta W_{flow} = P_e v_e dm_e - P_i v_i dm_i \tag{5-38}$$

Substituting everything into the First Law ($dE = \delta Q - \delta W$):

$$\begin{aligned}[E_{CV}(t + dt) - E_{CV}(t)] + [e_e dm_e - e_i dm_i]& \\ = \delta Q - [\delta W_{sh} + (P_e v_e dm_e - P_i v_i dm_i)]&\end{aligned} \tag{5-39}$$

Recognize that $E_{CV}(t + dt) - E_{CV}(t)$ is the change in energy within the control volume over time dt, which we can write as dE_{CV}.

Now, rearrange the equation to group the mass flow terms:

$$dE_{CV} = \delta Q - \delta W_{sh} - [e_e dm_e + P_e v_e dm_e] + [e_i dm_i + P_i v_i dm_i] \tag{5-40}$$

Recall that the specific energy $e\ is\ u + ke + pe$. Also, recall the definition of specific enthalpy:

$$h = u + Pv \tag{5-41}$$

Therefore, for the exiting mass:

$$\begin{aligned}e_e + P_e v_e = (u_e + ke_e + pe_e) + P_e v_e = (u_e + P_e v_e) + ke_e + pe_e \\ = h_e + ke_e + pe_e\end{aligned} \tag{5-42}$$

The same holds true for the incoming mass. Substituting this in:

$$dE_{CV} = \delta Q - \delta W_{sh} - [(h_e + ke_e + pe_e)dm_e] + [(h_i + ke_i + pe_i)dm_i] \tag{5-59}$$

This is a differential change over time dt. To find the rate equation, we divide all terms by dt:

$$\frac{dE_{CV}}{dt} = Q^{\cdot} - W^{\cdot}{}_{sh} - \left[m^{\cdot}{}_e\left(h_e + \frac{V_e{}^2}{2} + gz_e\right)\right] + \left[m^{\cdot}{}_i\left(h_i + \frac{V_i{}^2}{2} + gz_i\right)\right] \tag{5-43}$$

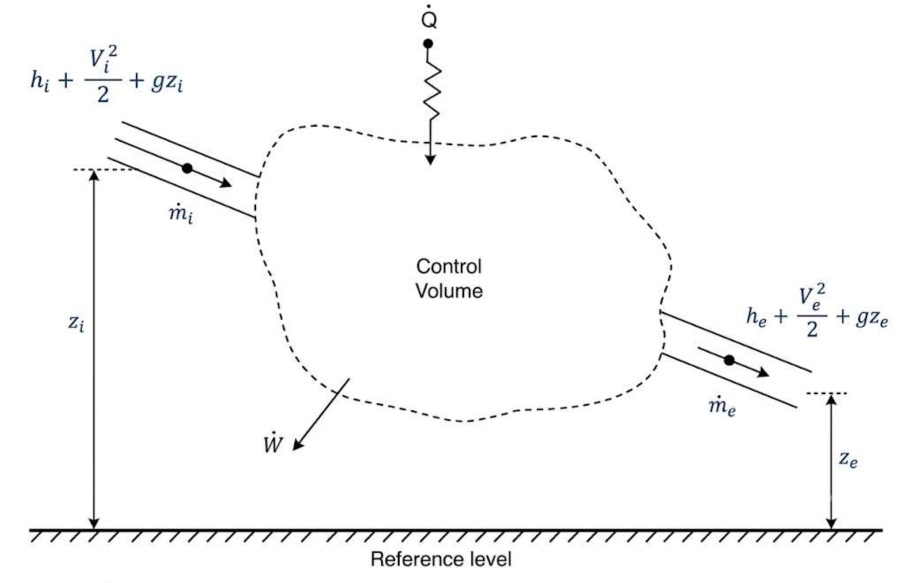


Figure 5-4: The first law of thermodynamics applied to an open system, depicting mass flow rates and energy transfers across the control surface.

where:

$\frac{dE_{CV}}{dt}$ is the rate of change of energy within the control volume.

$\dot{Q} = \frac{\delta Q}{dt}$ is the rate of heat transfer.

$\dot{W_{sh}} = \frac{\delta W_{sh}}{dt}$ is the shaft power.

$\dot{m} = \frac{dm}{dt}$ is the mass flow rate.

$\frac{V^2}{2}$ is the specific kinetic energy.

gz is the specific potential energy.

This is the general form of the First Law for a Control Volume.

5.19 The Steady-State, Steady-Flow (SSSF) Simplification

For most engineering devices, we assume steady-state and steady-flow (SSSF) conditions:

The properties within the CV do not change with time: $\frac{dE_{CV}}{dt} = 0$.

The mass flow rate in equals the mass flow rate out: $\dot{m}_\iota = \dot{m}_e = \dot{m}$.

Applying these assumptions, the general equation simplifies beautifully to:

$$\dot{Q} - \dot{W}_{sh} = \dot{m}\left[(h_e - h_i) + \frac{1}{2}\left({V_e}^2 - {V_i}^2\right) + g(z_e - z_i)\right] \tag{5-44}$$

Or, on a per-unit-mass basis:

$$q - w_{sh} = (h_e - h_i) + \frac{1}{2}\left({V_e}^2 - {V_i}^2\right) + g(z_e - z_i) \tag{5-45}$$

Remark: This is the main equation for analyzing turbines, compressors, pumps, nozzles, diffusers, and heat exchangers.

Summary: The First Law for a control volume account for mass flow by incorporating the energy carried by the mass and the flow work (Pv work) required to move it. This flow work term naturally leads to the appearance of enthalpy (h) as the central property for characterizing the energy of a fluid stream in an open system. The final form powerfully relates the heat and work interactions of a device to the change in the thermodynamic and mechanical properties of the fluid flowing through it.

Chapter 6: The second law of thermodynamics

To explain the second law of thermodynamics in this chapter the following sequence of reasoning is employed. First, the concept of a reversible process is presented. The reversible process is indeed the most important conceptual part for inducing the second law and deducing the concept of entropy as a state property. It is used to show that even for the case of the most ideal case (that can only be true in mind and not in practice), the nature plays a degrading role when heat is exchanged in a heat engine. The degradation is explained by the fact that for a heat engine working in a cycle, part of the heat it receives at high temperature is not converted to work, but simply becomes heat at a less hot or so-called cold temperature. From the operation of human invented engines, it will be induced that a cyclic machine needs at least two heat reservoirs: A hot reservoir to receive heat and a cold reservoir to lose heat. Heat at less hot temperature has less inherent 'power' to produce work in another heat engine in contact with a cold reservoir. Of course, at the end of the line we will have heat at a single temperature and no work can be obtained from it.

6.1 Introduction: Defining Reversibility

A reversible process is an idealization—a limit that real processes can approach but never fully achieve. For a process to be reversible, it must be possible to restore both the system and the surroundings to their original states after the process has occurred, with no net effects anywhere in the universe. This requires the process to be a continuous sequence of equilibrium states with no dissipative effects and also in equilibrium with the surroundings!

This overall idea is broken down into two components: internal and external reversibility.

6.2 Internally Reversible Process

An internally reversible process is one where no irreversibility occurs within the boundaries of the system. The system itself undergoes a quasi-equilibrium process. There is no friction, viscosity, inelastic deformation, turbulence, unrestrained expansion, or mixing within the system. If the process were reversed, the system would retrace its exact path on a property diagram (like $P - V$).

Remark: The internal state of the system and not the surrounding is under study. An internally reversible process is silent about what happens in the surroundings. A system can be internally reversible even if there are significant irreversibility outside of it.

Example: The classic frictionless piston-cylinder assembly. The gas inside is compressed or expanded infinitely slowly. At any point during the process, the gas properties (P, T) are uniform throughout. The path of the process can be perfectly plotted. The temperature gradient between system and surrounding is the source of external irreversibility to be explained in the sequel.

6.3 Externally Reversible Process

An externally reversible process is one where no irreversibility occurs outside the system's boundaries, in the immediate surroundings.

For this case to be true in heat transfer between system and its surroundings, any heat transfer must occur across an infinitesimally small temperature difference ($\Delta T \rightarrow 0$). Finite-temperature heat transfer, is a major source of irreversibility.

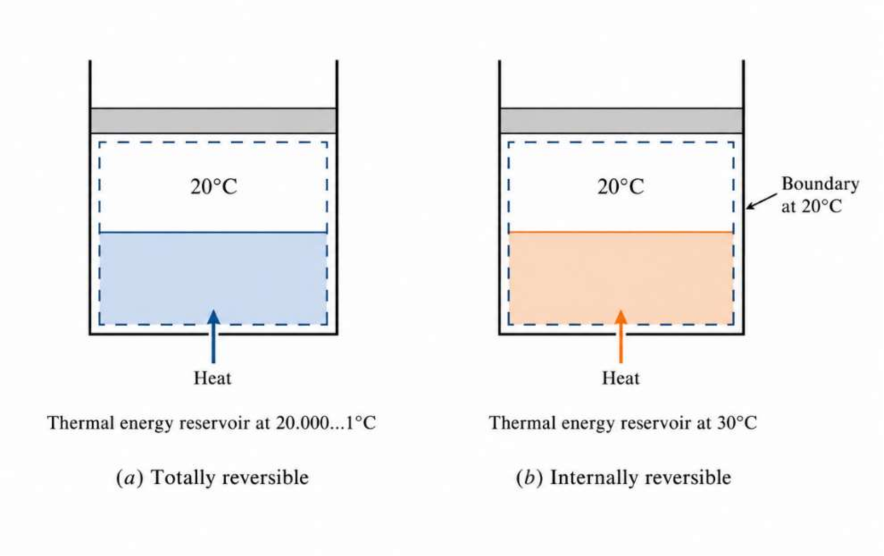
Remark: The interaction between the system and its surroundings is now the key issue.

Example: If a system is at temperature T_{sys}, and the reservoir (part of the surroundings) is at T_{res}. For an exchange of heat, the system must be at $T_{res} = T_{sys} \pm dT$. This is often idealized with "thermal reservoirs" that are so large that their temperature doesn't change when heat is transferred. Moreover, it is assumed that the infinitesimal temperature difference will make the heat transfer back from system to surrounding without any other change in the surrounding. In the sequel we will show that even for infinitesimal temperature gradient true external reversibility is not possible.

6.4 The Totally Reversible Process

A process is called totally reversible only if it is both internally and externally reversible. No irreversibility of any kind exists anywhere.

The system in the left of Figure 6-1 goes through an externally reversible process while the system at the right undergoes a quasi-equilibrium process (internal reversibility).



(*a*) Totally reversible

(*b*) Internally reversible

Figure 6-1: External reversible and internal reversible processes

Remarks:

1. A quasi-static process requires that the system remains essentially in equilibrium, which usually means temperature differences between the system and surroundings must be infinitesimally small and external pressure should be nearly equal to internal pressure. We cannot have a truly internally and externally reversible quasi-static process with finite heat transfer, because that would require a finite driving force, which always introduces irreversibility. However, the true process can be approximated or conceived by making heat transfer very slow. We have to reduce the heat flux by reducing the heat transfer coefficient or increasing the heat transfer area. This allows the gas to almost remain in equilibrium with the surroundings.
2. External reversibility is defined because it is needed to prove ultimate thermodynamic limits, like: maximum work and maximum efficiency (Carnot efficiency). To show no engine can beat a Carnot cycle, we conceptually convert the engine into a reversible heat pump. This requires the surroundings to be reversible, because only then can heat be exchanged and work "undone" (see the next chapter). Without external reversibility the Carnot engine cannot be reversed to work as a heat pump to prove that the most efficient engine is a totally reversible engine.

6.5 Quasi-Equilibrium Compression a limit of totally reversible process

To make this process externally reversible, we must use a mechanism that avoids this loss of potential energy. The theoretical solution is to use a sand pile on the piston instead of discrete weights.

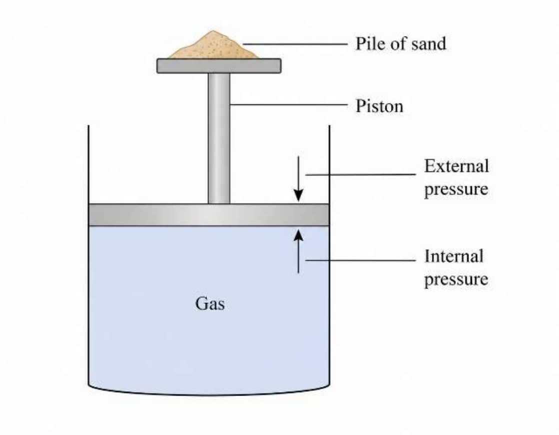


Figure 6-2: The "sand pile" thought experiment demonstrating an externally reversible process. Adding or removing individual grains of sand allows for gas compression and expansion without a net loss of potential energy in the surroundings.

Compression: Instead of adding macroscopic weights, we slowly add fine grains of sand one at a time. Each grain is added at the current height of the piston.

Expansion: To reverse the process, we slowly remove grains of sand one at a time. Each grain is removed from the top of the pile, at its current height.

Result: In this idealized case, every grain of sand is added and removed at the same elevation. There is no net change in the potential energy of the sand/surroundings. The work done on the gas during compression can be fully recovered as work done by the gas during expansion.

This "sand pile" method is the classic thought experiment to illustrate a truly reversible process. This example perfectly highlights why the discrete weight method, even if infinitely slow, fails to achieve total reversibility due to the irreversibility it introduces in the surroundings. This is a key insight for understanding the practical limitations of achieving the ideal cycles described by the Second Law.

Remark: Discussion on nature's magic preventing the exact external reversibility

Now, let's try to reverse the process to restore the system and its surroundings to their exact original states. To expand the gas, we must remove a weight (a grain of sand). Which weight do we remove first? We must remove the last weight we added, which is sitting at the top of the stack. However, to remove it, we must lift it off the piston. At this moment, the piston is at its lowest point. The gas pressure is at its maximum. Now we lift one by one the weights until the piston reaches to its highest point. All weights are removed. We need an extra weight and we can choose the last weight we added that is at the lowest height. To bring this weight from the lowest to highest point, work should be done. This work is needed from the surrounding. Therefore, surrounding is altered.
This was the crux of the issue. Each weight is added at a high potential energy state but is removed at a low potential energy state. To restore the surroundings (the weights) to their initial state, we must find an external source of work to lift them back up. The gas itself cannot provide this work.

6.6 Infinite heat reservoirs the limit of external reversibility

Imagine we have a system that needs to be heated from a cold temperature T_C to a hot temperature T_H. To avoid the irreversibility of finite temperature difference, we propose using an infinite series of heat reservoirs, each one infinitesimally warmer than the previous one, creating a continuous spectrum from T_C to T_H.

The process seems internally reversible: at each instant, the system temperature T_{sys} is only infinitesimally different from the reservoir temperature T_{res} it's contacting ($T_{sys} = T_{res} - dT$). Heat transfer δQ occurs across this infinitesimal difference.

Remark: A Problem is manifested due to the Asymmetry of the First and Last Step

The irreversibility is hidden in the state of the reservoirs themselves after the process.

We start with the system at T_C. We bring it into contact with the first reservoir at $T_C + dT$. Heat δQ flows *into* the system. This reservoir cools down by an infinitesimal amount. Let's say its temperature drops to $T_C + \varepsilon\ (where\ \varepsilon < dT)$. We repeat this, moving up the chain. Each reservoir gives up a finite amount of heat δQ and its temperature drops by a tiny, but non-zero, amount.

Now, to reverse the process, we need to cool the system from T_H back to T_C and restore every single reservoir to its exact original temperature and energy content.

We start with the system at T_H. To cool it reversibly, we must bring it into contact with a reservoir at $T_H - dT$. The reservoir that is supposed to be at $T_H - dT$ is no longer at that temperature! During the forward process, it was used to heat the system and its temperature dropped. It is now at $((T_H - dT) - \delta)$, where δ is its temperature decrease from accepting heat.

To restore the original state of the reservoirs, we would need an external source of “work” to "re-heat" each reservoir back to its original temperature, which is an irreversible act.

Remark: We have no intention to refute the external reversibility as a fundamental concept. We simply demonstrated that it is an ideal concept which can be used to obtain the upper bound of the efficiency of a heat engine. It is similar to finding the limit of an infinite sequence.

6.7 The Discovery and induction of second law from experiments

We begin this section by demonstrating the prime movers invented before the 18th century. They help to understand the proposition used to state verbally the second law.

The Savery Engine: Figure 6-3 shows a vertical section of the principal parts of Savery's engine invented and built around 1690s close to 18th century.

In the figure, letter a explains a receiver, in which the steam presses on the surface of the liquid water. Letter b shows an ascending pipe; c and d, one-way valves opening upwards. f denotes a boiler; g, is a steam pipe from boiler to receiver; h, cock, to open and close it. Letters i and k show combustion flues. l and m, are gauge cocks to ascertain the water level. o, condensing cock, to let a stream of cold water fall on the receiver, and condense the steam. The engine was worked by opening and closing the cocks h and o alternately. On opening h steam flows from the boiler and forces the water from the receiver a up through the pipe b; on closing h, and opening o, the steam was condensed, and the pressure of the atmosphere forces water up through the clack d, so as to fill the receiver again.

The engine was used for draining coal mine. It is shown here to outline the importance of cooling the heated steam in contrast to our intuition which might resist condensing the steam produced by consuming energy. The engine demonstrates that some heat is lost from the steam produced in the boiler. We conclude that all heat consumed in the boiler is not converted to work.

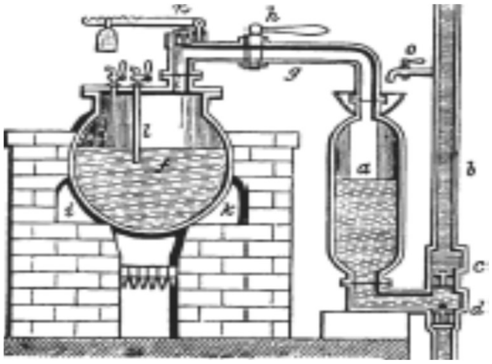


Figure 6-3: Vertical section of the Savery engine, an early thermal machine designed in the 1690s.

The Newcomen Engine (1712): Depicted in figure 6-4, a boiler produced low-pressure steam which filled a large cylinder beneath a piston. The steam valve was closed. A jet of cold water was sprayed into the cylinder, condensing the steam This condensation created a partial vacuum. The pressure of the outside atmosphere (hence "atmospheric engine") then pushed the piston down, which was connected to a pump via a rocking beam. The weight of the pump rods pulled the piston back up, and the cycle repeated.

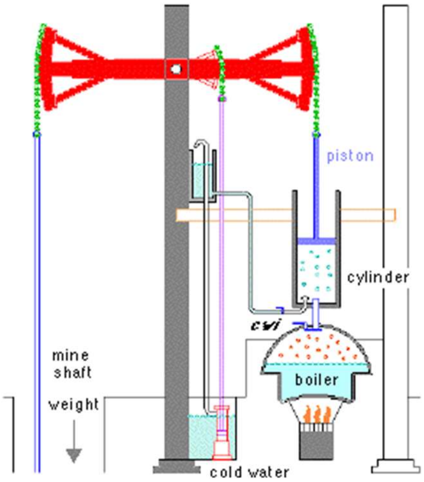


Figure 6-4: Schematic of the Newcomen atmospheric engine (1712).

Remark: The Necessity of Heat Transfer to Surroundings

The Newcomen engine's critical natural flaw was that it had to cool the entire cylinder each cycle. The cold-water spray cooled not just the steam, but the massive brass or iron cylinder itself.
On the next cycle, a large portion of the new steam was instantly condensed by the cold cylinder walls before it could do any work. This steam was used solely to reheat the cylinder. It's estimated that less than 1% of the heat from the coal was converted into useful work.
The heat transfer to the surroundings (the cylinder walls and the cooling water) was not a choice; it was the core mechanism of creating a vacuum. However, this very mechanism made the engine incredibly inefficient because the heat transfer was uncontrolled and excessive.

The Watt Engine (1769): James Watt's revolutionary insight was to realize that to avoid wasting steam totally, the condensation process had to be separated from the main cylinder (see figure 6-5).

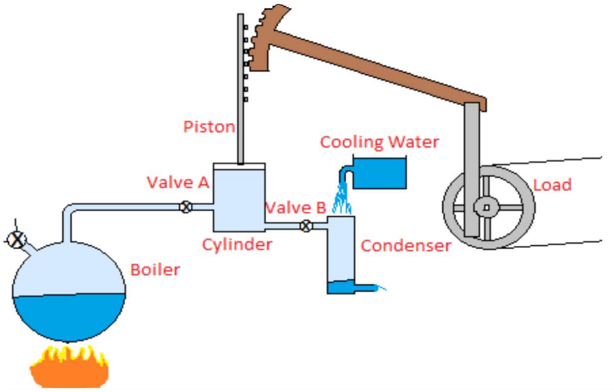


Figure 6-5: Schematic of the Watt engine (1769).

Steam from the boiler entered the main cylinder, pushing the piston up. The steam valve closed, and an exhaust valve opened. The steam was drawn into a separate, cold chamber (the condenser) where it was condensed by a spray of cold water, creating a vacuum. This vacuum pulled the piston down (Watt also sealed the top of the cylinder and used steam pressure for the downstroke as well, making it an engine not limited to atmospheric external force). The main cylinder remained hot throughout the entire cycle.

Watt's design drastically reduced the unnecessary heat transfer to the surroundings. The main cylinder stayed close to the steam temperature, so much less steam was wasted on reheating it each cycle. The heat rejection was now localized and optimized in the separate condenser. This simple change improved efficiency by a factor of more than two, reducing coal consumption by over 60%.

Remarks:

1. The Fundamental Impossibility is that we cannot achieve 100 percent efficiency. Newcomen and Watt engines, despite their radical difference in efficiency, share one unavoidable trait. They must reject a significant amount of waste heat to a cold reservoir (the condenser cooling water). This is not a design flaw but a manifestation of a fundamental law of the universe: the Second Law of Thermodynamics. A heat engine works by transferring heat from a high-temperature source (T_H) to a low-temperature sink (T_C). The flow of heat down this temperature gradient is what we harness to do work, just as a water wheel harnesses the flow of water downhill.
2. The evolution from Newcomen to Watt was a story of understanding and minimizing unnecessary and parasitic heat loss transfer to approach the fundamental limit. However, both engines were utterly dependent on the necessary heat transfer to a cold reservoir to function at all. This necessity is not an engineering limitation but a profound consequence of the Second Law, which dictates that a cyclic engine must always reject some energy as heat

to a cold reservoir to create the driving gradient and reset itself, making perpetual motion machine impossible (see section 6.3).

6.8 The Kelvin-Planck Statement of the Second Law

It is impossible to construct a device that operates in a cycle and whose sole effect is the absorption of heat from a single thermal reservoir and the performance of an equivalent amount of work.

This statement is not a theoretical conjecture; it is a generalization from every experimental attempt to build a certain kind of engine throughout history. It is indeed inferred from an induction method thanks to experiments. The operation of the engine can be conceptually depicted as in figure 6-6. Based on the first law of thermodynamics the work of the engine is the Q_H-Q_C. If we define efficiency as Work/Q_H, we conclude that the ratio must be always less than 1 or 100 percent for any heat engine that is constructed or will be constructed.

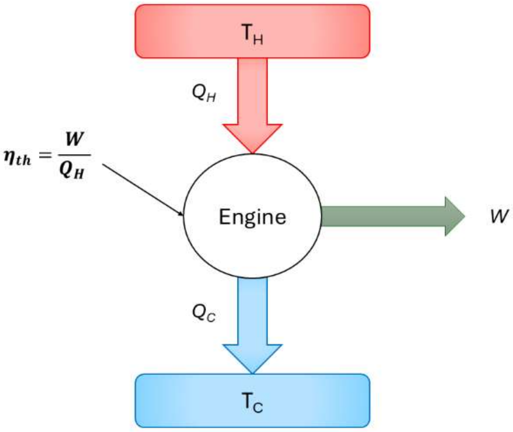


Figure 6-6: Operation of a heat engine between hot and cold reservoirs

Remark: The need for a cold reservoir, as stated in the Kelvin–Planck statement of the second law of thermodynamics, can be illustrated by considering how a magnet causes motion in a metal bar. While the magnet can perform work by attracting the bar, achieving continuous (cyclic) work requires us to expend work to separate the metal from the magnet—this acts as the necessary "reset" step, analogous to rejecting heat to a cold reservoir in a heat engine.

Note that the analogy is not a derivation of the Kelvin–Planck statement of the second law.

6.9 The Clausius Statement of the Second Law

Heat cannot spontaneously flow from a colder body to a hotter body.

In a more formal and complete phrasing:

It is impossible to construct a device that operates in a cycle and whose sole effect is the transfer of heat from a cooler to a hotter body.

Remarks: Key Implications and Explanation of Second Law

1. "Spontaneously" and "Sole Effect": These are the crucial words. The statement does not say that heat can never be transferred from cold to hot. This happens all the time in devices like refrigerators and air conditioners. What the Clausius statement forbids is doing this without any other change. In a refrigerator, work must be done (by the compressor) to force the heat to flow from the cold interior to the warm room. This input of work is the "other effect," making the process possible. In an absorption refrigeration cycle considerable heat plus pump work is needed for the operation.
2. Second law dictates the Direction of Heat Flow: It establishes the natural, irreversible direction of heat transfer, from high temperature to low temperature.

The Clausius statement is one of two classic, equivalent statements of the second law. The other is the Kelvin-Planck statement mentioned previously. While the Kelvin-Planck statement focuses on the impossibility of a perfect heat engine (100% efficiency), the Clausius statement focuses on the impossibility of an ideal refrigerator or heat pump (one that needs no energy input). It can be proven that if we could violate one, we could violate the other. They are two sides of the same coin (see section 6.2.3).

Just as water does not spontaneously flow uphill without a water pump, heat does not spontaneously flow from a cold object to a hot object without the "work" of a refrigerator that can be considered as a heat pump, in analogy.

For centuries, engineers and inventors have tried to create a device falsifying the second law. Every single attempt has failed. No engine, no matter how cleverly designed, has ever been observed. It is the outcome of a universal experimental failure.

The engine operates in a cycle (the working fluid returns to its initial state to run continuously). It is impossible to receive heat from a single source (e.g., the atmosphere, the ocean), and convert that heat entirely into useful work with 100% efficiency as shown in the Figure 6-7.

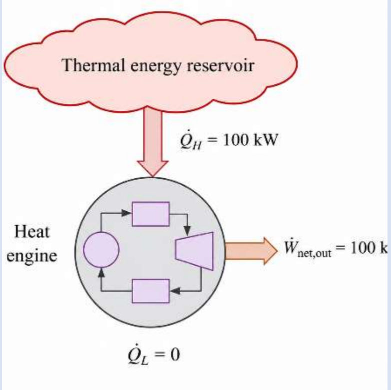


Figure 6-7: Schematic of a heat engine with 100% efficiency

The Kelvin-Planck statement is the formalization of this universal experimental observation. Since no experiment has ever violated this principle, we elevate it to a fundamental law of nature.

It is a common misconception that the Second Law of Thermodynamics forbids the conversion of heat into work. The law is more precise. The Kelvin-Planck statement explicitly forbids a cyclic device from performing this conversion while interacting with a single reservoir.

However, for a process (a non-cyclic, one-time transformation of a system from an initial state to a final state), it is indeed possible to convert heat entirely into work as in the following case. An ideal gas is placed in a piston-cylinder assembly and brought into contact with a single thermal reservoir at temperature T. The gas is allowed to expand slowly and isothermally (at constant temperature). For an ideal gas, internal energy U is a function of temperature only. Since $\Delta T = 0$, then $\Delta U = 0$. The First Law ($\Delta U = Q - W$) therefore simplifies to the following equation.

$$0 = Q - W \rightarrow Q = W$$

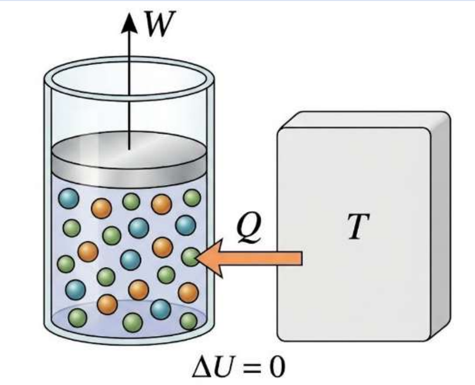


Figure 6-8: Schematic representation of the slow, isothermal expansion of an ideal gas in a piston-cylinder.

7. The Kelvin-Planck statement contains two critical clauses that the process explained in the item 9 does not satisfy: "...operates in a cycle...". The isothermal expansion is a process, not a cycle. The system ends in a different state (a larger volume, lower pressure) than it started. To reset the system and create a cycle, work would have to be done on the gas to compress it back to its original volume. This compression would require more work than the expansion produced, or would necessitate rejecting heat to a colder reservoir, thus violating the "sole effect" clause. "...whose sole effect...". The "sole effect" is not just the absorption of heat and performance of work. There is another, crucial effect, the system itself has changed (its volume has increased, and its pressure has decreased). In summary, the Second Law does not prohibit the complete conversion of heat into work in a single process. It prohibits the construction of a device that can do so continuously in a cycle without causing any other net change in the universe. This distinction is fundamental to understanding the difference between a one-time energy conversion and the sustainable operation of a heat engine.

6.10 The Thought Experiment: Equivalence of Kelvin-Planck and Clausius statement

Suppose, contrary to the Clausius statement, that a device X exists which can transfer heat from a cold reservoir to a hot reservoir with no other effect (i.e., without requiring work input). This is the "engine which transfers heat from cold to hot without needing work".

Now, operate a normal, reversible heat engine between the same two reservoirs. It absorbs heat Q_H from the hot reservoir, rejects heat Q_C to the cold reservoir, and produces work $W_{out} = Q_H - Q_C$.

Let the work output (W_{out}) from the reversible heat engine be used to drive a separate, unrelated process (e.g., lifting a weight). This is allowed. Crucially, the device X is operating for free.

Now, consider the combined system (Device X + Reversible Heat Engine) as a single "engine box".

Device X takes heat Q from the cold reservoir. The reversible heat engine rejects heat Q_C to it. The net heat transfer from the cold reservoir is $(Q - Q_C)$. The reversible heat engine takes heat Q_H from the hot reservoir. Device X dumps the same heat Q into it. The net heat transfer from the hot reservoir is $(Q_H - Q)$. The combined system produces a network output W_{out}.

Now, let's adjust the scale. Let the reversible heat engine be designed so that its rejected heat Q_C is exactly equal to the heat Q that device X pumps. Therefore,$Q_C = Q$.

With $Q_C = Q$, the net effect of the combined system is:

Net heat transfer to cold reservoir: $Q - Q_C = 0$.

Net heat transfer from hot reservoir: $Q_H - Q$.

The system produces work $W_{out} = Q_H - Q_C = Q_H - Q$.

The sole, net effect of this combined system is to absorb heat $(Q_H - Q)$ from a single thermal reservoir (the hot reservoir) and produce an equivalent amount of work $(W_{out} = Q_H - Q)$.

This is a direct violation of the Kelvin-Planck statement of the Second Law.

6.11 On the Impossibility of a Perpetual Motion Machine of the Second Kind (PMM2)

A Perpetual Motion Machine of the Second Kind (PMM2) is defined as a cyclic device that operates with 100% thermal efficiency. That is, it would convert all heat absorbed from a single thermal reservoir entirely into an equivalent amount of useful work, without producing any other effect on its surroundings.

The universal rejection of such a machine is not based on practical engineering challenges but is a direct consequence of the Second Law of Thermodynamics. The impossibility of a PMM2 can be proven by demonstrating that its existence would violate both fundamental statements of the Second Law.

We proceed by first Violating of the Kelvin-Planck Statement.

The Kelvin-Planck statement asserts that it is impossible for any device to operate in a cycle and produce no other effect than the exchange of heat with a single reservoir and the performance of an equivalent amount of work.

Let us assume, for the sake of argument, that a PMM2 is possible. This machine (M_1) would receive heat Q from a single reservoir at temperature T_H and produce an equal amount of work $W = Q$.

Now, let us use this work W to drive a reversible heat pump (M_2) operating between two reservoirs at T_H and T_L (where $T_H > T_L$). The heat pump consumes the work W to transfer heat Q_H from the low-temperature reservoir to the high-temperature reservoir. From the definition of a heat pump, the first law dictates that $Q_H = W + Q_L$, meaning it deposits more heat (Q_H) into the high-temperature reservoir than the work (W) it consumes.

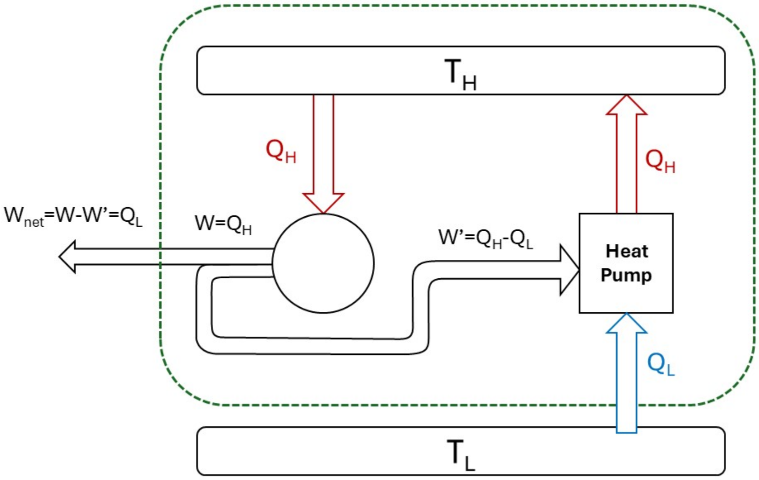


Figure 6-9: Illustrating the violation of the Kelvin-Planck statement leading to a hypothetical PMM2

The net effect of this combined system ($M_1 + M_2$) is:

The network input is zero (W produced by M_1 equals W consumed by M_2).

The heat Q taken from the high-temperature reservoir by M_1 is less than the heat Q_H dumped back into it by M_2.

The only final result is that a net amount of heat ($Q_H - Q$) has been transferred from the cold reservoir (T_L) to the hot reservoir (T_H) with no external work input.

This final result is a direct violation of the Clausius statement of the Second Law. Since the Clausius and Kelvin-Planck statements are equivalent, the initial assumption that the PMM2 (M_1) is possible must be false. Therefore, if a PMM2 violates the Kelvin-Planck statement the only final result is that heat Q_C has been transferred from the cold reservoir to the hot reservoir with no external work input or any other net effect. This is a direct and clear violation of the Clausius statement. Therefore, the initial assumption that a PMM2 is possible must be false.

The existence of a Perpetual Motion Machine of the Second Kind would violate the Second Law of Thermodynamics. This is not a limitation of engineering but a fundamental law of nature. The Second Law establishes a fundamental asymmetry in the universe: work can be completely converted into heat, but heat cannot be completely converted into work without rejecting a portion of it to a colder reservoir. This principle is the very foundation for the concept of efficiency limits in all heat engines.

Chapter 7 The Carnot Cycle an Ideal Internal and External Reversible Engine

Driven by the 19th century's pressing need to drain coal mines efficiently, Sadi Carnot in 1820s analyzed the practical limitations of engines like Newcomen's and Watt's. His seminal work proved that a heat engine's maximum possible efficiency is bounded solely by its operating temperatures, as calculated by $\eta_{max} = 1 - T_C/T_H$, where η is defined as thermal efficiency. This mathematical law finds its physical counterpart in the Kelvin-Planck statement of thermodynamics, discussed in section 6.2.

Since T_C is always greater than absolute zero, the efficiency is always less than 100%. The Newcomen and Watt engines, operating between T_H (boiling water) and T_C (cooling water), were subject to this same unbreakable limit. Watt didn't break the Second Law; he simply designed an engine that operated much closer to its theoretical maximum efficiency for its temperature range.

Nicolas Léonard Sadi Carnot did not build a physical, working version of the engine he described. However, his theoretical analysis of an idealized heat engine—now known as the Carnot engine—is one of the most fundamental and brilliant contributions to the science of thermodynamics.

Here's a breakdown of the story:

a) What Carnot Did (The Theory)

In 1824, Carnot published a groundbreaking book, *Reflections on the Motive Power of Fire*.

- **The Goal:** He wanted to understand and improve the efficiency of steam engines, which were driving the Industrial Revolution. The key question was: Is there a fundamental limit to the efficiency of any heat engine?
- **The Method:** He used a purely theoretical and conceptual approach. He imagined an idealized, perfectly reversible heat engine cycle (now called the Carnot Cycle) operating between two heat reservoirs at different temperatures.
- **The Discovery:** Through this thought experiment, he established what we now call the Carnot Principle:
    1. The efficiency of a heat engine depends only on the temperatures of the hot and cold reservoirs.
    2. No heat engine can be more efficient than a reversible Carnot engine operating between the same two temperatures (to be demonstrated later).
    3. All reversible engines operating between the same temperatures have the same efficiency (to be demonstrated later).

4. It seems that work produced by a water fall which is proportional to the difference in height has inspired him to infer that temperature difference would be similar to height difference.

b) He Didn't Build It

- **An Idealization:** The Carnot engine is a theoretical model. It assumes processes that are perfectly reversible (with no friction, turbulence, or heat loss) and infinitely slow. Such a machine is impossible to build in reality.
- **Limitations of the Era:** The materials and precision engineering required to even attempt an approximation of his cycle did not exist in the 1820s.

c) Analogy: Think of it like this: Physicists use the concept of a "frictionless surface" to understand the laws of motion, even though such a surface can't be built. Similarly, Carnot used the concept of a "reversible Carnot engine" to understand the ultimate limits of heat engines.

d) Discussion: So, while Carnot never built a physical Carnot engine, his theoretical work was so powerful and correct that it established the absolute benchmark for engine performance and became the cornerstone of a new scientific field: thermodynamics. His "engine" exists on paper and in the minds of scientists and engineers, guiding the design and understanding of all real-world engines, from car motors to power plants.

e) The Problem with Real Engines (The "Mess"): Real steam engines of his time were messy. They involved:

- Many different temperatures (the fire, various parts of the boiler, the cylinder walls, the condenser).
- Open cycles where steam was released.
- Irreversible processes like friction, rapid combustion, and uncontrolled heat flow.

This work laid the foundation for the Second Law of Thermodynamics, which would be formally stated by scientists like Clausius and Kelvin decades later and we discussed it in section 6.2.

7.1 Carnot's Stroke of Genius (The "Elegant Abstraction")

Carnot realized that to find the fundamental limit, he had to strip away all the mess and think about an ideal, perfect engine. His key decisions were:

- **Only Two Heat Reservoirs:** This is the masterstroke. By restricting the heat exchange to only two fixed temperatures (the source and the sink), he created a beautifully simple boundary for the problem. All heat input comes from one place; all heat rejection goes to another.

- **The Use of an "Ideal Gas":** While he initially thought in terms of a caloric fluid, his cycle works perfectly with an ideal gas. The ideal gas provides a simple, well-understood working substance where temperature is directly linked to internal energy and volume via a simple equation of state. This made the theoretical analysis mathematically tractable later during the second half 19th century.
- **The Two Adiabats: The "Crucial Bridge"**: They connect the two temperatures without heat transfer. An isothermal process is "stuck" at one temperature. To get from the high temperature T_{hot} to the low temperature T_{cold} (and back) without interacting with an infinite number of intermediate-temperature reservoirs, we need a process that changes temperature solely through work. That's what the adiabatic steps do.
- **The "Magic" of the 4-Step Cycle:** In the Isothermal Expansion at T_{hot} the gas receives heat Q_H from the hot reservoir and does work. In the Adiabatic Expansion the gas thermally isolates itself and cools down from T_{hot} to T_{cold} purely by doing work. In the Isothermal Compression at T_{cold} the gas rejects waste heat Q_C to the cold reservoir as work is done on the gas. In the adiabatic compression**,** the gas thermally isolates itself and is compressed, causing its temperature to rise from T_{cold} back to T_hot purely from the work done on it. The adiabatic steps are the perfect "glue" that seamlessly connects the two isothermal steps, creating a closed, reversible cycle that operates between only two reservoirs.
- **Epilogue:** Carnot's greatness wasn't in inventing a new machine, but in using a powerful theoretical model to ask the right question: "What is the absolute best any engine can possibly do?" By choosing the two-isothermal/two-adiabatic processes, he found the answer in the most elegant way possible, laying the groundwork for the entire field of thermodynamics. It was a conceptual leap of the highest order. In the 1830s and 1840s, other scientists, including Benoît Paul Émile Clapeyron, expanded upon Carnot's work. It was Clapeyron who later collaborated to formalize the Ideal Gas Law ($PV = nRT$) in 1834 and is widely credited with creating and using the P-V diagram to illustrate the Carnot cycle, making Carnot's ideas more accessible and easier to analyze.

7.2 Mathematical Formulation of Carnot Cycle (Engine)

The engine (the working fluid) absorbs heat Q_H isothermally from a hot reservoir at a constant T_H and rejects heat Q_c isothermally to a cold reservoir at a constant T_c. The cycle consists of two isothermal and two adiabatic processes. The shape and slope of the curves will be discussed later.

All heat transfer occurs at constant temperature. The system itself changes temperature adiabatically (during reversible compression/expansion), not by contacting a spectrum of reservoirs. When the system is at T_H, it is in contact only with the T_H reservoir. When the system is at T_C, it is in contact only with the T_C reservoir.

The reservoirs, by definition, are so large that their temperatures do not change when finite amounts of heat are added or removed (Q_H and Q_C). Therefore, the reservoir that accepted heat during the reverse process is still at precisely the correct temperature to donate it during the forward process, and vice-versa.

The Carnot cycle achieves true reversibility (internal and external reversibility) by ensuring that all processes are quasi-static and frictionless. A key to this is the condition that during the isothermal heat transfer stages, the temperature of the working gas differs only infinitesimally from that of the respective reservoir. This infinitesimal temperature gradient drives the heat transfer (Q_H in, Q_C out) at a rate slow enough to be reversed by an equally infinitesimal change in conditions, thus eliminating the irreversible dissipation of energy that occurs with a finite temperature difference. The infinitesimal temperature gradient is crucial when we will reverse the operation of the heat engine to a heat pump for proving the mathematical maximum efficiency of the Carnot engine (see the following section).

7.3 On the shape of Carnot Cycle

First, we find the slopes of each process for an ideal gas.

For any process, the First Law is expressed as:

$$dU = \delta Q - \delta W \tag{7-1}$$

For the adiabatic processes we have: $\delta Q = 0$

For Quasi-Equilibrium processes we have: The work is given by $\delta W = PdV$

Substituting these conditions into the First Law:

$$U = -PdV \tag{7-2}$$

For an ideal gas, internal energy U is a function of temperature only, $U = U(T)$. The change in internal energy is given by:

$$dU = mc_v dT \tag{7-3}$$

where m is mass and c_v is the specific heat at constant volume.

Substitute Equation 2 into Equation 1:

$$mc_v dT = -PdV \tag{7-4}$$

The ideal gas law is $PV = mRT$, where R is the specific gas constant. We can solve for pressure P:

$$P = \frac{mRT}{V} \tag{7-5}$$

Substitute this expression for P into Equation (7-4):

$$mc_v dT = -\left(\frac{mRT}{V}\right) dV \tag{7-6}$$

Or

$$\frac{c_v}{T} dT = -\frac{R}{V} dV \tag{7-7}$$

$$\int_{T_1}^{T_2} \frac{c_v}{T}\, dT = -\int_{V_1}^{V_2} \frac{R}{V} dV \tag{7-8}$$

Since c_v is constant for an ideal gas, we can take it out of the integral:

$$c_v \int_{T_1}^{T_2} \frac{1}{T}\, dT = -R \int_{V_1}^{V_2} \frac{1}{V} dV \tag{7-9}$$

Perform the integration:

$$c_v l\, n\left(\frac{T_2}{T_1}\right) = -R l\, n\left(\frac{V_2}{V_1}\right) \tag{7-10}$$

$$l\, n\left(\frac{T_2}{T_1}\right)^{c_v} = l\, n\left(\frac{V_1}{V_2}\right)^{R} \tag{7-11}$$

Since the natural logarithm is a one-to-one function, we can equate the arguments:

$$\left(\frac{T_2}{T_1}\right)^{c_v} = \left(\frac{V_1}{V_2}\right)^{R} \tag{7-12}$$

This is equivalent to:

$$T_2^{c_v} V_2^{R} = T_1^{c_v} V_1^{R} \tag{7-13}$$

Therefore, for any state during this process,

$$TV^{R/c_v} = constant \tag{7-14}$$

We know from the previous derivation that for an ideal gas, $c_p - c_v = R$. The ratio of specific heats is defined as:

$$\gamma = \frac{c_P}{c_v} \tag{7-15}$$

We can express $\frac{R}{c_v}$ in terms of γ:

$$R = c_P - c_v \tag{7-16}$$

$$\frac{R}{c_v} = \frac{c_P - c_v}{c_v} = \frac{c_P}{c_v} - 1 = \gamma - 1 \tag{7-17}$$

Substitute this into Equation (7-14):

$$TV^{\gamma-1} = constant \tag{7-18}$$

We now use the ideal gas law $PV = mRT$ to eliminate T. From the ideal gas law:

$$T = \frac{PV}{mR} \tag{7-19}$$

Substitute this into Equation (7-18):

$$\left(\frac{PV}{mR}\right) V^{\gamma-1} = constant \tag{7-20}$$

Since m and R are themselves constants, we can simplify this to:

$$PV^{\gamma} = constant \tag{7-21}$$

Thus, for a quasi-equilibrium adiabatic process of an ideal gas with constant specific heats, the relationship between pressure and volume is:

$$PV^{\gamma} = constant \tag{7-22}$$

where $\gamma = \frac{c_p}{c_v}$ is the ratio of specific heats.

For an isothermal process, temperature T is constant. We can write the ideal gas law as:

$$P = \frac{nRT}{V} \tag{7-23}$$

To find the slope on a P-V diagram (dP/dV), we differentiate p with respect to V, holding T constant:

$$\left(\frac{dP}{dV}\right)_{\text{iso}} = -\frac{nRT}{V^2} \tag{7-24}$$

We can substitute $P = nRT/V$ back into this equation to express the slope purely in terms of p and V:

$$\left(\frac{dP}{dV}\right)_{\text{iso}} = -\frac{P}{V} \tag{7-25}$$

For an adiabatic process, the governing equation is $PV^{\gamma} = K$ (where K is a constant).

We can write this as:

$$P = KV^{-\gamma} \tag{7-26}$$

Now, we differentiate p with respect to V:

$$\left(\frac{dP}{dV}\right)_{\text{adi}} = K(-\gamma)V^{-\gamma-1} \tag{7-27}$$

Notice that $KV^{-\gamma} = P$. Let's substitute this back in:

$$\left(\frac{dP}{dV}\right)_{\text{adi}} = -\gamma\frac{P}{V} \tag{7-28}$$

We now have the two slopes at a specific point (P, V) on the p-V diagram:

Isothermal Slope: $\left(\frac{dP}{dV}\right)_{\text{iso}} = -\frac{P}{V}$

Adiabatic Slope: $\left(\frac{dP}{dV}\right)_{\text{adi}} = -\gamma\frac{P}{V}$

Because $\gamma > 1$, it is clear that:

$$\left|\left(\frac{dP}{dV}\right)_{\text{adi}}\right| > \left|\left(\frac{dP}{dV}\right)_{\text{iso}}\right| \tag{7-29}$$

Both slopes are negative, but the adiabatic slope is more negative. On a P-V diagram, this means the adiabatic curve has a steeper downward slope.

The difference arises from what happens when we change the volume.

In an isothermal expansion, as volume V increases, pressure p decreases simply because the gas has more space ($P \propto 1/V$). The temperature is kept constant by absorbing heat from the surroundings. In an adiabatic expansion, as volume V increases, two things cause the pressure to drop. The volume increases ($P \propto 1/V$ effect). The gas does work to expand but cannot absorb any heat (adiabatic condition). Therefore, its internal energy decreases, and so does its temperature. A lower temperature further reduces the pressure (from $P \propto T$).

This combined effect of decreasing volume and decreasing temperature makes the pressure drop much more rapidly in an adiabatic process than in an isothermal one, resulting in a steeper slope on the p-V diagram (see Figure 7-1).

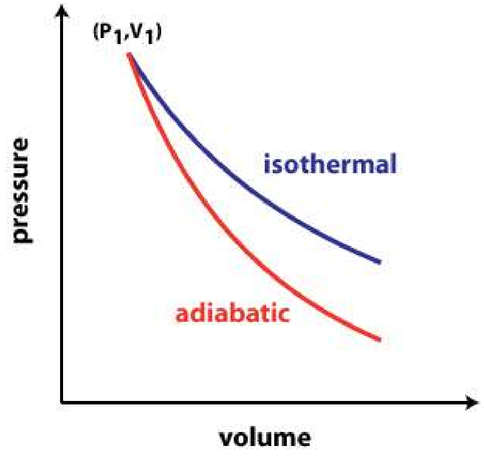


Figure 7-1: P-V diagram of isothermal and adiabatic process

7.4 The efficiency of Carnot engine (Figure 7-2 below)

1. **For the Isothermal Expansion (A → B)**

- Process is reversible, isothermal at T_H, so the energy for an ideal gas undergoing an isothermal process, the change in internal energy is zero ($\Delta U = 0$).
- From the first law: $\Delta U = Q + W$ implies $Q_H = -W_{AB}$.
- Work Done by the Gas: The work done by the gas in a reversible (quasi-equilibrium) isothermal expansion is:

$$W_{AB} = -\int_{V_A}^{V_B} P\,dV = -n\overline{R}T_H \int_{V_A}^{V_B} \frac{dV}{V} = -n\overline{RT_H}\ln\left(\frac{V_B}{V_A}\right) \quad (7\text{-}30)$$

- Heat Input: Since $Q_H = -W_{AB}$, we have:

$$Q_H = n\bar{R}T_H \ln\left(\frac{V_B}{V_A}\right) \tag{7-31}$$

2. **For the adiabatic Expansion (B → C)**

- **Process:** Reversible, adiabatic. $Q = 0$.
- **Energy:** The gas does work on the surroundings at the expense of its own internal energy, causing its temperature to drop from T_H to T_C. For a reversible adiabatic process in an ideal gas, $TV^{\gamma-1} =$ constant. Therefore:

$$T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1} \tag{7-32}$$

3. **For the Isothermal Compression (C → D)**

- The process is reversible, isothermal at T_C. Again, $\Delta U = 0$.
- From the First Law: $|Q_C| = -W_{CD}$. (Note: W_{CD} is positive because work is done on the gas).
- **Work Done on the Gas:**

$$W_{CD} = -\int_{V_C}^{V_D} P\,dV = -n\bar{R}T_C \ln\left(\frac{V_D}{V_C}\right) \tag{7-33}$$

- **Heat Rejected:** The magnitude of heat rejected to the cold reservoir is $|Q_C| = -W_{CD}$, so:

$$|Q_C| = n\bar{R}T_C \ln\left(\frac{V_C}{V_D}\right) \tag{7-34}$$

4. **For the Adiabatic Compression (D → A)**

- Process is reversible and adiabatic. $Q = 0$.
- Work is done on the gas, increasing its internal energy and temperature from T_C back to T_H. For an adiabatic process of ideal gas, we have:

$$T_H V_A^{\gamma-1} = T_C V_D^{\gamma-1} \tag{7-35}$$

5. **Manipulating Equations**: Now we use the adiabatic equations to relate the volumes. Dividing equation (7-32) by equation (7-35):

$$\frac{T_H V_B^{\gamma-1}}{T_H V_A^{\gamma-1}} = \frac{T_C V_C^{\gamma-1}}{T_C V_D^{\gamma-1}} \tag{7-36}$$

Canceling T_H and T_C, we get:

$$\frac{V_B^{\gamma-1}}{V_A^{\gamma-1}} = \frac{V_C^{\gamma-1}}{V_D^{\gamma-1}} \implies (\frac{V_B}{V_A})^{\gamma-1} = (\frac{V_C}{V_D})^{\gamma-1} \tag{7-37}$$

Taking the $(\gamma - 1)$-th root of both sides gives the crucial volume ratio identity:

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} \tag{7-38}$$

6. Calculation of Efficiency

We now substitute our expressions for heat into the efficiency formula.

From (1): $Q_H = nRT_H \ln(\frac{V_B}{V_A})$

From (3): $| Q_C | = nRT_C \ln(\frac{V_C}{V_D})$

From (5): $\frac{V_B}{V_A} = \frac{V_C}{V_D}$, so $\ln(\frac{V_B}{V_A}) = \ln(\frac{V_C}{V_D})$

Let's call this common logarithm value $\mathcal{L}$.

Now, plug into the efficiency formula:

$$\eta = 1 - \frac{| Q_C |}{Q_H} = 1 - \frac{n\bar{R}T_C\mathcal{L}}{n\bar{R}T_H\mathcal{L}} \tag{7-39}$$

Canceling the common factors n, R, and $\mathcal{L}$, we arrive at the final result:

$$\eta = 1 - \frac{T_C}{T_H} \tag{7-40}$$

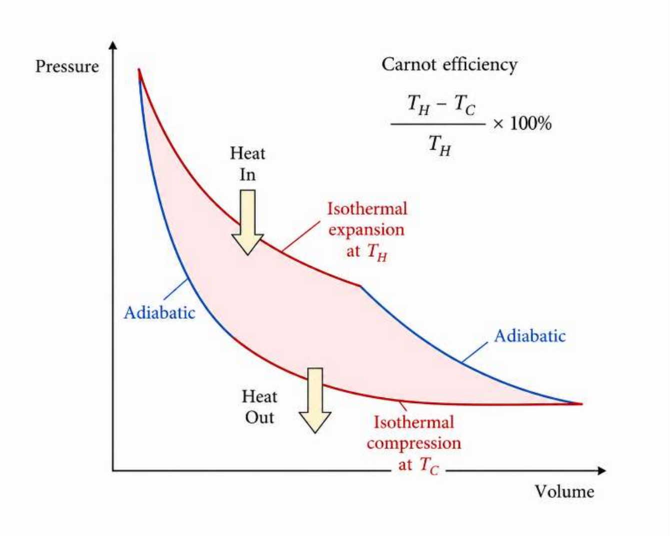


Figure 7-2: P-V diagram of Carnot engine cycle

7.5 Proof of the upper bound of efficiency of a reversible engine

Proving $\eta = 1 - T_C/T_H$ for an ideal gas doesn't automatically prove it's the universal maximum efficiency. This only shows that for an ideal gas Carnot engine with reversible processes, efficiency is $1 - T_C/T_H$.

It doesn't prove that no other engine (using different working substances or cycles either reversible or irreversible) could be more efficient.

The general proof relies on the Kelvin-Planck statement and the concept of reversible engines.

Here's the logic:

Step 1: Define Our Engines

Consider two engines operating between the same temperatures T_H and T_C:

- Engine R: A reversible Carnot engine (any working substance)
- Engine X: Any other heat engine (could be irreversible)

Step 2: The Coupling Argument (The Key Insight About Reversibility)

This is where the definition of ideal reversible process allows "reversing the engine" and becomes crucial:

1. Scale engine X so it absorbs the same Q_H as engine R
2. Reverse engine R to make it work as a heat pump (this is possible precisely because it's reversible)
3. Couple them together: Use the work output from engine X to drive the reversed engine R

Step 3: The Contradiction That Proves the Theorem

Now analyze the composite system:

- If $\eta_X > \eta_R$:
  - Engine X produces more work than needed to drive engine R
  - The excess work could be used externally
  - The net effect: Heat transferred from cold to hot reservoir with no external work input
  - This violates the Clausius statement of the second law
- If $\eta_X = \eta_R$:
  - The system is in perfect balance
  - No violation occurs
- If $\eta_X < \eta_R$:
  - Engine X cannot drive engine R
  - No violation occurs

Remarks:

a) Why Reversibility is Crucial.

1. Only reversible engines with externally reversible processes can be perfectly reversed to become heat pumps.
2. The temperature equality (infinitesimal ΔT during heat transfer) ensures external reversibility.
3. This allows us to create the "perfect coupling" between the engines

b) The Deeper Significance: The recognition that "the relation found from ideal gas is just a special case" shows an excellent physical intuition. The true power of Carnot's insight was recognizing that his conclusion must be general, even though he could only analyze specific cases This general proof, developed by Clausius and Kelvin, is what elevates Carnot's principle from an interesting observation about steam engines to a fundamental law of nature governing all energy conversion processes. No engine can be more efficient than a reversible engine (a Carnot engine) operating between the same two reservoirs. All reversible engines operating between the same two reservoirs have the same efficiency.

c) At this point we conclude that two reversible Carnot engines, even when using different working fluids, have the same efficiency when operating between the same two thermal reservoirs. Therefore, the efficiency cannot depend on the nature of the working substance; the only remaining free variables are the temperatures of the hot and cold reservoirs.

Or more formally: Since all reversible Carnot engines operating between the same two reservoirs possess identical efficiencies regardless of working fluid, the efficiency must be a universal function depending only on the reservoir temperatures.

Readers may think that the proof of Carnot efficiency is valid only for ideal gases. On the contrary, suppose that in the isothermal heat-receiving process, the working fluid is a liquid that is converted to vapor at constant temperature and pressure, and in the heat-releasing process, the working fluid partially condenses, also at constant temperature and pressure

7.6 Mathematical Proving of the Carnot efficiency for any reversible engine in contact with only two heat reservoirs

In the section 74, we proved the Carnot cycle efficiency. In the proof we implicitly assumed quasi-equilibrium processes to be able to integrate using working fluid properties. Moreover, we did not discuss the temperature gradient necessary for the two isothermal heat transfer processes. In section 7.3 we proved that the efficiency of a reversible engine is greater than the any irreversible engine in contact with similar heat reservoirs. However, we should prove that irrespective of detail and assumptions of Carnot cycle the algebraic efficiency formula or mathematical efficiency function for any cycle in contact with two reservoirs depends only on T-H and T-C.

If other variables other than the temperatures of heat reservoirs are responsible then Carnot ideal gas case fails. If the efficiency of a reversible engine depended on something else besides temperature, then the ideal gas Carnot engine, which we can calculate, would give a formula $\eta = 1 - T_c/T_h$ in the special case. If that formula were not universal – if a different working substance gave a different efficiency at the same T_c, T_h – then the ideal gas would be just one of many possibilities, and Carnot's theorem would be false. But experiments (and the Second Law) show that it is universal, within the precision of measurement. Classical thermodynamics asserts (and experiments confirm) that for pure thermal reservoirs (no chemical reactions, no magnetic fields, no other work interactions), no such extra variables matter. This is an empirical fact, not a logical deduction.

Proof:

Let engine R_1 absorb heat Q_A from reservoir at T_A and reject heat Q_B to reservoir at T_B.

Since R_1 is reversible, the heat ratio is a function of temperatures:

$$\frac{Q_A}{Q_\mathrm{B}} = g(T_\mathrm{A}, T_\mathrm{B}) \tag{7-41}$$

Let engine R_2 absorb heat Q_B from reservoir at T_B and reject heat Q_C to reservoir at T_C.

Since R_2 is reversible:

$$\frac{Q_{\mathrm{B}}}{Q_{\mathrm{C}}} = g(T_{\mathrm{B}}, T_{\mathrm{C}}) \tag{7-42}$$

Combined Engine (R_1+ R_1R_2+ R_2) between T_{A} and T_{C}:

The heat rejected by R_1 to T_{B} is exactly absorbed by R_2 from T_{B}, so there is no net heat exchange with T_{B}.

The combined engine absorbs heat Q_A from T_A and rejects heat Q_C to T_C.

The heat ratio for the combined engine is:

$$\frac{Q_A}{Q_{\mathrm{C}}} = \frac{Q_A}{Q_{\mathrm{B}}} \cdot \frac{Q_{\mathrm{B}}}{Q_{\mathrm{C}}} = g(T_A, T_{\mathrm{B}}) \cdot g(T_B, T_C) \tag{7-43}$$

Let engine R_3 absorb heat $Q_A{}'$ from T_A and reject heat $Q_C{}'$ to T_C.

Since $R3$ is reversible:

$$\frac{Q_A{}'}{Q_C{}'} = g(T_A, T_C) \tag{7-44}$$

Both the combined engine (R_1+ R_1R_2+ R_2) and engine R_3 operate reversibly between T_A and T_C. Therefore, they must have the same heat ratio:

$$g(T_A, T_C) = g(T_A, T_B) \cdot g(T_B, T_C) \tag{7-45}$$

This functional equation must hold for any temperatures T_A, T_B, and T_C.

The equation $g(T_A, T_C) = g(T_A, T_B) \cdot g(T_B, T_C)$ implies that g can be expressed as a ratio of functions of a single temperature:

$$g(T_H, T_C) = f(T_H)/f(T_C) \tag{7-46}$$

where f is a function depending only on temperature.

Remark:

Proof of equation (7-46) **is demonstrated below:**

We start with the functional equation

$$\phi(T_1, T_3) = \phi(T_1, T_2) \cdot \phi(T_2, T_3) \tag{7-47}$$

Assume $\phi > 0$ and define:

$$\psi(T_a, T_b) = \ln\left(\phi(T_a, T_b)\right) \tag{7-48}$$

Taking the logarithm of the original equation gives

$$\psi(T_1, T_3) = \psi(T_1, T_2) + \psi(T_2, T_3) \tag{7-49}$$

Differentiate with respect to the intermediate variable T_2.

The left-hand side $\psi(T_1, T_3)$ does **not** depend on T_2, so its partial derivative is zero:

$$0 = \frac{\partial}{\partial T_2}\psi(T_1, T_2) \ + \ \frac{\partial}{\partial T_2}\psi(T_2, T_3) \tag{7-50}$$

Thus:

$$\frac{\partial}{\partial T_2}\psi(T_1, T_2) = -\frac{\partial}{\partial T_2}\psi(T_2, T_3) \tag{7-51}$$

The left-hand side depends only on T_1 and T_2; the right-hand side depends only on T_2 and T_3. For this to hold for all T_1, T_2, T_3, each side must equal a function of T_2 alone. Call it $h(T_2)$:

$$\frac{\partial}{\partial T_2}\psi(T_1, T_2) = h(T_2) \tag{7-52}$$

Integrate with respect to T_2:

$$\psi(T_1, T_2) = \int h(T_2)\, dT_2 \ + \ C(T_1) \tag{7-53}$$

where $C(T_1)$ is an arbitrary function of T_1.

Let:

$$G(T) = \int h(T)\,dT, \tag{7-54}$$

So that:

$$\psi(T_1, T_2) = G(T_2) + C(T_1). \tag{7-55}$$

Use the symmetry condition $\phi(T, T) = 1$ since for any temperature T, a trivial cycle with zero efficience gives $\phi(T, T) = 1$. Hence:

$$\psi(T, T) = \ln(1) = 0. \tag{7-56}$$

Plugging into the expression for ψ:

$$0 = G(T) + C(T) \Longrightarrow C(T) = -G(T) \tag{7-57}$$

Therefore

$$\psi(T_1, T_2) = G(T_2) - G(T_1) \tag{7-58}$$

Recall $\psi = \ln\ \phi$:

$$\ln(\phi(T_1, T_2)) = G(T_2) - G(T_1) \tag{7-59}$$

Exponentiate:

$$\phi(T_1, T_2) = e^{\,G(T_2) - G(T_1)} = \frac{e^{G(T_2)}}{e^{G(T_1)}} \tag{7-60}$$

Define $g(T) = e^{G(T)}$. Then

$$\phi(T_1, T_2) = \frac{g(T_2)}{g(T_1)} \tag{7-61}$$

Thus, for any reversible engine:

$$\frac{Q_H}{Q_C} = f(T_H)/f(T_C) \tag{7-62}$$

The thermodynamic temperature scale is defined such that $f(T)$is proportional to the absolute temperature T, leading to the well-known result for Carnot engines:

$$\frac{Q_H}{Q_C} = \frac{T_H}{T_C} \tag{7-63}$$

This derivation shows that the heat ratio depends solely on the temperatures and not on the working substance, emphasizing the universality of the Second Law.

Remarks:

a) Indeed, we could choose f to be an exponential function, such as $f(T) = e^{kT}$ for some constant k, which would imply $\frac{Q_H}{Q_C} = \frac{e^{kT_H}}{e^{kT_C}} = e^{k(T_H - T_C)}$ However, this choice would result in a logarithmic temperature scale, which would be highly inconvenient for practical temperature measurement. For example, temperature differences would not be additive, and the scale would not align with the linear behavior observed in common thermometers.

b) Instead, the linear choice $f(T) = T$(where T is the absolute temperature) is adopted because it is consistent with the ideal gas law and gas thermometer measurements. A constant-volume gas thermometer relies on the pressure P of an ideal gas to measure temperature. The choice $f(T) = T$ ensures that the thermodynamic temperature scale (based on Carnot cycles) is identical to the ideal gas temperature scale. This makes temperature measurement straightforward and reproducible using gas thermometers, which are highly accurate for defining standard temperature points (e.g., the triple point of water).

c) According to the ideal gas law, $P \propto T$ at constant volume, so the temperature scale is linear. This linearity is empirically well-established and matches everyday experiences.

d) If we analyze a Carnot cycle using an ideal gas as the working substance (see section 7.4), we can derive directly that $\frac{Q_H}{Q_C} = \frac{T_H}{T_C}$, where T_H and T_C are the absolute temperatures measured on the ideal gas scale. This derivation confirms that the linear relationship is natural and consistent.

e) Thus, while mathematically other functions are possible, the linear case is chosen for its practical utility and consistency with physical laws. It simplifies thermodynamics and aligns with experimental evidence, making it the standard for the International System of Units (SI).

7.7 Generalization to any number of heat and sink sources

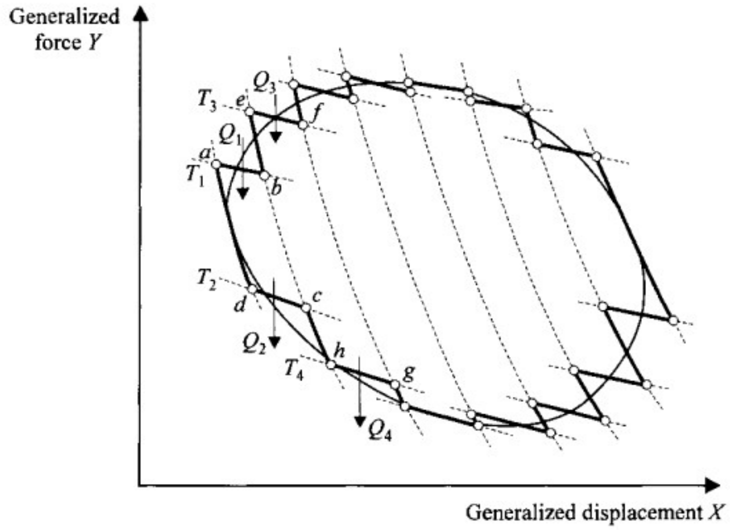


Figure 7-3: Generalized work diagram, where the smooth closed curve is a reversible cycle and the zigzag closed path is made up of alternating reversible isothermal and reversible adiabatic processes.

Conceptually a reversible cycle or engine can be conceived as a curved closed path in P-v diagrams (see Figure 7-3). In this case more than 2 heat reservoirs would be in contact.

Imagine plotting any arbitrary thermodynamic cycle on a P-V diagram. The cycle will form a closed loop, but it might be an irregular shape, not the simple Carnot cycle.

Imagine a complex, reversible heat engine that operates by exchanging heat with a series of n different thermal reservoirs at temperatures T1, T2, T3, ..., Tn.

We can analyze this cycle by mentally breaking it down. For each infinitesimal heat exchange $đQ_i$ at a temperature T_i, we can imagine it as part of a tiny, reversible isothermal step. We connect these isothermal steps with reversible adiabatic processes. This allows us to view the entire complex cycle as a network of many infinitesimal Carnot cycles operating between different pairs of temperatures.

When we sum (integrate) this over the *entire* complex cycle, the result is still zero:

$$\oint \frac{đQ_{rev}}{T} = \sum_{i=1}^{n} \frac{đQ_{i,rev}}{T_i} = 0 \tag{7-64}$$

where the sum is over all the heat interactions with all the different reservoirs.

Discussion:

The ability to handle any number of reservoirs is not a modification of the theorem but rather a demonstration of its immense generality. The simple two-reservoir Carnot cycle is the fundamental "atom" of reversible heat engine operation. By proving the concept for that case and then showing that any complex reversible cycle can be built from—or analyzed as—a collection of these atomic cycles, we prove that the conclusions about efficiency and the definition of entropy hold universally.

Since any cycle can be broken down into Carnot cycles, and the Carnot efficiency $(1 - \frac{T_c}{T_h})$ is the maximum possible for any heat engine operating between two temperatures, it follows that no cycle can be more efficient than a Carnot cycle operating between the same 'average' maximum and 'average' minimum temperatures.

It's important to note that the generalization for reversible arbitrary path engine is an idealization. The cancellation of internal processes is perfect only if the original cycle is reversible. For an irreversible cycle, the internal paths might not perfectly cancel, but the conclusion of Clausius's inequality $(\oint \frac{\partial Q}{T} < 0)$ still holds.

Furthermore, the most accurate way to state this is that the network of Carnot cycles approximates the network and heat transfer of the original cycle. The actual fluid path in the original cycle is not literally the same as the sum of these Carnot cycles, but the overall energy exchange with the surroundings is equivalent.

In summary, by approximating an arbitrary cycle as a sum of many Carnot cycles, we can extend the powerful, simple results of the Carnot cycle to any thermodynamic process, thereby proving the most general statements of the Second Law and defining the property of entropy. It's a brilliant conceptual tool that reveals the universal principles limiting all heat engines.

This simplicity allows us to clearly see the crucial role that temperature plays in converting heat to work. It's not just about the quantity of heat (Q_H), but the quality (the temperature at which it is available).

It's the difference between proving a rule for a single, perfect building block (the Carnot cycle) and then showing that any structure built perfectly from such blocks must also obey the rule.

Chapter 8: Entropy

8.1 Clausius Equality-A Path forward to deduce a new property (entropy)

The Clausius's inequality is another cornerstone of the Second Law deduced from it.

For each infinitesimal Carnot cycle of a general reversible cycle as discussed in section 7.5 and 7.8, the efficiency is $1-\frac{T_{low}}{T_{high}}$. This means

$$\frac{Q_{in}}{T_{high}}-\frac{Q_{out}}{T_{low}}=0 \qquad (8\text{-}1)$$

for a reversible Carnot cycle.

When we sum this for all the tiny cycles approximating an arbitrary reversible cycle, we get

$$\oint\left(\frac{\partial Q_{rev}}{T}\right)=0 \qquad (8\text{-}2)$$

If the original cycle was irreversible, based on lower efficiency, the sum would be

$$\oint\ (\frac{\partial Q}{\mathrm{T}})\ <\ 0 \qquad (8\text{-}3)$$

For the simple case of Carnot engine, we can write:

$$\frac{Q_H}{T_H}=-\frac{Q_C}{T_C} \qquad (8\text{-}4)$$

The sum around the entire cycle is therefore mathematically expressed as:

$$\oint\left(\frac{\delta Q}{T}\right)_{rev}=\frac{Q_H}{T_H}-\frac{Q_C}{T_C} \qquad (8\text{-}5)$$

This is the critical result. For a reversible general cycle,

$$\oint\left(\frac{\delta Q}{T}\right)_{rev}=0 \qquad (8\text{-}6)$$

This proves that the quantity $\frac{\delta\, Q_{rev}}{T}$ behaves like a state function—its integral around a closed path is zero, meaning it depends only on the state, not the path taken to get there (see section 8.7 for the analogy between potential energy change which is independent of path although we may take a zigzag path).

Remark:

a) We moved from the Specific to the General case. Once we have this result for the simple, two-reservoir Carnot cycle, we can use the "sum of many Carnot cycles" logic to generalize it to any arbitrary reversible cycle. If every infinitesimal Carnot cycle that makes up the arbitrary cycle has

$$\oint \frac{\delta Q}{T} = 0 \tag{8-7}$$

Therefore, for *any* reversible cycle,

$$\oint \left(\frac{\delta Q}{T}\right)_{\text{rev}} = 0 \tag{8-8}$$

b) We focus on the Carnot cycle not because it's common, but because it's the simplest possible model that contains the essential physics of heat engines and allows us to cleanly isolate and define the property of entropy. It is the strategic "key" that unlocks the door to the Second Law's most profound implications.

8.2 Entropy a property of the system

To prove a quantity is a property, we must prove that its change depends only on the initial and final states, not on the path taken between them.

Consider a closed system undergoing a process from state 1 to state 2 as in Figure 8-.

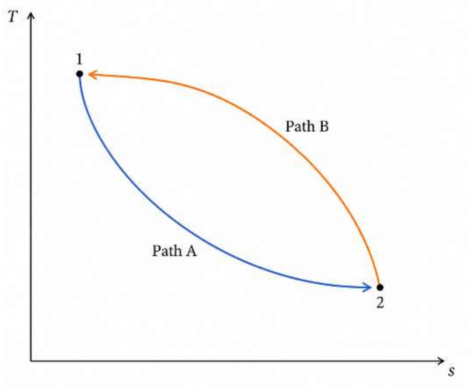


Figure 8-1: Closed system diagram between state 1 to state 2 with two path A and B.

Let Path A be any reversible path (R) from 1 to 2.

Let Path B be any other reversible path from 2 back to 1.

Together, Paths A and B form a reversible cycle: $1 \rightarrow 2\ (via\ R^1) \rightarrow 1\ (via\ R^2)$.

We apply Clausius theorem for a reversible cycle. The Clausius Theorem states that for any reversible cycle, the cyclic integral is zero:

$$\oint \frac{\delta Q_{rev}}{T} = 0 \tag{8-9}$$

Now we break the cyclic integral into two paths. We can split the integral for the entire cycle into the sum of the integrals for the two paths:

$$\oint \frac{\delta Q_{rev}}{T} = \oint \frac{\delta Q}{T} = \int_1^2 (\frac{\delta Q}{T})_{R_1} + \int_2^1 (\frac{\delta Q}{T})_{R_2} \; = \; 0 \tag{8-10}$$

Rearranging the terms, we get:

$$\int_1^2 (\frac{\delta Q}{T})_{R_1} \; = \; -\int_2^1 (\frac{\delta Q}{T})_{R_2} \tag{8-11}$$

Since reversing the limits of integration changes the sign, this simplifies to:

$$\int_1^2 (\frac{\delta Q}{T})_{R_1} = \int_1^2 (\frac{\delta Q}{T})_{R_2} \tag{8-12}$$

The integral $\int_1^2 \frac{\delta Q_{rev}}{T}$ has the same value for any reversible path between states 1 and 2. Its value depends only on the end states, not the path. This is the definition of a point function, or a property.

We define this property as the change in Entropy (S):

$$S2 - S1 = \int_1^2 \frac{\delta Q_{rev}}{T} \tag{8-13}$$

8.3 Principle of increase of entropy of an irreversible process with respect to reversible counterpart

Now, we prove that for any irreversible process, entropy generation is positive.

Construct a cycle where:

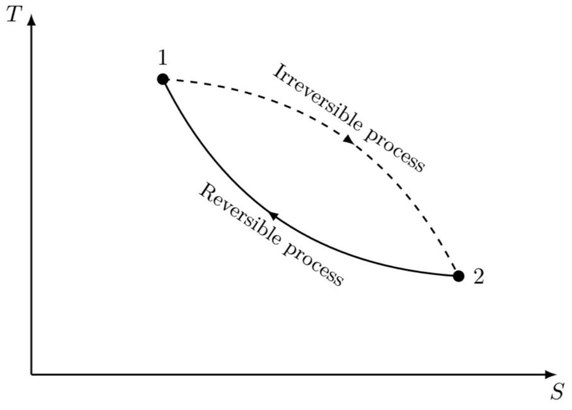


Figure 8.2: A cycle with irreversible and reversible process

As shown in Figure 8.-2, the process from state 1 to state 2 is irreversible (I). The process from state 2 back to state 1 is reversible (R).

This forms a cycle that is overall irreversible: $1 \rightarrow 2(via I) \rightarrow 1(via R)$.

The Clausius Inequality states that for any cycle (reversible or irreversible), the cyclic integral is less than or equal to zero, with equality holding only for the reversible case:

$$\oint \frac{\delta Q}{T} \leq 0 \tag{8-14}$$

Note that the inequality is for the case of an irreversible engine losing moreheat to the cold reservoir.

For our irreversible cycle, the inequality holds:

$$\oint \frac{\delta Q}{T} = \int_1^2 (\frac{\delta Q}{T})_I + \int_2^1 (\frac{\delta Q}{T})_R \ < \ 0 \tag{8-15}$$

From the section 8.2, we know that the reversible integral from 2 to 1 is related to the entropy change:

$$\int_2^1 (\frac{\delta Q}{T})_R \ = S_1 - S_2 = -(S_2 - S_1) \tag{8-16}$$

Substitute this into the inequality:

$$\int_1^2 (\frac{\delta Q}{T})_I - (S_2 - S_1) < 0 \tag{8-17}$$

Rearranging the terms gives the final, crucial result:

$$S_2 - S_1 > \int_1^2 (\frac{\delta Q}{T}) \tag{8-18}$$

This can be written more generally by introducing the concept of entropy generation (S_{gen}):

$$S_2 - S_1 = \int_1^2 (\frac{\delta Q}{T}) + S_{gen} \tag{8-19}$$

where $S_{gen} > 0$ for an irreversible process and $S_{gen} = 0$ for a reversible process.

The equation $S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{\text{gen}}$ is the entropy balance for a process, where $S_{\text{gen}} \geq 0$ accounts for entropy generation due to irreversibilities. For a reversible process, $S_{\text{gen}} = 0$ and the integral becomes path-independent, equal to the entropy change. However, for an irreversible process, $S_{\text{gen}} > 0$, and the integral $\int \delta Q/T$ alone does not give the entropy change; one must also determine S_{gen}. The difficulty lies in the fact that $\int \delta Q/T$ depends on the actual path and on the temperature at the system boundaries where heat transfer occurs, which may be non-uniform and unsteady. Moreover, S_{gen} cannot be directly measured; it must be inferred by calculating the entropy change via a reversible path between the same states and subtracting the $\int \delta Q/T$ evaluated along the irreversible path. Thus, while the equation is exact, its practical application to irreversible processes is not straightforward because both terms are path-dependent and require detailed knowledge of the process.

Remarks:

1. For irreversible work (e.g., a rapid expansion against a constant external pressure), the work done is $W = \int P_{\text{ext}}\, dV$, where P_{ext} is the surroundings pressure — not the system pressure, which may be undefined or non-uniform during the process. Similarly, for the term $\int \frac{\delta Q}{T}$ that appears in the entropy balance for an irreversible process, the temperature T in the denominator must be the temperature at the boundary where the heat transfer occurs. This boundary temperature is determined by the surroundings, not by the bulk system temperature (which may be ill-defined or varying).
2. In many practical cases, if the system exchanges heat with a single reservoir at temperature T_{res}, then the boundary temperature is T_{res} (assuming a thin, conductive wall with

negligible resistance). Then $\int \delta Q/T = \frac{Q}{T_{\text{res}}}$, where Q is the actual heat transferred irreversibly, as the reservoir follows an internally reversible change (see section 8.4).

3. If the surroundings consist of multiple reservoirs at different temperatures, or if the boundary temperature changes along the process, one must use the local boundary temperature at each instant, which again comes from external conditions (e.g., a heating fluid's temperature).
4. Thus, information about the surroundings is indeed essential for evaluating $\int \delta Q/T$ in an irreversible process, just as P_{ext} is needed for work. Without it, the integral cannot be computed from system properties alone.
5. Both work and heat "losses" (or entropy generation) are governed by external constraints (external pressure, external temperature), while the reversible path uses system properties (P_{sys}, T_{sys}) exclusively.

8.4 The entropy change of an infinite thermal reservoir

We can calculate the entropy change of a reservoir (at constant temperature T_{res}) simply as $\frac{Q}{T_{\text{res}}}$ — regardless of whether the overall process is reversible or irreversible — lies in the definition of a thermal reservoir and the nature of entropy as a state function.

A reservoir is internally reversible. A reservoir is idealized as having an infinite heat capacity, so its temperature remains constant no matter how much heat is added or removed. Moreover, it is always in internal equilibrium — there are no temperature gradients inside it. Any heat transfer to or from the reservoir occurs at its boundary, which is at the uniform temperature T_{res}. From the perspective of the reservoir alone, the heat transfer is *quasistatic* because the reservoir's state changes through a sequence of equilibrium states. Thus, the reservoir undergoes a reversible process internally.

The reservoir remains in internal equilibrium at all times.

For such a body, $dS = \delta Q_{\text{rev}}/T$ along any actual path, since the path itself is reversible for the reservoir.

Entropy is a state function. For any process (reversible or irreversible) that takes the reservoir from an initial state to a final state, the entropy change ΔS_{res} depends only on those two states. The reservoir's only relevant state variable is its temperature (which is constant) and possibly its internal energy, but the relation $dS_{\text{res}} = \frac{\delta Q_{\text{res}}}{T_{\text{res}}}$ holds for any infinitesimal heat transfer δQ_{res} because the reservoir is always in internal equilibrium. In other words, the Clausius inequality for the reservoir alone is an equality:

$$dS_{\text{res}} = \frac{\delta Q_{\text{res}}}{T_{\text{res}}} \tag{8-20}$$

irrespective of how the heat is exchanged with another system. This is not true for a finite body that develops temperature gradients.

The irreversibility arises from the finite temperature difference between the system and the reservoir, or from other dissipative effects within the system. The reservoir itself does not "see" that irreversibility — it only experiences a heat transfer at its boundary, and because it is always in equilibrium, the entropy production is zero inside the reservoir. All entropy generation occurs in the system or in the combined system-reservoir boundary layer, but not inside the reservoir.

8.5 Principle of increase of entropy of the universe

Assume the system (which is not a reservoir) may undergo an irreversible process and exchange heat with the surroundings.

The reservoir, however, simply loses or gains heat Q_{res} (with sign convention: positive into reservoir) at constant T_{res}. Its entropy change is $\Delta S_{\text{res}} = \frac{Q_{\text{res}}}{T_{\text{res}}}$.

The entropy balance for the system is written as:

$$\Delta S_{\text{sys}} = \int \frac{\delta Q}{T_{\text{sys,b}}} + S_{\text{gen}} \qquad (8\text{-}21)$$

where $S_{\text{gen}} \geq 0$ (entropy generation inside the system), and $T_{\text{sys,b}}$ is the temperature of the system boundary where heat is transferred.

Now we sum to find the entropy change of the combined system and surrounding which may be called a hypothetical universe isolated from outside.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \int \frac{\delta Q}{T_{\text{sys,b}}} + S_{\text{gen}} - \int \frac{\delta Q}{T_{\text{surr}}} = \int \delta Q \left(\frac{1}{T_{\text{sys,b}}} - \frac{1}{T_{\text{surr}}}\right) + S_{\text{gen}} \qquad (8\text{-}22)$$

Now consider the sign of the integral term. For any heat transfer, the second law imposes that δQ and $\left(1/T_{\text{sys,b}} - 1/T_{\text{surr}}\right)$ have the same sign? Actually, if heat flows from surroundings to system ($\delta Q > 0$), then $T_{\text{surr}} \geq T_{\text{sys,b}}$, so $1/T_{\text{sys,b}} \geq 1/T_{\text{surr}}$, hence the difference is non-negative. If heat flows from system to surroundings ($\delta Q < 0$), then $T_{\text{sys,b}} \geq T_{\text{surr}}$, so $1/T_{\text{sys,b}} \leq 1/T_{\text{surr}}$, making the difference non-positive; but multiplied by negative δQ yields a non-negative product. In both cases:

$$\delta Q\left(\frac{1}{T_{\text{sys,b}}}-\frac{1}{T_{\text{surr}}}\right) \geq 0 \tag{8-23}$$

Therefore, the integral term is ≥ 0. And $S_{\text{gen}} \geq 0$. Hence:

$$\Delta S_{\text{univ}} \geq 0 \tag{8-24}$$

Equality holds only if both:

The integral term is zero (which requires either $\delta Q = 0$ or $T_{\text{sys,b}} = T_{\text{surr}}$ during all heat transfer), and
$S_{\text{gen}} = 0$ (no internal irreversibilities).

These two conditions together define a reversible process.

We have proven that for any process (reversible or irreversible) in a system interacting with surroundings at constant temperature,

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0 \tag{8-25}$$

This is the principle of entropy increase for the universe. For an isolated system (where there are no surroundings to consider), the proof reduces to the earlier one showing $\Delta S_{\text{isolated}} \geq 0$.

Thus, the second law of thermodynamics can be succinctly stated: The entropy of an isolated system never decreases; it increases for any real process.

Remarks:

a) For any real process (which is irreversible), the total entropy of the universe (system + surroundings) always increases. This is the most profound implication of the Second Law of Thermodynamics.
b) The Concept of Lost Work (or irreversibility) is the difference between the maximum possible work that could be obtained from a process (if it were perfectly reversible) and the actual work obtained from the real, irreversible process. In simpler terms Lost work is the useful energy that becomes permanently unavailable for doing work due to irreversibilities.
c) Why Does Work Get "Lost"? Irreversibilities (like friction, unrestrained expansion, or heat transfer across a finite temperature difference) generate entropy. This entropy must be discarded into the environment. To discard this entropy, a certain amount of energy must also

be discarded as waste heat, instead of being converted into useful work. In a reversible process, there is no entropy generation $\left(S_{gen} = 0\right)$, so there is no lost work $(W_{lost} = 0)$.

d) For the case of a Heat Engine operating between a source (T_H) and the environment (T_0). The maximum possible work output is $W_{rev} = Q_{in}\left(1 - \frac{T_0}{T_H}\right)$. For the Irreversible case due to irreversibilities (friction in moving parts, heat transfer across a large ΔT), the actual work output is $W_{actual} < W_{rev}$.

8.6 On the energy degradation

Consider a Carnot engine operating reversibly between two reservoirs, the total entropy change of the universe is zero as follows:

Given:

- Hot reservoir at $T_h = 2000$ K, loses $Q_h = 1000$ J
- Cold reservoir at $T_c = 1000$ K, gains $Q_c = 500$ J (since Carnot efficiency $\eta = 1 - T_c/T_h = 0.5$, work $W = 500$ J, and $Q_c = Q_h - W = 500$ J)

Entropy changes:

$$\Delta S_{\text{hot}} = \frac{-Q_h}{T_h} = \frac{-1000}{2000} = -0.5\ \text{J/K}$$

$$\Delta S_{\text{cold}} = \frac{+Q_c}{T_c} = \frac{500}{1000} = +0.5\ \text{J/K}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{hot}} + \Delta S_{\text{cold}} = 0$$

Thus, the entropy change of the universe is 0 J/K.

Even in a reversible Carnot cycle, some energy ends up in the cold reservoir at a lower temperature, seemingly “degraded.” Yet the total entropy change of the universe is zero. How can that be, if degradation is usually associated with entropy increase?

The resolution lies in distinguishing between energy degradation (loss of ability to do work) and entropy generation.

The Carnot engine converts part of the heat from the hot reservoir into work. The remaining heat is rejected to the cold reservoir because the second law forbids complete conversion, not because of irreversibility. This rejected heat still contains available work potential relative to a reservoir at absolute zero, but relative to the cold reservoir (1000 K) its potential is zero. So, the “degradation” is just the unavoidable fact that some heat must be thrown away at a lower temperature to enable the cycle to be reversible.

The work produced (500 J) is entirely available to do anything. If that work is later dissipated into heat (e.g., by friction or electrical resistance), that subsequent process will increase the entropy of the universe. But the Carnot cycle itself does not cause that increase. The cycle leaves the universe in a state where the hot reservoir has lost 1000 J, the cold reservoir gained 500 J, and 500 J of work exists. The total entropy change is zero.

The "degradation" we sense is the loss of temperature level, not an increase in entropy.

The apparent degradation (heat at 1000 K instead of 2000 K) is not an increase in entropy — it's a redistribution of energy that allows work extraction.

Thus, the Carnot cycle itself is not the source of degradation; it merely sets the maximum possible work. The philosophical unease arises because we conflate the *inevitable* rejection of heat in a cycle with *irreversible* degradation. The reversible cycle achieves zero entropy change, meaning no net degradation in the sense of the second law — only a transformation that respects the law's limits.

So, degradation is not a sign of irreversibility; it's an unavoidable consequence of the finite temperature difference between the hot source and the cold sink. What reversibility changes is the amount of degradation.

In a reversible engine, degradation is the *minimum* possible (here, 500 J of the 1000 J).

In an irreversible engine, even more heat is degraded (e.g., 600 J rejected, only 400 J work) for the same Q_h and reservoirs.

"Degradation of energy is nature's law when we produce work and it is inevitable." The only choice is how much degradation occurs — less if the process is more reversible, more if it is irreversible. The reversible limit sets the floor, not zero.

For any real engine operating between the same reservoirs, more heat is rejected to the cold reservoir (say $Q_c' > Q_c$), so work output is less ($W' < W$). The extra degradation is directly linked to entropy generation:

$$\Delta S_{\text{universe}} = \frac{Q_c'}{T_c} - \frac{Q_h}{T_h} > \mathbf{0} \tag{8-26}$$

Since Q_h is the same, and $W = Q_h - Q_c$, $W' = Q_h - Q_c'$, the lost work (compared to Carnot) is:

$$W_{\text{lost}} = W - W' = Q_c' - Q_c \tag{8-27}$$

And the entropy generation is:

$$\Delta S_{\text{universe}} = \frac{Q_c' - Q_c}{T_c} = \frac{W_{\text{lost}}}{T_c} \tag{8-28}$$

Thus, entropy increase is exactly proportional to lost work (when the cold reservoir is at T_c).

8.7 A Deeper Connection between lost work and irreversibility of a process

For a reversible, quasi-equilibrium process we have:

- Entropy balance: $dS = \frac{\delta Q_{\text{rev}}}{T} \Rightarrow \delta Q_{\text{rev}} = T\,dS$
- Work (only $P\,dV$ work): $\delta W_{\text{rev}} = P\,dV$
- First law: $\delta Q_{\text{rev}} = dU + \delta W_{\text{rev}}$ (consistent with the above)

For an irreversible process (same initial and final states, i.e., same dS)

$$dS = \frac{\delta Q_{\text{irr}}}{T_{\text{boundary}}} + \delta S_{\text{gen}}, \delta S_{\text{gen}} > 0 \tag{8-29}$$

The derivation implicitly assumes that the heat transfer occurs at the **system temperature** T (i.e., $T_{\text{boundary}} = T$). This is a common simplification when irreversibilities are internal (friction, viscosity, etc.) and heat exchange is with a reservoir at the same instantaneous temperature.

Under that assumption:

$$\delta Q_{\text{irr}} = T\,dS - T\,\delta S_{\text{gen}} \tag{8-30}$$

From the first for the irreversible process:

$$\delta Q_{\text{irr}} = dU + \delta W_{\text{irr}} \tag{8-31}$$

For a simple compressible substance, regardless of path by combining the first and second law:

$$T\,dS = dU + P\,dV \tag{8-32}$$

This holds because it involves only state functions (T, S, U, P, V).

Substitute δQ_{irr} and dU into the first law for irreversible process:

$$T\,dS - T\,\delta S_{\text{gen}} = (T\,dS - P\,dV) + \delta W_{\text{irr}} \tag{8-33}$$

Cancel $T\,dS$ on both sides:

$$-T\,\delta S_{\text{gen}} = -P\,dV + \delta W_{\text{irr}} \tag{8-34}$$

$$\delta W_{\text{irr}} = P\,dV - T\,\delta S_{\text{gen}} \tag{8-35}$$

Interpretation

Compared to the reversible work $\delta W_{\text{rev}} = P\,dV$, the actual work is reduced by $T\,\delta S_{\text{gen}}$. This reduction is the lost work (also called irreversibility). It represents the work that could have been obtained but is wasted due to entropy generation.

The term $T\,\delta S_{\text{gen}}$ is not a work or energy that disappears; it is a lost opportunity to do work – the energy still exists but has degraded in quality.

8.8 Entropy change of an ideal gas

We start from the first law and write:

$$\delta Q = dU + \delta W \tag{8-36}$$

and then substitute $\delta Q = T\,dS$ (which is only valid for a reversible process) and $\delta W = p\,dV$ (only valid for a quasi-equilibrium, frictionless process), we are indeed assuming reversibility and quasi-equilibrium. From that, for an ideal gas, we derive:

$$dS = C_v \frac{dT}{T} + R\frac{dV}{V} \Rightarrow \Delta S = C_v \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} \tag{8-37}$$

And

$$dS = C_p \frac{dT}{T} - R\frac{dP}{P} \Rightarrow \Delta S = C_p \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{V_1} \tag{8-38}$$

Because entropy is a state function. Once we have expressed ΔS in terms of state variables (T, V or T, P), the formula no longer contains any reference to the path. It holds for any process connecting the two equilibrium states – regardless of whether that process was reversible or irreversible, quasi-static or violent.

Remark:

Quasi-equilibrium (or quasistatic) means the process is internally reversible—no finite gradients in pressure, temperature, or chemical potential inside the system. That's exactly the condition needed to write $\delta W = p\, dV$ (with p being the system's uniform pressure) and $\delta Q = T\, dS$ (with T being the system's uniform temperature). Internally reversible means quasistatic + no friction / dissipation inside. Totally reversible would also require no external irreversibilities (e.g., heat transfer across finite temperature difference to reservoirs).

Example:

Initial state: Ideal gas at P_1, T_1, volume V_1.

Path A (reversible, quasi-static adiabatic expansion): Remove small weights gradually. The gas expands adiabatically and reversibly until its pressure equals P_{atm}. Final temperature $T_{2,\text{rev}}$. Since $\Delta S = 0$ for a reversible adiabatic process, the logarithmic formula yields:

$$\Delta S = C_p \ln \frac{T_{2,\text{rev}}}{T_1} - R \ln \frac{P_{\text{atm}}}{P_1} = 0$$

Path B (irreversible adiabatic expansion): Remove a large weight suddenly (or let the gas expand against constant external pressure P_{atm}). The process is adiabatic but irreversible. The gas expands until its pressure equals P_{atm}, but the final temperature $T_{2,\text{irr}}$ is different from $T_{2,\text{rev}}$ (it will be higher because the gas does less work).

The final states are different (same P_{atm}, but different T and V). So, we cannot directly compare ΔS using the same final state.

We need a different path for the irreversible process to obtain exactly the same initial and final states.

First, expand adiabatically and irreversibly to some intermediate state (P_2, T_{mid}) where $T_{\text{mid}} > T_2$. Then, add a heat transfer step (e.g., put the gas in contact with a cold reservoir) to cool it at constant pressure P_2 down to T_2. The overall path is irreversible (due to the sudden expansion and finite-temperature heat transfer), but the initial and final states match those of Path 1.

Now, we cannot directly integrate $\delta Q/T$ because the path is irreversible. However, we know entropy is a state function, so ΔS must be the same as for Path 1. That is exactly why we can use the logarithmic formula (which came from a reversible path) for the irreversible process.

8.9 Analogy of potential energy change and entropy change

Elevation is a property of a point on a hill. Every point has a unique elevation.
How do we measure the elevation difference between Point A and Point B? We can't measure it directly in a messy, friction-filled walk. We take a plumb line and a level – a reversible, lossless, ideal method.
Once we know that elevation is a property, we can calculate the change in potential energy for *any* path (even a crazy, zigzag, friction-heavy one) by simply using the elevation difference: mgΔh. We don't care that the actual path had friction; the property change is fixed.

Entropy is exactly the same. dS = δQ_rev/T is our "plumb line and level." It's the ideal, lossless way to measure the change in the property.

8.10 On the Clausius integrating factor

Clausius showed that using the first law and a specific equation of state, we can demonstrate that for that particular substance, the quantity $\frac{\delta Q_{\text{rev}}}{T}$ happens to be an exact differential. For example:

- For an ideal gas: $\frac{\delta Q_{\text{rev}}}{T} = C_v \frac{dT}{T} + R\frac{dV}{V}$ → exact.
- For a van der Waals gas: $\frac{\delta Q_{\text{rev}}}{T} = C_v \frac{dT}{T} + \frac{R}{v-b} dv$ → exact.

But this only proves that for an ideal gas (or van der Waals gas), entropy defined this way is a state function. It does not prove that the same is true for all possible substances (liquids, solids, two-phase mixtures, real gases that don't follow these simple equations).

Without the second law, we have no guarantee that:

- The same integrating factor $1/T$ works for every substance.
- The cyclic integral $\oint \delta Q_{\text{rev}}/T$ is zero for all reversible cycles involving arbitrary materials.

Without the second law (i.e., without the Carnot principle and/or Kelvin-Planck statement), we cannot prove that $\oint \delta Q_{\text{rev}}/T = 0$ for a general substance. The ideal gas derivation is merely a consistency check for one special case, not a general proof.

8.11 On the Carathéodory's approach to second law

Carathéodory formulates the second law as:

In every neighborhood of any given state, there exist states that cannot be reached by adiabatic processes (often summarized as "there exist adiabatically inaccessible states").

This formulation yields a rigorous existence theorem for entropy without invoking heat engines.

However, the approach has limitations:

- It assumes the concept of heat (via the definition of adiabatic processes) without explaining it physically.
- It does not explain why some processes are irreversible in practice—it merely encodes irreversibility as "adiabatic inaccessibility."
- It does not directly connect the second law to empirical facts, such as the impossibility of a 100% efficient heat engine.

In contrast, Clausius' original insight derives the physical origin of entropy from experimental observations.
No engine can convert all heat into work—some heat must be rejected to a colder reservoir. Clausius combines Carnot's efficiency principle with a statement of the second law to deduce entropy as a property of a system.

Carathéodory's theorem can feel "mysterious."

It is mathematically elegant and rigorous, but it replaces empirical content with a geometric hypothesis. It proves the existence of entropy but does not explain why entropy matters physically. In essence, Carathéodory's theorem is a mathematical existence proof, whereas Clausius' approach is a physical derivation from experimental facts, giving entropy its physical meaning.

The second law is fundamentally an empirical law, not merely a geometric fact.

8.12 Entropy Balance for a Control Volume

We derive the entropy balance for a control volume starting from the entropy change of a closed system (the "system") and applying the Reynolds transport theorem. For any closed system, the second law gives

$$\frac{dS_{\text{sys}}}{dt} = \int_{\text{boundary}} \frac{\delta \dot{Q}}{T} + \dot{S}_{\text{gen}}, \dot{S}_{\text{gen}} \geq 0 \tag{8-39}$$

where S_{sys} is the total entropy of the system, $\delta \dot{Q}$ is the heat transfer rate through an infinitesimal boundary element at absolute temperature T, and $\dot{S}_{\text{gen}}$ is the entropy generation rate due to irreversibilities inside the system.

Now consider a fixed control volume (CV) in space, with control surface (CS). At time t, the closed system coincides exactly with the CV. As time advances to $t + \Delta t$, the system moves with the flow, carrying entropy across the CS. The rate of change of entropy of the *system* can be related to the CV quantities by the Reynolds transport theorem for an extensive property $B = S$ with specific entropy $b = s$:

$$\frac{dS_{\text{sys}}}{dt} = \frac{d}{dt}\int_{\text{CV}} \rho s \, dV + \int_{\text{CS}} \rho s \, (\mathbf{v}_{\text{rel}} \cdot \mathbf{n}) \, dA, \tag{8-40}$$

where ρ is density, v_{rel} is the velocity of the fluid relative to the CS (for a fixed CS, it is simply the absolute velocity v), and n is the outward unit normal. The first term on the right is the rate of entropy accumulation inside the CV, and the second term is the net entropy outflow rate by mass flow.

Remark:

Proof of Reynolds Transport Theorem

Let $B_{\text{sys}}(t)$ be the total amount of property B in the system at time t.

Let $b(\mathbf{x}, t) = dB/dm$ be the intensive (field) representation.

Then:

$$B_{\text{sys}}(t) = \int_{V_{\text{sys}}(t)} \rho(\mathbf{x}, t) \, b(\mathbf{x}, t) \, dV \tag{8-41}$$

At the initial instant t_0, the system occupies exactly the fixed CV volume V_{CV}.

We want $\frac{dB_{\text{sys}}}{dt}$ at $t = t_0$. Use the definition of derivative:

$$\frac{dB_{\text{sys}}}{dt}\,|_{t_0} = \lim_{\Delta t \to 0} \frac{B_{\text{sys}}(t_0 + \Delta t) - B_{\text{sys}}(t_0)}{\Delta t} \tag{8-42}$$

At t_0, System and CV coincide, so

$$B_{\text{sys}}(t_0) = \int_{V_{\text{CV}}} \rho(\mathrm{x}, t_0) \, b(\mathrm{x}, t_0) \, dV \tag{8-43}$$

At $t_0 + \Delta t$, the system has moved. It consists of three regions:

- Region I: fluid that remains inside the CV at $t_0 + \Delta t$ (some of the original fluid).

- Region II: fluid that has left the CV (outflow through CS).
- Region III: fluid that has entered the CV (inflow).

Thus:

$$B_{\text{sys}}(t_0 + \Delta t) = \int_{V_{\text{I}}(t_0+\Delta t)} \rho b \, dV \; + \; \int_{V_{\text{II}}(t_0+\Delta t)} \rho b \, dV \; + \; \int_{V_{\text{III}}(t_0+\Delta t)} \rho b \, dV \qquad (8\text{-}44)$$

But note that at $t_0 + \Delta t$, the fluid originally in the CV has moved. The volume V_{I} is the part still inside, V_{II} is the part that left. Meanwhile, region III is new fluid that came in from outside.

We write:

$$B_{\text{sys}}(t_0 + \Delta t) = \left[\int_{V_{\text{CV}}} \rho \, b \, dV\right]_{t_0+\Delta t} \; - \; \left(\int_{V_{\text{outflow}}} \rho \, b \, dV\right)_{\text{during } \Delta t} \; + \; \left(\int_{V_{\text{inflow}}} \rho \, b \, dV\right)_{\text{during } \Delta t} \qquad (8\text{-}45)$$

Because the integral over the CV at $t_0 + \Delta t$ includes the fluid originally inside that remained (region I) plus fluid that entered (region III). So:

$$\int_{V_{\text{CV}}(t_0+\Delta t)} \rho b \, dV = \int_{V_{\text{I}}} \rho b \, dV + \int_{V_{\text{III}}} \rho b \, dV \qquad (8\text{-}46)$$

Then:

$$B_{\text{sys}}(t_0 + \Delta t) = \int_{V_{\text{I}}} \rho b \, dV + \int_{V_{\text{III}}} \rho b \, dV + \int_{V_{\text{II}}} \rho b \, dV \qquad (8\text{-}47)$$

But:

$$\int_{V_{\text{I}}} \rho b \, dV = \int_{V_{\text{CV}}(t_0+\Delta t)} \rho b \, dV - \int_{V_{\text{III}}} \rho b \, dV \qquad (8\text{-}48)$$

Substitute:

$$B_{\text{sys}}(t_0 + \Delta t) = \left[\int_{V_{\text{CV}}} \rho \, b \, dV\right]_{t_0+\Delta t} - \int_{V_{\text{III}}} \rho b \, dV + \int_{V_{\text{II}}} \rho b \, dV \qquad (8\text{-}49)$$

The negative sign on the inflow term (III) appears because the volume integral over the CV at $t_0 + \Delta t$ already includes inflow; we must subtract it and add the outflow to get the *system* property.

Thus:

$$B_{\text{sys}}(t_0+\Delta t) - B_{\text{sys}}(t_0) = \left[\int_{V_{\text{CV}}} \rho\, b\, dV\right]_{t_0+\Delta t} - \left[\int_{V_{\text{CV}}} \rho\, b\, dV\right]_{t_0} + \int_{V_{\text{II}}} \rho b\, dV - \int_{V_{\text{III}}} \rho b\, dV \tag{8-50}$$

Dividing by Δt and taking limit:

$$\frac{dB_{\text{sys}}}{dt} = \lim_{\Delta t\to 0} \frac{\int_{V_{\text{CV}}} \rho b\, dV\ |_{t+\Delta t} - \int_{V_{\text{CV}}} \rho b\, dV\ |_{t}}{\Delta t} + \lim_{\Delta t\to 0} \frac{1}{\Delta t}\left(\int_{V_{\text{II}}} \rho\, b\, dV - \int_{V_{\text{III}}} \rho\, b\, dV\right) \tag{8-51}$$

The first limit is the partial derivative with respect to time inside the fixed CV:

$$\frac{\partial}{\partial t}\int_{V_{\text{CV}}} \rho b\, dV \tag{8-52}$$

The second limit: V_{II} is the volume that crossed the CS outward. During Δt, an infinitesimal patch dA on the CS with outward normal **n** sweeps a volume $(\mathbf{v}\cdot\mathbf{n})\Delta t\, dA$. The mass crossing outward is $\rho(\mathbf{v}\cdot\mathbf{n})\Delta t\, dA$ (positive for outflow). The amount of B crossing is $b \times$ that mass: $b\rho(\mathbf{v}\cdot\mathbf{n})\Delta t\, dA$. Summing over the CS, the outflow contribution is:

$$\int_{CS} \rho b(\mathbf{v}\cdot\mathbf{n})\Delta t\, dA \tag{8-53}$$

Similarly, inflow (negative $\mathbf{v}\cdot\mathbf{n}$) contributes negatively. Thus the net outflow of B across the CS in time Δt is:

$$\int_{CS} \rho b(\mathbf{v}\cdot\mathbf{n})\, dA\, \Delta t \tag{8-54}$$

Hence:

$$\lim_{\Delta t\to 0} \frac{1}{\Delta t}\left(\int_{V_{\text{II}}} \rho\, b\, dV - \int_{V_{\text{III}}} \rho\, b\, dV\right) = \int_{CS} \rho b\, (\mathbf{v}\cdot\mathbf{n})\, dA \tag{8-55}$$

Combining, we obtain the **Reynolds Transport Theorem** for a fixed control volume:

$$\frac{dB_{\text{sys}}}{dt} = \frac{\partial}{\partial t}\int_{V_{\text{CV}}} \rho b \, dV \; + \; \int_{CS} \rho b \, (\mathbf{v} \cdot \mathbf{n}) \, dA \tag{8-56}$$

Because the system and the CV coincide at time t, the heat transfer term in the second law also applies to the same boundary. Hence the heat transfer through the system boundary equals the heat transfer through the CS (for a fixed CS, work crossing the boundary does not carry entropy). Therefore, we write:

$$\int_{\text{boundary}} \frac{\delta \dot{Q}}{T} = \int_{\text{CS}} \frac{\dot{q}}{T} \, dA \tag{8-57}$$

where $\dot{q}$ (W/m²) is the local heat flux across the CS, and T is the absolute temperature on the CS at that location. The entropy generation $\dot{S}_{\text{gen}}$ is now understood to be that occurring *inside* the CV, because the system and CV occupy the same region at the instant of analysis.

Substituting the Reynolds transport expression into the second-law equation yields the general entropy balance for a control volume:

$$\frac{d}{dt}\int_{\text{CV}} \rho s \, dV \; + \; \int_{\text{CS}} \rho s \, (\mathbf{v} \cdot \mathbf{n}) \, dA \; = \; \int_{\text{CS}} \frac{\dot{q}}{T} \, dA \; + \; \dot{S}_{\text{gen}}, \qquad \dot{S}_{\text{gen}} \geq 0. \tag{8-58}$$

This is the fundamental equation. Each term has the unit W/K (or J/(s·K)). For most engineering applications, the control volume operates at steady state (no accumulation), so the first term vanishes. If, in addition, the flow is one-dimensional at inlets and outlets (with uniform properties), the mass-flow entropy transport reduces to sums over discrete ports:

$$\sum_{\text{out}} \dot{m}_e \, s_e \; - \; \sum_{\text{in}} \dot{m}_i \, s_i \; = \; \int_{\text{CS}} \frac{\dot{q}}{T} \, dA \; + \; \dot{S}_{\text{gen}} \tag{8-59}$$

For an adiabatic control volume ($\dot{q} = 0$ everywhere on the CS), we obtain the simple relation

$$\sum_{\text{out}} \dot{m}_e \, s_e \; - \; \sum_{\text{in}} \dot{m}_i \, s_i \; = \; \dot{S}_{\text{gen}} \geq 0 \tag{8-60}$$

which states that the net entropy outflow by mass flow equals the entropy generated inside the CV. For a single inlet and outlet (e.g., a turbine or compressor), this reduces to $\dot{m}(s_e - s_i) = \dot{S}_{\mathrm{gen}} \geq 0$, directly linking entropy rise to irreversibilities such as friction, mixing, or internal heat transfer across finite differences.

Extending entropy analysis from a closed system to a control volume (open system) fundamentally changes the accounting framework. For a closed system, entropy change is due solely to heat transfer across the boundary and internal irreversible generation. For a control volume, however, mass flow physically transports entropy across the boundary, introducing a new convective term. The general entropy balance for a control volume thus becomes: the rate of entropy accumulation within the volume equals the net entropy inflow with mass, plus entropy transfer via heat transfer across the boundary (integral of $\delta\dot{Q}/T$), plus the entropy generation rate due to irreversibilities inside the volume. This formulation is essential because many practical engineering devices—turbines, compressors, nozzles, heat exchangers—operate as steady-flow control volumes, where the accumulation term is zero. In such cases, the entropy leaving with the outflow must equal the entropy entering with the inflow, plus entropy from heat transfer, plus the internally generated entropy.

A particularly powerful extension arises when analyzing steady-flow devices with a single inlet and outlet. The entropy balance reduces to $\dot{m}(s_e - s_i) = \int \frac{\delta\dot{Q}}{T} + \dot{S}_{gen}$. In the adiabatic limit ($\dot{Q} = 0$), this simplifies dramatically: entropy generation becomes $\dot{S}_{gen} = \dot{m}(s_e - s_i) \geq 0$. This relation directly quantifies irreversibilities from friction, turbulence, shock waves, or non-equilibrium effects. For example, in an adiabatic turbine, expansion ideally occurs at constant entropy (isentropic), but real turbines experience entropy rise due to fluid friction and internal heat transfer across finite temperature differences. The isentropic efficiency of the turbine is precisely a measure of how closely the actual entropy rise approaches the ideal zero value. Similarly, for a compressor or pump, the entropy generation manifests as additional work input required beyond the reversible minimum.

Chapter 9: ENTROPY vs DISORDER

Unlike most quantities in physics and chemistry, the change of entropy of the system and its surroundings is not conserved, rather, it increases. In order to appreciate the concept of entropy, let us consider natural processes and look for insights that are consistent with calculations.

For example, consider the phase change of sublimation, the transition of a solid to a vapor that occurs in dry ice. The change of entropy, which is the amount of heat absorbed during the sublimation divided by the sublimation temperature, increases as expected. But what can be said about the microscopic changes that occur when carbon dioxide molecules of dry ice escape from the solid into the vapor. A solid is capable of supporting itself, whether in a crystalline state or amorphous state. Moreover, the material in the solid phase retains its size and shape, which means that the microscopic components (particles) of the system form a rigid structure. Simply stated, each particle retains its location in an organized structure; that is, the solid is in a state of *order*. As latent heat is supplied to a solid, the process of sublimation changes the solid into a vapor with no change of temperature. A vapor has no fixed size and shape; in fact, a vapor must be placed in a closed container or it is lost. The particles in the vapor are not individually restrained into any organized structure; rather, the vapor particles are free to move independently throughout the volume of the container. In other words, the vapor is in a state of disorder, relative to its solid phase. An increase in entropy of a system can be described as an increase in the disorder of the system. Notice that the concept of disorder is relative to a reference state, just as entropy is. The use of disorder as a synonym for entropy can be extended beyond phase transitions as the following examples show.

The temperature of an ideal gas does not change and heat is not added to the system during a free expansion, yet the entropy increases. The only difference between the initial state and the final state of the ideal gas is an increase of volume, which provides the gas particles with more space for their motion. Disorder, in this case, is not linked to a structural change that provides freedom of movement, as in the case of sublimation, but, rather, more freedom of movement is provided in a larger volume.

In the case of conduction of heat through a metal bar from a high-temperature reservoir to a low-temperature reservoir, there is no change of phase, volume, or temperature of the conductor, but the entropy of the universe increases. The internal energy becomes disordered in its passage between reservoirs, because the internal energy has been dissipated in the low-temperature reservoir and cannot be used to run a heat engine.

All these examples, involving irreversible processes, show that the entropy of the universe increases. It is possible to regard all natural processes from the point of view of orderliness, and, in all cases, the result obtained is that isolated systems or systems plus surroundings experiencing irreversible processes proceed toward a state of greater disorder.

Nevertheless, "order" and "disorder" are somewhat subjective interpretations of entropy increase. When we mix two liquids, entropy increases—but is the mixture truly in disorder?

A better interpretation of entropy increase is the growth in the number of available microstates for the energy of molecules. This is best explained within the context of statistical thermodynamics.

9.1 Entropy and the Human Sensorium

Our journey through thermodynamics has been an exercise in intellectual abstraction, moving from what we can directly feel to what we must deduce through reason.

We, as humans, are equipped with five senses. We can feel temperature (thermos reception) as a direct sensation of hot and cold. We can feel pressure (mechanoreception) as a force on our skin. These are direct, visceral experiences.

Entropy is different from ordinary sensory properties. We cannot see, hear, smell, taste, or touch entropy directly. It is not a tangible quantity like temperature or pressure, which we can feel as heat or sense as touch. Yet, entropy exists as a fundamental property of matter and energy transformations.

Entropy is a transcendental property — a concept that goes beyond what our immediate senses can detect. Similar to how energy was an unknown abstract concept to early humans, entropy is a modern scientific insight revealed through careful measurement, logic, and experiments.

Energy, however, is different. We do not have an "energy receptor." We feel its effects—the ability to lift a weight, to run, to think. We operationalize it as "the capacity to do work," but we never measure it directly. A thermometer measures temperature; a barometer measures pressure. But there is no "energy-meter." We calculate energy indirectly through its manifestations. The concept of "having energy" when we wake up is a felt, internal assessment of our potential for action, our ability to perform "work" in the broadest biological and psychological sense.

This is why entropy presents the greatest conceptual challenge. It is a property even more abstract than energy. It has a unit (J/K) never used in everyday conversation. No device measures it directly; it is always calculated from other measurements. It is not conserved; it is generated, constantly and irrevocably.

The lack of a direct measurement for entropy should not limit our intellectual ability to understand it, just as the lack of an energy-meter does not limit our understanding of physics. We understand it by its consequences, its unwavering mathematical definition $\left(dS = \frac{\delta Q_{rev}}{T}\right)$ and its profound governing principle: $\Delta S_{universe} \geq 0$.

Early humans had no direct concept of energy, despite experiencing effects like fire, muscle work, and motion. It took centuries to formalize energy as a property, starting from work and heat observations.

Similarly, entropy is a property inferred from patterns in how heat and work behave, not something we directly experience.

Let us stare the following thought:

"I have energy but I am confused, meaning my entropy is increased."

After rest, our body has minimized its entropy production and stored high-quality energy. We feel the potential for organized, purposeful action—low internal entropy.

A nightmare represents a state of psychological disorder and chaos. Upon waking, the memory of that chaotic, unpredictable narrative persists. Our mind is not in a state of equilibrium; it is in a disordered, high-probability configuration of thoughts. The energy is there, but its quality has diminished because it is now coupled with a disorganized state.

The feeling of "confusion" is the subjective, conscious experience of a high-entropy cognitive state. The energy is present, but it cannot be cleanly directed toward purposeful "work"; it is dissipated into unstructured, random thought. In this state, we have not lost energy (First Law), but we have lost the ability to effectively harness it (Second Law). The potential to do useful mental work has decreased because our internal state has become more disordered. Our entropy has increased.

Thus, entropy transcends physics. It is the fundamental measure of disorder, the arrow of time, the tax collector on all transactions in the universe, and the silent parameter that governs everything from the cooling of a cup of coffee to the exhaustion of a star, and even the tangled thoughts of a mind emerging from a dream. It is the price of existence itself, and in understanding it, we understand the most fundamental rule of the cosmic game.

Finally, there are other abstract properties in science. Electric charge cannot be sensed by our five senses but is fundamental in physics. Magnetic fields are invisible, yet real. The same is true for gravitational field.

Our five senses are incredibly powerful, but they are not perfect—they can mislead us in ways that are often predictable. Here's a structured list with examples:

Optical illusions

The famous Müller-Lyer illusion (two lines of equal length look different because of arrow-like ends) shows how context tricks perception.

Ames room: A distorted room makes people appear huge or tiny depending on where they stand.

Mirages: Heat gradients bend light, making water appear on a hot road.

Peripheral vision errors: Things moving in the periphery can appear larger, faster, or differently shaped than they are.

Hearing

Phantom words: In "speech illusion" experiments, repeating ambiguous sounds can be heard as words your brain expects.

McGurk effect: Seeing someone's lips say "ga" while hearing "ba" makes the brain perceive "da".

Tinnitus: Ringing in the ears is not an external sound but an internal misfiring of auditory neurons.

Hearing is not a direct readout of sound; the brain interprets signals and fills in gaps.

Touch illusions

Holding a warm object while your hand is in cold water can make the cold feel hotter than it is.

Phantom limb sensation: Amputees feel touch or pain in a limb that no longer exists.

Touch perception depends on the brain's integration of multiple signals, which can be tricked.

Taste

Flavor influenced by smell: Smell contributes ~80% of what we perceive as taste. A blocked nose can make food taste bland

Color altering taste: Red-colored drinks are often perceived as sweeter than blue ones, even if sugar content is identical.

Temperature illusion: Warm beverages taste sweeter than cold ones with the same sugar content.

Taste is multisensory; the brain combines smell, sight, temperature, and expectation.

Smell

Adaptation: When exposed to a constant odor, the brain stops noticing it (e.g., perfumes or garbage).

Cross-modal influence: Visual cues can make an odor seem more or less pleasant.

Smell is interpreted, not directly sensed; the brain decides which signals are important.

Our senses provide incomplete, noisy, or context-dependent information.

The brain does its best to construct a coherent picture of the world—but that picture can be wrong based on our senses.

Many illusions arise because the brain assumes patterns or expectations based on prior experience.

There are many fundamental physical concepts that we do not perceive directly through our senses, yet we know they exist because the brain can infer them from observations, measurements, and mathematical reasoning.

Time

We experience change and duration, but we do not directly sense time itself. We infer time from clocks, periodic motions, aging, and memory. Modern physics treats time as a dimension, something far more subtle than our subjective feeling of its passage.

Gravity

We feel weight, but we do not directly sense gravity. An astronaut in orbit experiences weightlessness even though Earth's gravity is still strong. What we actually feel is the force exerted by the floor, chair, or ground on our bodies.

Electric Fields

We do not directly perceive electric fields surrounding charged objects. Their existence is inferred from the motion of charged particles, voltages, sparks, and countless experiments.

Magnetic Fields

Most humans have no conscious sense for magnetic fields. Yet magnetic fields shape compass needles, guide charged particles, and influence many natural phenomena. Some animals appear to possess a limited magnetic sense, but humans generally do not.

Atmospheric Pressure

At sea level, every square meter of our bodies experiences roughly 100,000 newtons of force from the atmosphere. We are almost completely unaware of this immense pressure because it acts nearly equally in all directions.

Momentum

We feel impacts and forces, but momentum itself is not a sensation. It is a conserved quantity discovered through analysis of motion.

Energy

Energy is one of the most important concepts in physics, yet no sense organ detects "energy" directly. We observe motion, temperature, light, and chemical changes and infer the transfer and conservation of energy.

Entropy

Entropy belongs in this category. We may feel warmth or observe decay and mixing, but entropy itself is not directly sensed. It is calculated from the possible arrangements of matter and energy and from energy flows.

Curvature of Space-Time

According to Albert Einstein, gravity can be understood as the curvature of space-time. Nobody sees or feels space-time curvature directly. Its existence is inferred from planetary motion, light bending around massive objects, and precision measurements.

Quantum Wave Functions

In quantum mechanics, particles are described by wave functions. No one observes a wave function directly. We infer its existence because it accurately predicts experimental results.

Atoms

Nobody has ever seen an atom with their naked eyes. Even modern images are indirect representations produced by sophisticated instruments. The concept of atoms arose from reasoning about chemical reactions and experimental evidence.

Concluding, the scope of human knowledge is much larger than the scope of human senses.

Science advances because the brain extends the reach of the senses through measurement, mathematics, and logical reasoning. We cannot directly see gravity, energy, momentum, atoms, or entropy, yet we understand them so well that we can predict eclipses, build computers, send spacecraft to other planets, and estimate the entropy produced by our own bodies.

In that sense, one might say that mathematics and scientific reasoning function as an extension of our sensory system, allowing us to perceive aspects of reality that no biological sense organ can detect directly.

9.2 Entropy balance in living systems

We often encounter entropy as an abstract quantity appearing in equations and thermodynamic tables, making it difficult to connect with physical intuition. One way to develop that intuition is to recognize that each of us is a living thermodynamic system. In a sense, a human being is an entropy-generating machine. Every moment of our lives, we consume organized forms of energy stored in food and convert them into mechanical work, chemical activity, heat, and waste products. While our bodies maintain a remarkable degree of internal order, they do so only by increasing the entropy of their surroundings.

Although we do not carry instruments that measure entropy directly, we experience its effects continuously. The warmth of our skin after exercise, the heat released by metabolism, the need to consume food to sustain life, and the gradual dissipation of energy throughout our daily activities are all manifestations of entropy production. Life does not escape the Second Law of Thermodynamics; rather, it operates in full accordance with it. The highly organized structure of a living organism is maintained by exporting entropy to the environment at an even greater rate. Seen in this light, entropy is not an abstract concept confined to textbooks—it is an integral part of our everyday existence.

Plants operate under the same principle!

Just like humans, plants are living systems that maintain internal order at the expense of their surroundings. They capture organized energy from sunlight through photosynthesis, storing it in chemical bonds of sugars and other molecules. That energy allows them to build complex structures — leaves, stems, roots, and even flowers — maintaining highly ordered arrangements of cells and tissues. Yet in the process, plants also increase the entropy of their environment. They release heat, shed waste products, and eventually return materials to the soil, contributing to the overall increase in disorder.

Even without instruments, we can sense this entropy production: the warmth of sunlight on a leaf, the gentle decay of fallen leaves, the spread of seeds carried by wind — all are reminders that living systems, whether human or plant, sustain themselves by exporting entropy. Recognizing this makes the abstract concept of entropy tangible: it is not merely a number in an equation but a fundamental aspect of life, observable in the everyday processes of the natural world.

9.3 Entropy a Design Tool

Note that we deduced entropy from a macroscopic experimentally based approach and nothing about disorder is required. In engineering, entropy is valuable because it quantifies irreversibility, degradation of energy quality, lost work potential and inefficiency. Entropy generation directly measures thermodynamics imperfection. There are enormously practical applications such as turbine loss, compressor inefficiency, heat exchanger optimization, pressure drop penalties, combustion irreversibility and refrigeration performance. In design entropy is not a mysterious concept but it is an engineering tool. Finally, entropy helps understand: How to design engines that are more efficient and environmentally friendly. Though entropy is abstract, it plays a crucial role in engineering. It tells us how efficiently we can convert heat into work. It helps us predict the performance limits of engines, refrigerators, turbines, and many other devices. It shows us where energy losses occur and cannot be recovered.

While illuminating, Boltzmann’s statistical interpretation applies rigorously only to highly simplified models—assuming non-interacting particles in equilibrium. The statistical approach although revolutionized our understanding of nature, specially regarding the arrow of time, yet the second law of thermodynamics, by contrast, was discovered through empirical observation, not derived from microscopic probability. Engineers define and use entropy based on measurable relationships between heat and temperature, not on counting invisible microstates. Therefore, applying Boltzmann’s model beyond its domain risks transforming a practical and vital thermodynamic quantity into a speculative abstraction not suited for the engineering world.

9.4 The limits of explanations

According to Kant's “thing in itself” (*Ding an sich*) refers to the mind-independent reality that cannot be experienced directly, because all human intuition is necessarily conditioned by the a priori forms of space and time. While we can never have knowledge of things as they are in themselves, the concept of this noumenal reality serves as a necessary limiting notion: it marks the boundary of possible experience and thereby secures the domain of empirical science, which is confined to appearances (phenomena).

We say the ideal gas law $PV = nRT$ is "explained" by kinetic theory: molecules collide with walls, transferring momentum proportional to their kinetic energy, which is related to temperature.

But that simply replaces one description with another. Why do molecules have kinetic energy proportional to temperature? Because of equipartition. Why equipartition? Because of statistical mechanics. Why statistical mechanics? Because of the postulate of equal a priori probability. Why that postulate? Because it works. At every step, we have not reached a terminal "why"—only a new description.

Similarly, we may say entropy increases because disorder is more probable. But that is just re-describing the Second Law in the language of combinatorics. It does not tell us why nature prefers disorder. It just tells us that if we assume all microstates are equally likely, then disorder dominates. But why that assumption?

The kinetic theory and statistical mechanics appendices are not offered as "ultimate explanations." They are alternative formulations—different languages that describe the same phenomena. They are useful for prediction and intuition, but they do not terminate the chain of "why."

We should not mistake microscopic models (kinetic theory, statistical mechanics) for foundational explanations of thermodynamics. They are parallel descriptions, not deeper causes. The laws of thermodynamics stand on their own empirical footing. Any attempt to 'explain' them will lead to an infinite regress of new questions. Science describes how nature behaves; it does not—and cannot—answer why nature behaves that way in any ultimate sense.

The chain of "why" is infinite. Science is not in the business of final explanations. It is in the business of systematic description and predictive modeling.

We may feel unsatisfied when told that the ideal gas law is 'explained' by molecular motion, or that entropy is 'explained' by disorder. This unease is philosophically sound. Science never reaches a final, fundamental 'why.' It only ever replaces one description with another, more general or more detailed, description. The chain of explanation is infinite. Thermodynamics is an empirical science: its laws summarize what we observe. Kinetic theory and statistical mechanics are powerful reformulations, not ultimate foundations. Accepting this humility—that science describes, but does not explain in any absolute sense—liberates the learner from chasing an infinite regress.

Appendix A

Postulate (or Axiom): A fundamental statement that is accepted as true and evident without proof within a specific theory.

Example 1: Everyday Observation (Biology/Botany)

- Observation: We notice that the basil plant on your windowsill is leaning heavily toward the sunlight coming through the glass.
- Question: Why is the plant growing toward the light?
- Hypothesis: "If a plant is exposed to light from a single direction, then it will grow toward that light source to maximize photosynthesis."

Why this is a good hypothesis:

- Testable: We can design an experiment to test this. For example, we could rotate the plant 180 degrees each day and see if it continues to lean or grows straight.
- Falsifiable: If we rotate the plant and it still grows toward the original direction (perhaps due to a draft or gravity), the hypothesis would be proven false.
- Clear and Specific: It identifies the key variables: the independent variable (direction of light) and the dependent variable (direction of plant growth).

Example 2: Formal Scientific Context (Psychology)

- Observation: Previous studies suggest that short bursts of physical activity can improve cognitive function in adults.
- Question: Can a short, 10-minute walk improve memory recall in high school students?
- Hypothesis: "If high school students engage in a 10-minute brisk walk before a memory test, then they will score significantly higher than students who remain sedentary for the same period."

Why this is a good hypothesis:

- Testable: We can conduct a controlled experiment. One group of students (the experimental group) takes a 10-minute walk. Another group (the control group) sits quietly for 10 minutes. Both groups then take the same memory test.
- Falsifiable: The data might show no significant difference in test scores, or even that the walking group scored lower, which would falsify the initial prediction.
- Measurable: The outcome (memory recall) is measured by a quantitative test score, making the results objective and analyzable.

In both cases, the hypothesis serves as the foundation for an experiment. The results will either support the hypothesis or lead to its rejection, both of which are valuable outcomes that advance understanding.

The principle of falsification

A cornerstone of the modern scientific method is the principle of falsification, advanced by philosopher Karl Popper. It states that for a hypothesis, theory, or law to be considered scientific, it must be falsifiable. This means it must be possible to imagine empirical evidence that would contradict and therefore invalidate it.

For example, the First Law of Thermodynamics (conservation of energy) is falsifiable. One could propose an experiment demonstrating the creation of energy from nothing. If such an experiment were rigorously validated, the First Law would be falsified and would require fundamental revision.

This principle highlights that scientific knowledge is not built on absolute proof, but on the progressive elimination of error. Theories that withstand persistent and rigorous attempts at falsification are provisionally accepted as the best available explanations of how the universe works.

Unlike a mathematical proof a scientific theory is empirical and is always open to falsification. Newton's law of generation is a famous example of an established law that was later found and not to be universal. It does not hold in experiments involving motion at speeds close to the speed of light or in close proximity of strong gravitational fields.

So, Popper suggests that a scientist should try to refute her/his theory, rather than establish its truth. This goal could be accomplished without the use of induction.

The weakness of Popper's argument is obvious. For the goal of science is not solely to refute theories, but also to determine which theories are true (or probably true). When a scientist collects experimental data, their aim might be to show that a particular theory—their arch-rival's theory perhaps—is false. But much more likely, they are trying to convince people that their own theory is true. However, it seems that Popper's concerned about other branches of science such as economy, astronomy, biology, psychology and similar subjects that could have influence in the ontological and epistemological branched of philosophy rather the engineering practical subjects. The most critical non-scientific subject is ideology. When faced any evidence that falsifies a belief, ideology supports it with new justifications that are not subject to empiricism and observation.

Example:

Imagine we encounter an empty, deserted region in a forest.

Non-scientific theory: A gardener is responsible. He is invisible and acts without explaining his motives. We cannot falsify this claim.

Scientific theory: An underground activity has made this part of forest empty. We can test the geology of the earth in that region, and every physical theory conjectured can be examined by observation and instrumentation. At each step the theory is refined, and we get closer to the cause of the anomaly in that region of forest, without claiming to have discovered the ultimate cause.

Appendix B: Induction and deduction

In the context of logic, only deductive arguments are valid. An inductive argument is invalid as a logical argument; even though its premises might well be true (and so might its conclusion), they are not sufficient to allow us to infer the truth of the conclusion, as we will see. Let us consider some simple examples of inductive and deductive arguments. Remember, a deductive argument is just one such that the truth of premises implies the truth of the conclusion – and in this sense, the premises "contain" the conclusion already. An inductive argument is simply one for which this isn't the case. An example of a deductive argument is:

Premise 1: All Iranians drink tea in the morning

Premise 2: Siamak is Iranian

Therefore (deduced), Siamak drinks tea in the morning

This is a perfectly valid deductive argument. If someone were to use this argument to try to really argue that Siamak, some Iranian does not drink tea in the morning, then we can simply say that one of the premises is not true. True premises must take us to a true conclusion. In other words, if all Iranians really do drink tea, and if Siamak really is an Iranian, then it must be the case that he drinks real tea in the morning as a matter of logic.

Now consider an inductive argument:

Premise 1: All the Iranians I've ever met drink tea in the morning

Premise 2: Siamak, whom I've not met, is an Iranian

Therefore: Siamak drinks tea in the morning.

Here the conclusion could be quite manifestly invalid or merely probable. The two premises may be absolutely true, yet we can hold the premises to be true and yet deny the conclusion without contradicting the premises. Siamak could be the exception to the rule. Thus, induction is not capable of taking us from true premises to a guaranteed true conclusion.

In the context of thermodynamics, we can replace premises 1 and 2 of the induction argument with the following:

Premise 1: All heat engines that work in a cycle lose heat to a cold reservoir.

Premise 2: Someone has invented a novel engine, but I have not yet seen its operation.

Therefore: The novel engine also loses heat to a cold reservoir.

Deductive inference is safer than its inductive cousin. When we reason deductively, we can be certain that if we start with true premises we will end up with a true conclusion. By contrast, inductive reasoning is quite capable of taking us from true premises to a false conclusion. Despite this defect, we seem to rely on inductive reasoning throughout our lives. For example, when we turn on our computer in the morning, we are confident it will not explode in our face. Why? Because we turn on our computer every morning, and it has never exploded up to now. But the inference from up until now, my computer has not exploded when I turned it on my computer will not explode this time is inductive, not deductive. It is logically possible that our computer will explode this time, even though it has never done so before.

The conclusion of a deductively valid argument will always contain no more information than the premises of the argument. In fact, the conclusion of a deductive argument generally contains dramatically less information than the premises of that argument. We could actually think of this as the function of a deductive argument. Its conclusion allows us to focus on the particular implication of the information contained in the premises that interests usu. However, one should always remain prudent about the conclusion deduced as sometimes the premises are far from being true and they may be misleading.

The reason inductive arguments are useful, however, is that—unlike deduction—inductive arguments can actually add new information to the information that we already have. For example, the ideal gas law is obtained by an empirical inductive method upon examining the behavior of limited number of gases. However, the mathematical relation called the state equation can be applied to any gases that we have not even put on experience or may even exist in reality. A gas thermometer works on the principle of ideal gas law and is a useful application of the inductive approach.

Once a theory or law is established from an inductive method, we can deduce special argument or statement from it. The process of deduction after establishing the theory inductively is logically valid and contains no inconsistencies. For example, accepting the conservation of energy leads deductively or mathematically to the conclusion that energy is a property of a substance, as will be elucidated in chapter 5. The existence of entropy follows inevitably from the first and second laws of thermodynamics which is to be formulated by deduction (see chapter 8).

It should be mentioned that the problem of induction today is not applied to established sciences such as classical engineering thermodynamics. However, a general theory for turbulence in fluids if ever discovered in future would remain falsifiable for a long time.

Therefore, we should be careful to generalize the laws of thermodynamics derived from engineering applications. Using a deductive method to explain the phenomena related to biology, to analyze economic growth or to predict the future of universe is not straightforward and requires caution.

Appendix C: Microscopic Model of a Monatomic Ideal Gas

The behavior of ideal gas presented as an equation of state only describes how a gas behaves under variations of pressure, volume and temperature. The microscopic model presented in this appendix goes beyond the description and attempts to explain why the gas reacts consistent with the state equation.

An ideal gas assumed of collection of non-interacting particles. Each particle has mass and obeys classical Newtonian mechanics The mechanical energy is translational kinetic energy already known from dynamics course and expressed as

$$E = \frac{1}{2} m v^2 \tag{C-1}$$

Consider one particle (atom or molecule) in a cubic box of volume V, and compute the force on one wall from particle collisions.

The Momentum Change from One Collision is obtained as follows:

When a particle hits the wall perpendicular to the x-axis, the change in momentum is:

$$\frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L} \tag{C-2}$$

Time interval between collisions with same wall is the time molecule travels between hits and is $2L/v_x$. Factor 2 appears because the molecule moves 2L between each collision. The time between consecutive collisions with the same wall is the time to travel to the opposite wall and back.

Therefore, the average force from one particle:

$$F_x = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L} \tag{C-3}$$

Now for N molecules, we average over all their momentum exchange:

$$F_x^{\text{total}} = \sum_{i=1}^{N} \frac{mv_{x,i}^2}{L} = \frac{Nm\langle v_x^2 \rangle}{L} \tag{C-4}$$

Note that every molecule has its own velocity.

Pressure is force/area. Then:

$$P = \frac{F_x}{A} = \frac{Nm\langle v_x^2 \rangle}{L \cdot A} = \frac{Nm\langle v_x^2 \rangle}{V} \tag{C-5}$$

Remarks:

1. Pressure is defined as force per unit area. Force is the rate of change of momentum delivered to the wall. A single molecule colliding elastically with a wall transfers momentum $2mv_x$ (for the perpendicular component). But that transfer happens in an extremely short time. The instantaneous force from one collision is a huge spike. However, pressure gauges (or our sense of pressure) do not respond to individual spikes—they respond to the average over billions of collisions per second.

2. Not all collisions are identical. Molecules have different speeds. They hit the wall at different angles (only the perpendicular velocity component matters). They hit different spots at different times. So, the momentum transfer per collision varies widely. A fast molecule hitting head-on transfers more momentum than a slow one hitting at a grazing angle.

3. The justification comes from statistical averaging. We consider a wall of area A over a time interval Δt that is: Long compared to the time between collisions (so many collisions occur). Short compared to macroscopic changes (so the gas remains in equilibrium). In that time, the total momentum transferred to the wall is the sum of $2mv_{x,i}$ over all collisions. The average force is:

   $$F = \frac{\text{Total momentum transferred}}{\Delta t}$$

   Pressure is then $P = F/A$.

   Because the gas is in equilibrium and isotropic, the average over many molecules yields the same result as the average over time (ergodic hypothesis). The derivation uses the average of v_x^2, not any single v_x. But the key is that every collision, regardless of the molecule's speed, contributes to pressure according to the same physical law ($\Delta p = 2mv_x$). The "same effect" here means the same mechanism: momentum transfer via elastic collision. The magnitude differs, but when we average, the result is proportional to $\langle v_x^2 \rangle$.

4. Even if we started with all molecules at the same speed (but random directions), collisions would immediately create a spread of speeds. Elastic collisions between molecules of equal mass exchange velocities. After just a few collisions per molecule, the distribution becomes the familiar Maxwell–Boltzmann form. So, assuming different velocities is not a hypothesis we impose arbitrarily; it's the inevitable outcome of molecular motion and collisions.
5. The elastic collision is recalled from dynamics as follows.

Consider two identical particles having mass m. Their velocities before collision are $\vec{u}_1, \vec{u}_2$ and after collision are $\vec{v}_1, \vec{v}_2$.
The Conservation of momentum is written:

$$m\vec{u}_1 + m\vec{u}_2 = m\vec{v}_1 + m\vec{v}_2 \Rightarrow \vec{u}_1 + \vec{u}_2 = \vec{v}_1 + \vec{v}_2 \qquad \text{(C-6)}$$

The Conservation of kinetic energy in elastic is expressed as:

$$\frac{1}{2}mu_1^2 + \frac{1}{2}mu_2^2 = \frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 \Rightarrow u_1^2 + u_2^2 = v_1^2 + v_2^2 \qquad \text{(C-7)}$$

Let $\hat{e}$ be the unit vector along the line joining the centers at the moment of contact (line of impact).
Define:

$$u_{1\parallel} = \vec{u}_1 \cdot \hat{e}, u_{1\perp} = | \vec{u}_1 - (u_{1\parallel}\hat{e}) | \qquad \text{(C-8)}$$

and similarly for particle 2.
During the infinitesimally short collision, the forces act only along $\hat{e}$ (smooth, frictionless surfaces). Therefore, Momentum along $\hat{e}$ is conserved for the system. Momentum perpendicular to $\hat{e}$ is conserved for each particle individually (no force in that direction).
Thus:

$$u_{1\perp} = v_{1\perp}, u_{2\perp} = v_{2\perp} \qquad \text{(C-9)}$$

Momentum conservation along $\hat{e}$ is written as:

$$mu_{1\parallel} + mu_{2\parallel} = mv_{1\parallel} + mv_{2\parallel} \Rightarrow u_{1\parallel} + u_{2\parallel} = v_{1\parallel} + v_{2\parallel} \qquad \text{(C-10)}$$

Because perpendicular velocities do not change, the energy equation becomes:

$$u_{1\parallel}^2 + u_{1\perp}^2 + u_{2\parallel}^2 + u_{2\perp}^2 = v_{1\parallel}^2 + v_{1\perp}^2 + v_{2\parallel}^2 + v_{2\perp}^2 \qquad \text{(C-11)}$$

Cancel $u_{1\perp}^2 = v_{1\perp}^2$ and $u_{2\perp}^2 = v_{2\perp}^2$:

$$u_{1\parallel}^2 + u_{2\parallel}^2 = v_{1\parallel}^2 + v_{2\parallel}^2 \tag{C-12}$$

We have equations (C-10) and (C-12):

$$\begin{cases} u_{1\parallel} + u_{2\parallel} = v_{1\parallel} + v_{2\parallel} \\ u_{1\parallel}^2 + u_{2\parallel}^2 = v_{1\parallel}^2 + v_{2\parallel}^2 \end{cases} \tag{C-13}$$

From (C-10), let $S = u_{1\parallel} + u_{2\parallel} = v_{1\parallel} + v_{2\parallel}$.

From (C-12), $u_{1\parallel}^2 + u_{2\parallel}^2 = v_{1\parallel}^2 + v_{2\parallel}^2$.

Note that $\left(v_{1\parallel} + v_{2\parallel}\right)^2 = S^2 = v_{1\parallel}^2 + v_{2\parallel}^2 + 2v_{1\parallel}v_{2\parallel}$.

But also $u_{1\parallel}^2 + u_{2\parallel}^2 = S^2 - 2u_{1\parallel}u_{2\parallel}$.

Equating the expressions for S^2 from the two sides:

$$u_{1\parallel}^2 + u_{2\parallel}^2 + 2u_{1\parallel}u_{2\parallel} = v_{1\parallel}^2 + v_{2\parallel}^2 + 2v_{1\parallel}v_{2\parallel} \tag{C-14}$$

Since $u_{1\parallel}^2 + u_{2\parallel}^2 = v_{1\parallel}^2 + v_{2\parallel}^2$ from (C-12), we get:

$$u_{1\parallel}u_{2\parallel} = v_{1\parallel}v_{2\parallel} \tag{C-15}$$

Now we have $v_{1\parallel} + v_{2\parallel} = S$ and $v_{1\parallel}v_{2\parallel} = u_{1\parallel}u_{2\parallel}$.

Thus $v_{1\parallel}$ and $v_{2\parallel}$ are the two roots of the quadratic $x^2 - Sx + u_{1\parallel}u_{2\parallel} = 0$.

The roots are exactly $u_{1\parallel}$ and $u_{2\parallel}$. Therefore:

$$\{v_{1\parallel}, v_{2\parallel}\} = \{u_{1\parallel}, u_{2\parallel}\} \tag{C-16}$$

The two possible assignments are:

a) $v_{1\parallel} = u_{1\parallel}$, $v_{2\parallel} = u_{2\parallel}$ (no collision, trivial)

b) $v_{1\parallel} = u_{2\parallel}$, $v_{2\parallel} = u_{1\parallel}$ (swap)

The physical collision (non-trivial) gives exchange of parallel components:

$$v_{1\parallel} = u_{2\parallel}, v_{2\parallel} = u_{1\parallel} \tag{C-17}$$

From (C-9) and (C-17), the full final velocities are:

$$\vec{v}_1 = u_{2\parallel}\,\hat{e} + \vec{u}_{1\perp}, \vec{v}_2 = u_{1\parallel}\,\hat{e} + \vec{u}_{2\perp} \tag{C-18}$$

Now we show that same initial speeds can give different final speeds

Let initial velocities have the same magnitude u_0. Choose a coordinate system where $\hat{e} = \hat{x}$. Then:

$$\vec{u}_1 = (u_{1x}, u_{1y}), \vec{u}_2 = (u_{2x}, u_{2y}), \text{with } u_{1x}^2 + u_{1y}^2 = u_{2x}^2 + u_{2y}^2 = u_0^2 \tag{C-19}$$

After collision:

$$\vec{v}_1 = (u_{2x}, u_{1y}), \vec{v}_2 = (u_{1x}, u_{2y}) \tag{C-20}$$

Now compute speeds squared:

$$v_1^2 = u_{2x}^2 + u_{1y}^2, v_2^2 = u_{1x}^2 + u_{2y}^2 \tag{C-21}$$

For $v_1^2 = v_2^2$ we need $u_{2x}^2 + u_{1y}^2 = u_{1x}^2 + u_{2y}^2$, or $u_{2x}^2 - u_{2y}^2 = u_{1x}^2 - u_{1y}^2$. This is not generally true.

In three dimensions, using the Boltzmann distribution (a foundational result of statistical mechanics), the average kinetic energy of a molecule is:

$$\langle E \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \tag{C-22}$$

Equation (C-22) is a special case of the equipartition theorem for an ideal gas. It provides the key link between microscopic motion and macroscopic temperature. The theorem states that each quadratic degree of freedom of a molecule contributes an average energy of $\frac{1}{2} k_B T$ per molecule, or equivalently $\frac{1}{2} RT$ per mole, where R is the universal gas constant, T is the absolute temperature, and k_B is Boltzmann's constant. As noted in Chapter 5, this lecture note does not cover the details of statistical mechanics; we ask the reader to accept this result as given or refer to the appendix F that briefly discusses how the Equipartition theorem can be justified.

Now, assuming isotropy:

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\langle v_x^2 \rangle \Rightarrow \langle v_x^2 \rangle = \frac{1}{3}\langle v^2 \rangle \tag{C-23}$$

So:

$$\langle v_x^2 \rangle = \frac{2k_B T}{m} \tag{C-24}$$

Plugging into pressure formula we obtain:

$$P = \frac{Nm\langle v_x^2 \rangle}{V} \tag{C-25}$$

$$\langle v_x^2 \rangle = \frac{1}{3}\langle v^2 \rangle \tag{C-26}$$

$$\rightarrow P = \frac{Nm}{V} \cdot \frac{1}{3}\langle v^2 \rangle = \frac{1}{3} \cdot \frac{Nm\langle v^2 \rangle}{V} \tag{C-27}$$

But from kinetic theory:

$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T \Rightarrow m\langle v^2 \rangle = 3k_B T \tag{C-28}$$

So:

$$P = \frac{1}{3} \cdot \frac{N(3k_B T)}{V} = \frac{Nk_B T}{V} \tag{C-29}$$

The relation between pressure, volume and temperature is derived as:

$$PV = Nk_B T \tag{C-30}$$

Or, using and number of moles n for $N_k B$, we find the classical equation of ideal gas.

$$PV = n\bar{R}T \tag{C-31}$$

The ideal gas law is not just an empirical equation; it emerges naturally from the postulates of statistical mechanics (applied to non-interacting particles), which themselves connect microscopic mechanics to macroscopic thermodynamics. This derivation, however, relies on the fundamental postulate that for a system in thermal equilibrium, all accessible microstates of the same energy are equally probable.

Remark:

1. Temperature does not appear in Newton's equations. It is not a property of a single particle. It emerges when we have many particles and look at their average kinetic energy. It's a statistical, macroscopic concept. The underlying reality is molecular motion and collisions. What we call "temperature" is a convenient label for the average kinetic energy per degree of freedom.
2. Hot and cold are subjective notions. Human perception of "hot" and "cold" is relative to our own body temperature (~37°C). A 40°C day feels hot because heat flows into our body (we need to cool down). A 20°C day feels cool because heat flows out of our body.
3. What is objectively real is the average kinetic energy of molecules. Our subjective sensation of "hot" is just our nervous system's response to the rate and direction of heat transfer.
4. The relationship $\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT$ is a bridge between the microscopic world (masses, velocities, kinetic energy) – which is fundamental and the macroscopic world (thermometers, temperature scales) – which is convenient for human purposes.
5. So, temperature is not a primitive. It is derived. The primitive is the kinetic energy of molecules. That is a correct, reductionist view of physics.

A thermometer does not measure some abstract, intrinsic "temperature" floating in the substance. What it does:

1. It is placed in contact with the substance.
2. Heat flows (via molecular collisions) until thermal equilibrium is reached.
3. At equilibrium, the average kinetic energy per molecule of the thermometer's working fluid (e.g., mercury, alcohol, or thermistor electrons) equals that of the substance.
4. The thermometer then displays a number (e.g., 37°C) that is calibrated against known fixed points (ice/steam at standard pressure).
5. That number is not a direct reading of the substance's "heatiness" – it's a proxy for the equilibrium condition reached through energy transfer.
6. Temperature is an inferred, relational property. It only exists in the context of energy exchange and equilibrium. If a substance were perfectly isolated with no way to transfer energy, we could assign it a temperature in theory, but we could never measure it. And that

temperature would still just be a label for the average kinetic energy of its molecules. So, a thermometer doesn't "see" temperature; it experiences energy exchange and then reports a number we've agreed means something.

7. Energy is a fundamental conserved quantity. It exists for a single particle, an atom, a system, or the entire universe. It can appear as kinetic, potential, chemical, electrical, nuclear, and other forms. Temperature is an emergent property of a collection of many particles. It describes the thermal state of a system and is closely related to the average microscopic energy of its particles.

Appendix D: Macroscopic Derivation of Ideal Gas Law

Avogadro law (1811): It would be simpler if we use the results of microscopic approach of appendix C. The reason is that Avogadro's was a conjecture laid before the recognition of atoms and molecules and the notion of molar mass was defined a century later. The physical argument proposed by Avogadro is very conjectural, although his brilliant law was proved to be true later after the establishment of Chemistry as a separate branch of science. The law was verified later by measurements in late 19th beginning of 20th century.

Consider two different gases, 1 and 2, placed in separate containers of equal volume V and under the same pressure P and temperature T.

From equation B?, we can write:

For Gas 1:

$$P = \frac{1}{3}\frac{N_1 m_1}{V}\bar{v}_1^2 \tag{D-1}$$

For Gas 2:

$$P = \frac{1}{3}\frac{N_2 m_2}{V}\bar{v}_2^2 \tag{D-2}$$

Since their pressures and volumes are equal, we can set the two equations equal to each other:

$$\frac{1}{3}\frac{N_1 m_1}{V}\bar{v}_1^2 = \frac{1}{3}\frac{N_2 m_2}{V}\bar{v}_2^2 \tag{D-3}$$

Simplifying this gives:

$$N_1 m_1 \bar{v}_1^2 = N_2 m_2 \bar{v}_2^2 \tag{D-4}$$

A crucial point of the kinetic theory is that the average translational kinetic energy of a gas molecule depends only on its absolute temperature.

$$\frac{1}{2}m\bar{v}^2 = \text{Constant for a given temperature} \tag{D-5}$$

Therefore, for Gas 1 and Gas 2 at the same temperature T, their average kinetic energies are equal:

$$\frac{1}{2}m_1\bar{v}_1^2 = \frac{1}{2}m_2\bar{v}_2^2 \tag{D-6}$$

which simplifies to:

$$m_1\bar{v}_1^2 = m_2\bar{v}_2^2 \tag{D-7}$$

We now have two equations:

- Equation A: $N_1m_1\bar{v}_1^2 = N_2m_2\bar{v}_2^2$
- Equation B: $m_1\bar{v}_1^2 = m_2\bar{v}_2^2$

If we divide Equation A by Equation B, the terms $m_1\bar{v}_1^2$ and $m_2\bar{v}_2^2$ cancel out, leaving us with:

$$N_1 = N_2 \tag{D-8}$$

This derivation conclusively shows that for two different gases under the same conditions of temperature, pressure, and volume, the number of molecules must be identical. This is the exact statement of Avogadro's Law stated as:

Equal volumes of gases, at the same temperature and pressure, contain equal numbers of molecules.

The key insight is that while heavier molecules (larger m) move slower (smaller $\bar{v}^2$), the product $m\bar{v}^2$ (related to kinetic energy) is the same for all gases at a given temperature. To exert the same pressure on the walls of identical containers, the number of molecules doing the "bombarding" must be the same.

From Boyle's Law (1662), for a fixed amount of gas at constant temperature:

$$P \propto \frac{1}{V} \text{ or } PV = \text{constant} \tag{D-9}$$

From Charles's Law (1787), for a fixed amount of gas at constant pressure:

$$V \propto T \text{ or } \frac{V}{T} = \text{constant} \tag{D-10}$$

Definition of a mole: Based on Avogadro's law, one mole of any gas is defined as 6.022 × 10^{23} particles. This amount of particle, at standard pressure and temperature conditions (273.15 K and 1 atm), occupies approximately the same volume.

Combine Boyle and Charles

For a fixed amount of gas:

$$V \propto \frac{T}{P} \Rightarrow \frac{PV}{T} = \text{constant} \tag{D-11}$$

Accurate experimental measurements show that at standard conditions 1 mole of any ideal gas occupies approximately 22.414 L.

We can therefore calculate a molar gas constant$\overline{R}$:

$$R = \frac{PV}{T} \text{for 1 mole of gas} \tag{D-12}$$

For n moles of gas, since volume is directly proportional to the number of moles (Avogadro's Law), we can generalize to n moles using Avogadro's Law as expressed below:

$$\frac{PV}{T} = n\overline{R} \tag{D-13}$$

Or:

$$PV = nRT \tag{D-14}$$

Alternative: The Kinetic Theory Route

From kinetic theory, we derived:

$$PV = \frac{1}{3} Nm\bar{v}^2 \tag{D-15}$$

And

$$\frac{1}{2} m\bar{v}^2 = \frac{3}{2} k_B T \tag{D-16}$$

Combining:

$$PV = Nk_B T \tag{D-17}$$

Recognizing that N (number of molecules) = nN_a (moles × Avogadro's number):

$$PV = n(N_a k_B)T = n\overline{R}T \tag{D-18}$$

where $\overline{R} = N_a k_B$ is the universal gas constant.

Both paths lead to the same result, but starting with a clear definition of 'n' provides the most rigorous foundation.

Remarks:

1. n is indeed the generalized molecular count. We use n (the number of moles) to represent the amount of substance. It is directly proportional to the number of molecules, N with respect to N_A, the Avogadro's number.

$$n = \frac{N}{N_A} \tag{D-19}$$

2. Molar mass (M) is the mass of one mole of a chemical substance. The definition of the mole is based on a fixed number of entities (like atoms, molecules, or ions). Specifically, the mole is defined by setting the value of the Avogadro constant (N_A) to exactly $6.02214076 \times 10^{23}$ elementary entities per mole. Therefore, molar mass can be understood as the mass of 6.022×10^{23} particles of a substance. The molar mass of any substance is a physical property that is determined through experimental measurement.

3. Determination of Molar Mass**:** The molar mass of a substance is a critical property that influences its material and chemical characteristics. It is often determined experimentally using various techniques.

4. The Link to Measurable Mass: This is the key to applying the theory. We define n by using m the total mass of the sample (in grams or kilograms) and M the molar mass (in g/mol or kg/mol). Thus, n is written as:

$$n = \frac{\text{Total Mass of the Substance}}{\text{Molar Mass}} = \frac{m}{M} \tag{D-20}$$

This definition ($n = m/M$) bridges the gap between the abstract world of molecule counts and the concrete world of laboratory measurements. We can't count molecules directly. (N is immeasurable directly). But we can measure mass perfectly easily. (m is easily measurable with a balance).

On the Interaction of Pressure, Temperature, and Volume

We cannot directly measure the speed of a single gas molecule—it is far too small and fast. However, we can measure properties of the gas as a whole, such as pressure and volume.

Pressure arises from billions of gas molecules colliding with the walls of their container every second. The faster a molecule moves, the harder it strikes the wall. Therefore, if we increase the average speed of the molecules while keeping the volume fixed, the pressure increases.

Experiments show that for a fixed amount of gas in a fixed volume, the pressure is proportional to the temperature (measured in kelvin). Thus:

- Higher temperature → higher pressure
- Lower temperature → lower pressure

Higher pressure means that molecules are hitting the walls with greater force. Greater impact force implies a higher average molecular speed—more precisely, a higher average kinetic energy. Consequently, higher temperature leads to higher average molecular speed and kinetic energy.

Now consider a different situation: the volume is decreased while the temperature remains constant. In this case, the average molecular speed does not change, but the molecules travel a shorter distance between collisions with the walls. As a result, the frequency of collisions increases, which raises the pressure. This explains why reducing the volume of a gas (at constant temperature) increases its pressure—a relationship known as Boyle's law.

Appendix E: On the Mechanical Energy

The discovery of the conservation of energy in mechanics of motion was a gradual process spanning the 17th to 19th centuries, driven by both theoretical insights and experiments on falling bodies, pendulums, and collisions.

Key steps and contributors:

1. Galileo Galilei (c. 1600s) – Through experiments with pendulums and inclined planes, Galileo observed that a pendulum always rises to nearly its original height (air resistance aside) and that a ball rolling down one incline climbs to the same height on another, regardless of slope. This hinted at a conserved quantity related to height and motion, though he did not formalize it as energy.
2. Christiaan Huygens (1650s–70s) – Studying elastic collisions, Huygens showed that the sum of the products of mass and squared speed (mv^2) was conserved in certain interactions, alongside momentum. This “vis viva” (living force) was an early precursor to kinetic energy.
3. Gottfried Wilhelm Leibniz (1686) – Explicitly distinguished “vis viva” (mv^2) from Descartes’ momentum (mv). He argued that vis viva is conserved in mechanical processes where no friction or inelastic losses occur, laying a foundation for energy conservation in ideal systems.
4. Johann Bernoulli and Daniel Bernoulli (18th century) – Applied vis viva to fluid mechanics and linked it to “potential” height (gravitational potential), introducing the idea that work done by gravity converts into vis viva.
5. Joseph-Louis Lagrange (1788) – In *Mécanique Analytique*, Lagrange derived equations of motion that directly imply conservation of total mechanical energy (kinetic + potential) for systems under conservative forces, though the term “energy” wasn’t yet standard.
6. Gaspard-Gustave Coriolis (1829) – Introduced the modern term “kinetic energy” ($\frac{1}{2}mv^2$) and the work-energy theorem, showing that work done by forces equals the change in kinetic energy.
7. William Robert Grove, Hermann von Helmholtz, James Prescott Joule (1840s) – Established the general principle of conservation of energy, incorporating heat, electricity, and mechanical work. Joule’s paddle-wheel experiment demonstrated that mechanical work (e.g., falling weights) produces a proportional amount of heat, showing that energy is not lost but transformed. Helmholtz (1847) gave a unified mathematical formulation, including mechanical energy as a special case.

In the 17th and 18th centuries, natural philosophers were trying to find a quantity that remained constant in mechanical processes (like collisions), believing that the universe should obey such a conservation law.

There were two main competing ideas:

René Descartes (1644): He proposed that the important conserved quantity was momentum ($mass \times velocity$), or as he called it, the "quantity of motion." For Descartes, this quantity was simply $m \times v$. A small object moving very fast could have the same "quantity of motion" as a large object moving slowly.

Gottfried Wilhelm Leibniz (1686): He argued against Descartes. Through experiments with pendulums and falling bodies, Leibniz became convinced that the truly conserved quantity was not $m \times v$, but $m \times v^2$. He named this quantity vis viva ("living force"). He argued that this quantity, not momentum, was the true measure of a body's "power" to do work, like how high a pendulum can swing or how deeply a hammer can drive a nail.

Leibniz's key insight came from the physics of falling objects. He realized that the height a body falls is related to its potential to create motion. The square of the velocity (v^2) it gains is directly proportional to that height.

Therefore, $m \times v^2$ seemed to be the quantity that was exchanged, transformed, and ultimately conserved in these mechanical processes. It represented the "living," active force in motion, as opposed to "dead" force (like the pressure of a stationary object).

The debate raged for decades because both sides seemed to have evidence. The reason was that both momentum *and* vis viva are conserved, but under different conditions:

Momentum ($m \times v$) is conserved in all collisions (elastic and inelastic).

Vis viva ($m \times v^2$) is only conserved in perfectly elastic collisions.

This is why the debate was so difficult to resolve—both quantities are fundamental, but they describe different things.

The resolution came with a crucial refinement. It was later recognized (particularly by Émilie du Châtelet and others) that when calculating the *work* done by a constant force (F) over a distance (d), the integral leads naturally to $\frac{1}{2} \times m \times v^2$, not $m \times v^2$.

In the early 19th century, the term "energy" was beginning to be used more broadly. The British physicist Lord Kelvin (William Thomson) and others started to distinguish between different forms this conserved quantity could take.

The energy of motion, which was Leibniz's *vis viva*, was formally renamed kinetic energy by Lord Kelvin. He defined it as $K = \left(\frac{1}{2}\right) mv^2$. The "energy of position" or stored energy was named potential energy, P.E.

The work of physicists like James Prescott Joule demonstrated that heat was not a fluid ("caloric") but a form of energy itself—thermal energy. This proved that *vis viva* could transform into other forms (heat, light, etc.).

This finally led to the modern principle of the Conservation of Energy: Energy cannot be created or destroyed, only transformed from one form to another (e.g., kinetic $\left(\frac{1}{2}\right) mv^2$ to potential (mgh) to thermal, etc.). The total sum of all these forms remains constant.

So, vis viva was the historical precursor and conceptual foundation for our modern term kinetic energy. The journey from $m \times v^2$ to $\left(\frac{1}{2}\right) mv^2$ represents the shift from a brilliant intuition to a precise physical definition integrated into the universal law of conservation of energy.

Appendix F: Proof of Equipartition Theorem

F.1 Microscopic definition of entropy

Statistical mechanics connects the **microscopic** world (individual molecules, their positions and velocities) to the **macroscopic** world (temperature, pressure, entropy).

The central formula is:

$$s = \ln \Omega \text{ or } S = k_B \ln \Omega \tag{F-1}$$

where s is the dimensionless entropy, S the thermodynamic entropy, and Ω the number of microstates consistent with a given macrostate.

Fundamental Postulate: Equal a Priori Probability

For an **isolated system** at equilibrium (fixed total energy E, fixed number of particles N, fixed volume V – but here we ignore volume because energy depends only on velocity) we postulate that:

Every microstate that satisfies the macroscopic constraints is equally probable.

That is, if we list all possible ways the molecules can have velocities such that the total kinetic energy equals E, each of those ways is equally likely to occur.

This is not a mathematical theorem; it is a physical postulate (assumption) that has been tested countless times and agrees with experiments.

Microstate vs. Macrostate

- **Microstate**: A complete specification of the velocity of every molecule. Example for two molecules: $(v_1, v_2) = (+1, -2)$.
- **Macrostate**: A specification of only a few global properties – here, only the total kinetic energy E (and N, but N is fixed).
- Example: “$E = 2$” (in some unit).

The number of microstates that give the same macrostate E is called $\Omega(E)$.

Simple Discrete Model: Two Molecules in 1D

Let’s make the problem so simple that we can count Ω by hand.

- **Molecules**: $N = 2$, distinguishable (we can label them A and B).

- **Motion**: One-dimensional (velocity is just a signed number).
- **Mass**: Set $m = 2$ so that kinetic energy of one molecule is $e = v^2$ (since $\frac{1}{2}mv^2 = v^2$ when $m = 2$).
- **Allowed velocities**: To keep the count finite, let velocity take only **integer values** from -2 to $+2$:
  $v = -2, -1, 0, +1, +2.$
  Then the possible energies are:

  $$e = v^2 : 0,\ 1,\ 4.$$

- **Macrostate**: Fixed total energy $E = 2$ (exact, not a range).
- We count the microstates

We need all pairs (v_A, v_B) such that $v_A^2 + v_B^2 = 2$.

The squares are 0, 1, 4. The only way to sum to 2 is $1 + 1$.

So each molecule must have $v^2 = 1 \rightarrow v = +1$ or $v = -1$.

- Molecule A: 2 choices
- Molecule B: 2 choices

Total microstates:

$$\Omega = 2 \times 2 = 4.$$

Let us list them explicitly:

1. $(+1, +1)$
2. $(+1, -1)$
3. $(-1, +1)$
4. $(-1, -1)$

All four have total energy $1 + 1 = 2$.

We calculate the entropy from counting

The entropy (dimensionless) is the natural logarithm of Ω:

$$s = \ln\ \Omega = \ln\ 4 \approx 1.386.$$

If we wanted the usual thermodynamic entropy, we would multiply by Boltzmann's constant: $S = k_B \ln\ 4$.

Let us check another constant macrostate: $E = 5$

Now let the macrostate be $E = 5$ exactly.
We need $v_A^2 + v_B^2 = 5$.
Possibilities: $4 + 1$ or $1 + 4$.

- **Case 4+1**: $v_A = \pm 2$ (2 choices), $v_B = \pm 1$ (2 choices) → $2 \times 2 = 4$ microstates.
- **Case 1+4**: $v_A = \pm 1$ (2 choices), $v_B = \pm 2$ (2 choices) → another 4 microstates.

Total $\Omega = 8$.

$$s = \ln\, 8 = 3\ln\, 2 \approx 2.079.$$

So as E increases, Ω increases, and entropy increases.

Why Does Entropy Increase with Energy? – "Molecules Are Innocent, *E* Is Guilty"

When we heat a gas at constant volume, we add energy E.

- The molecules themselves do not change.
- But the constraint on total energy becomes looser: a larger E means the system can access more velocity combinations.

In our discrete model, $E = 2$ gave $\Omega = 4$; $E = 5$ gave $\Omega = 8$. In a real continuous gas, Ω grows as $E^{3N/2}$, a huge increase.

Thus, the rise in entropy when heating is entirely due to the increase in E – the molecules are innocent, E is guilty.

For an ideal gas expanding isothermally (constant T):

- The total kinetic energy E stays constant because $E = \frac{3}{2} N k_B T$.
- Since E is unchanged, the momentum (velocity) microstates remain exactly the same set as before – nothing changes in how energy is distributed among velocities.
- What *does* change is the volume V available to each molecule. In the full phase space, the number of microstates is proportional to V^N (for distinguishable particles) or $V^N/N!$ (indistinguishable).

Thus:

$$\Omega_{\text{total}} = \Omega_{\text{momentum}} \times \Omega_{\text{position}} \tag{F-2}$$

and Ω_{position} increases with V.

The entropy change for isothermal expansion from V_i to V_f is:

$$\Delta S = N k_B \ln\left(\frac{V_f}{V_i}\right) \tag{F-3}$$

which comes entirely from the position part.

The word “disorder” suggests something like molecules becoming more jumbled or chaotic in their motions. But during isothermal expansion:

- The velocities (hence the kinetic energy distribution) are identical before and after.
- The only new thing is that each molecule has more possible positions to occupy.

That’s not “disorder” in any intuitive sense – it’s simply a larger set of microstates because a new degree of freedom (position) now has more options. The entropy increases because the system’s microstate count increases, but the motion (velocities) is unchanged.

F.2 Proving equipartion theorem

Definition: Let $\Omega(E)$ be the number of distinct microscopic states (microstates) of a system with total energy E.

Consider a small system in thermal contact with a large reservoir at temperature T.

Total energy: $E_{\text{total}} = E_{\text{system}} + E_{\text{reservoir}} = \text{constant}$.

The number of microstates of the combined system is

$$\Omega_{\text{total}}(E_{\text{system}}) = \Omega_{\text{system}}(E_{\text{system}}) \cdot \Omega_{\text{reservoir}}(E_{\text{total}} - E_{\text{system}}) \tag{F-4}$$

Since the reservoir is large, expand $\ln \Omega_{\text{reservoir}}$ around E_{total}:

$$\ln\ \Omega_{\text{reservoir}}(E_{\text{total}} - E_{\text{system}}) = \ln\ \Omega_{\text{reservoir}}(E_{\text{total}}) - \frac{\partial \ln\ \Omega_{\text{reservoir}}}{\partial E_{\text{reservoir}}} |_{E_{\text{total}}}\ E_{\text{system}} + \cdots \tag{F-5}$$

Define

$$\beta \equiv \frac{\partial \ln\ \Omega_{\text{reservoir}}}{\partial E_{\text{reservoir}}} |_{E_{\text{total}}} \tag{F-6}$$

The probability that the system has energy E_{system} is proportional to $\Omega_{\text{total}}(E_{\text{system}})$, hence

$$P(E_{\text{system}}) \propto \Omega_{\text{system}}(E_{\text{system}})\ e^{-\beta E_{\text{system}}} \tag{F-7}$$

For a single particle (or a system where the density of states is nearly constant over the relevant energy range), this reduces to

$$P(E) \propto e^{-\beta E} \tag{F-8}$$

which is the Boltzmann distribution.

From statistical thermodynamics, entropy is $S = k\ln\ \Omega$. For the reservoir,

$$\frac{1}{T} = \frac{\partial S_{\text{reservoir}}}{\partial E_{\text{reservoir}}} = k\ \frac{\partial \ln\ \Omega_{\text{reservoir}}}{\partial E_{\text{reservoir}}} = k\beta \tag{F-9}$$

Thus

$$\beta = \frac{1}{kT} \tag{F-10}$$

The Boltzmann distribution becomes $P(E) \propto e^{-E/(kT)}$.

For a particle of mass m with velocity component v_x, the kinetic energy contribution is $\frac{1}{2}mv_x^2$.

The probability density for v_x is

$$P(v_x) \propto e^{-\frac{mv_x^2}{2kT}} \tag{F-11}$$

Average $\langle v_x^2 \rangle$ is expressed as:

$$\langle v_x^2 \rangle = \frac{\int_{-\infty}^{\infty} v_x^2 \ e^{-\frac{mv_x^2}{2kT}} \, dv_x}{\displaystyle\int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2kT}} \ dv_x} \tag{F-12}$$

Set $a = \frac{m}{2k}$. The denominator is the Gaussian integral $\sqrt{\pi/a}$.

The numerator is

$$\int_{-\infty}^{\infty} x^2 \, e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a^3}} \tag{F-13}$$

Thus

$$\langle v_x^2 \rangle = \frac{\frac{1}{2}\sqrt{\pi/a^3}}{\sqrt{\pi/a}} = \frac{1}{2a} = \frac{1}{2} \cdot \frac{2kT}{m} = \frac{kT}{m} \tag{F-14}$$

Average kinetic energy per degree of freedom

$$\langle \frac{1}{2} m v_x^2 \rangle = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} kT \tag{F-15}$$

In three dimensions, $v^2 = v_x^2 + v_y^2 + v_z^2$, and by symmetry each component contributes the same:

$$\langle K \rangle = \frac{1}{2} kT + \frac{1}{2} kT + \frac{1}{2} kT = \frac{3}{2} kT \tag{F-16}$$

This completes the derivation of the equipartition theorem for translational kinetic energy.

Appendix G: Constant Gas Volume Thermometer

Scientists measured the coefficient of expansion of various substances (like mercury and metals) and used them to build thermometers, *assuming* a linear relationship with a "temperature" scale they defined arbitrarily (e.g., 0° for ice, 100° for steam).

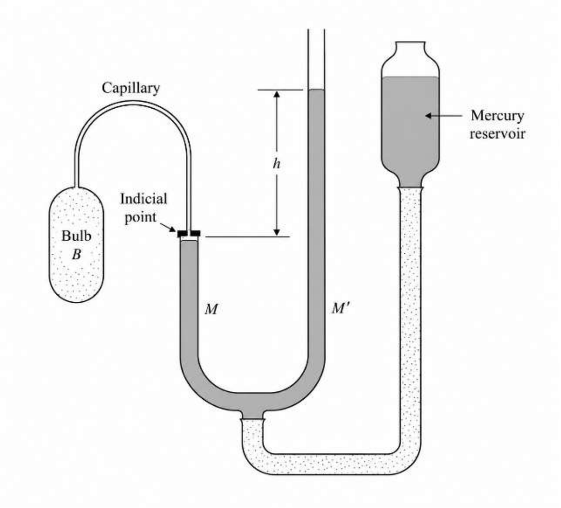


Figure G-1: Simplified constant-volume gas

This inconsistency forced them to search for a truly universal and fundamental temperature scale. This led to the concept of the absolute temperature scale based on the properties of gases themselves, which then retroactively redefined the meaning of the coefficient of expansion.

The scale between reference points was divided linearly. This meant that the coefficient of expansion k for the thermometric fluid (e.g., mercury) was defined *as* constant. The change in length ΔL (or volume ΔV) was assumed to be directly proportional to "temperature" (t):

$$\Delta L = L_0 \cdot k \cdot t \tag{G-1}$$

where k was just a constant of proportionality. The number on the thermometer *was* the temperature.

Scientists like Boyle, Charles, and Gay-Lussac began studying gases and discovered elegant relationships. But a critical problem arose: the value of the "temperature" T in these laws depended on the thermometer used.

If we used a mercury thermometer to measure the temperature of a gas, we would get one value for the coefficient in Charles's law $\left(\frac{V}{T} = \text{constant}\right)$.

If we used an alcohol thermometer, we would get a slightly different value for the "constant."

This was scientifically unacceptable. The laws of physics should be independent of the tool used to measure them.

Principles of gas thermometer

Scientists realized that among all substances, gases exhibited the most consistent and regular thermal behavior. They began using a gas itself (in a constant-volume thermometer) as the standard instrument (see figure G-1).

We perform measurements of the pressure ratio for a gas bulb immersed first in boiling water (temperature T_s) and then in an ice-water steam mixture (called triple pint temperature), each time reducing the amount of gas in the bulb. We plot the measured pressure ratio P_s/P_{TP} against the pressure P_{TP} (at the triple point) and extrapolate to $P_{TP} = 0$. On the y-axis, we put the measured pressure ratio $\frac{P_s}{P_{TP}}$. On the x-axis, we put the pressure of the gas in the bulb at the triple point, P_{TP}.

We will get a curve that is not perfectly horizontal. However, we will see that as the pressure P_{TP} approaches zero, the calculated ratio $\frac{P_s}{P_{TP}}$ approaches a limiting value (see figure G-2).

If we perform the experiment above with different gases (e.g., oxygen, nitrogen, helium) at the same starting pressure, we will get slightly different pressure readings (P) in the hot water bath.

Real gases deviate from ideal behavior due to intermolecular forces (attraction between molecules) and the finite size of the molecules themselves. These forces are unique to each type of gas. See the discussion on Joule Thompson coefficient below.

This limiting value, the Y-intercept of the graph where $P_{TP} = 0$, is the ratio that a perfectly ideal gas would give. For the boiling and triple points of water, this extrapolated value is indeed very close to 1.3661.

The ideal gas law gives $\frac{P_s}{P_{TP}} = \frac{T_s}{T_{TP}} = \frac{T_s}{T_i}$ where T_i is the temperature of ice point. We define the temperature difference $T_s - T_i = 100$ K (or 100°C). Hence:

$$\frac{P_s}{P_i} = \frac{T_i + 100}{T_i} = 1 + \frac{100}{T_i}$$

Solving for T_i:

$$\frac{P_s}{P_i} - 1 = \frac{100}{T_i} \Rightarrow T_i = \frac{100}{(P_s/P_i) - 1}$$

Using the extrapolated ideal ratio $(P_s/P_i)_{\text{ideal}} \approx 1.3661$ from the figure G-2gives

$$T_i = \frac{100}{1.3661 - 1} = \frac{100}{0.3661} \approx 273.15\text{ K}$$

Therefore, the ice point is approximately 273.15 K, and the boiling point is $T_s = T_i + 100 = 373.15$ K. This experimental procedure is the foundation of the Kelvin temperature scale.

(Modern measurements using this method define the triple point of water as $273.16\ K$, which sets the ice point at approximately $273.15\ K$).

Conclusion

By measuring the pressure ratio at progressively lower gas densities and extrapolating to zero pressure, we effectively eliminate the non-ideal behavior of the real gas we are using. This allows us to find the pressure ratio that a hypothetical, perfectly ideal gas would have.

This ratio is directly related to the ratio of the absolute temperatures. Since we have defined the interval between the fixed points as 100 degrees, we can then solve for the absolute temperatures of the fixed points themselves, arriving at $\sim 273\ K$ and $\sim 373\ K$. This process is the fundamental experimental basis for the Kelvin scale.

Measuring an Unknown Temperature with a Gas Thermometer

To accurately measure an unknown temperature T using a constant-volume gas thermometer, we account for non-ideal gas behavior by extrapolating to the ideal gas limit. Here's the step-by-step procedure:

Initial Measurements:

Fill the thermometer bulb with a gas (e.g., nitrogen or helium).

Measure the pressure P_{ice} when the bulb is at the ice point (defined as $273\ K$).

Measure the pressure P when the bulb is at the unknown temperature T.

Compute the ratio $\frac{P}{P_{\text{ice}}}$.

Reducing Gas Density:

Remove some gas from the bulb to reduce the initial pressure.

Repeat the measurements of P_{ice} and P at this lower density.

Compute the ratio $\frac{P}{P_{\text{ice}}}$ again.

Continue this process several times, each time with less gas (lower pressure).

Extrapolation to Zero Pressure:

Plot the computed ratios $\frac{P}{P_{\text{ice}}}$ on the vertical axis against the pressure at the ice point P_{ice}.

Extrapolate the curve to where $P_{\text{ice}} = 0$. The vertical intercept gives the ideal gas limit of the ratio, denoted $(\frac{P}{P_{\text{ice}}})$ideal .

Calculating the Unknown Temperature:

For an ideal gas, pressure is proportional to absolute temperature: $\frac{P}{P_{\text{ice}}} = \frac{T}{T_{\text{ice}}}$.

Assuming the ice point is $273\ K$, the unknown temperature is:

$$T = 273 \times (\frac{P}{P_{ice}})_{\text{ideal}} \tag{G-2}$$

This method ensures that the measurement is based on the ideal gas law, eliminating errors due to real gas effects such as intermolecular forces and finite molecular size. The extrapolation to zero pressure yields a result that is independent of the specific gas used, providing a fundamental and accurate determination of the absolute temperature.

$$T = 273 \times \left(\frac{P}{P_{\text{ice}}}\right)_{\text{ideal}} \tag{G-3}$$

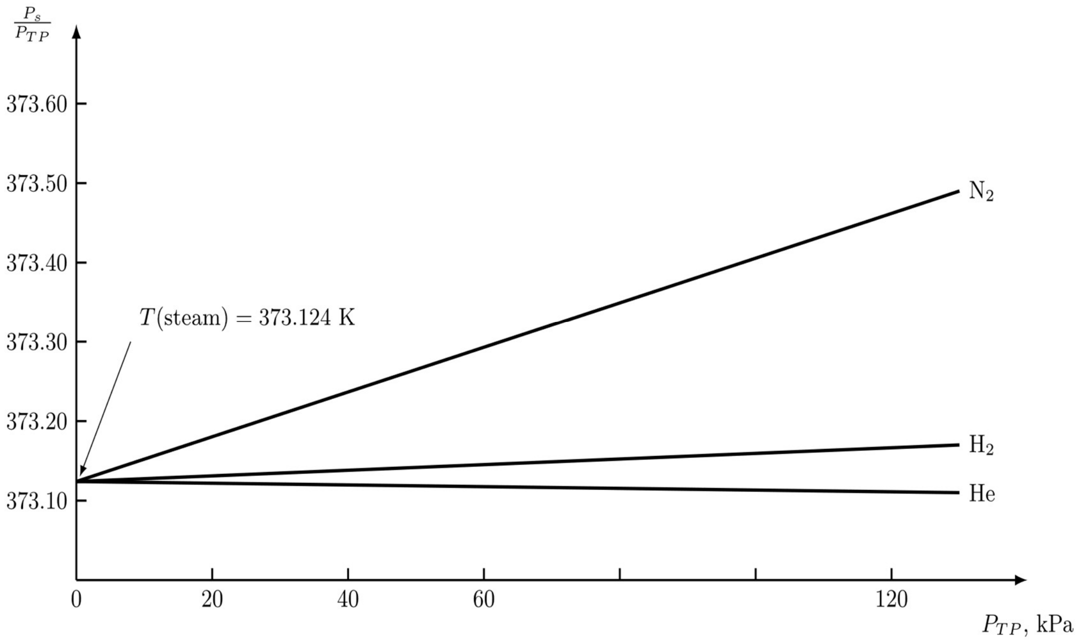


Figure G-2: Readings of a constant-volume gas thermometer for the temperature of steam when different gases are used at various arbitrary values of triple point pressure

The Key Advantage: Independence from Substance

A paramount advantage of this method is that the final result is independent of the type of gas used in the thermometer.

The process of extrapolating the pressure ratio to zero pressure effectively corrects for the unique non-ideal properties (molecular size, intermolecular forces) of any specific gas. Whether we use helium, nitrogen, or argon, the extrapolated intercept $\left(\frac{P}{P_{\mathrm{TP}}}\right)_{\mathrm{ideal}}$ will converge to the same value. This is because all gases behave as ideal gases in the limit of zero pressure.

Contrast with Mercury/Liquid Thermometers: This is in stark contrast to thermometers based on the thermal expansion of a liquid, like a mercury or alcohol thermometer.

These thermometers rely on the empirical fact that the liquid expands more than its glass container. The reading depends directly on the coefficient of thermal expansion of that specific liquid.

If we built two identical thermometers, one with mercury and one with alcohol, they would likely give slightly different readings at the same temperature (outside of the calibrated points) because the two liquids expand at slightly different rates. Their operation is based on a material property that is *not* universal.

The gas thermometer, through its extrapolation procedure, allows us to define a universal temperature scale (the Kelvin scale) based on the fundamental laws of thermodynamics and ideal gas behavior. Liquid thermometers, on the other hand, measure temperature relative to the arbitrary expansion properties of a specific substance, making them secondary instruments that must be calibrated against a primary standard like a gas thermometer. This is why the gas thermometer is the primary standard for defining the International Temperature Scale.

In figure G-2 we notice that the slope of the curves for different gases is different. It can be explained by the Joule Thomson Coefficient as explained in the following remark.

Remark: The Joule-Thomson Coefficient (μ)

This is the quantity that measures the sign of the slope we observed. It is defined as:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \qquad \text{(G-4)}$$

Translation: The change in temperature per change in pressure at constant enthalpy.

- If μ is positive: The gas cools down upon expansion (or heats up upon compression). ($\frac{dP}{\mathrm{dT}}$ is positive)
- If μ is negative: The gas heats up upon expansion (or cools down upon compression). ($\frac{dP}{\mathrm{dT}}$ is negative)

- If μ is zero: The gas behaves like an ideal gas in this regard. This happens at the inversion temperature.

For any given real gas, there is a specific temperature called the inversion temperature.

Below the inversion temperature the attractive forces dominate. When the gas expands, molecules pull away from each other. To overcome these attractive forces, they use their own kinetic energy.

This loss of kinetic energy means the gas cools down ($\mu > 0$).

Above the inversion temperature the Kinetic energy is high, and repulsive forces dominate.

When the gas expands, the molecules are already moving so fast that the repulsive forces from collisions are the main effect. As they move apart, these high-energy collisions become less frequent.

The overall effect is a decrease in the potential energy associated with repulsion, which results in an increase in kinetic energy and the gas heats up ($\mu < 0$).

This is beautifully illustrated by the classic experiment. A gas is forced through a porous plug (a throttling process). The pressure drops, and the temperature on the other side is measured.

The curves can be drawn for different gases are isochores (constant volume lines). Their slope is $\left(\frac{dP}{dT}\right)_V$.

The sign and value of this slope are deeply connected to the Joule-Thomson coefficient and the equation of state for the real gas. A negative slope on a P-T diagram for an isochore implies that for a given volume, *an increase in temperature* leads to a decrease in pressure. This counter-intuitive result is a direct consequence of the strong intermolecular forces and the complex relationship between pressure, volume, and temperature for real gases far from ideal conditions.

Appendix H: The Mathematical Link: The Maxwell Relations & The Ideal Gas Law

The experimental result can be derived mathematically from the ideal gas equation of state using thermodynamic relations. This is where the Maxwell relations come in. The relations are covered in part 2 of the lecture notes.

From the fundamental thermodynamic relations, we can derive an important equation for the volume dependence of internal energy:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{G-1}$$

This equation is always valid.

Now, we assume the ideal gas law:

$$P = \frac{RT}{V} \tag{G-2}$$

We calculate the partial derivative:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \tag{G-3}$$

We substitute back:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V}\right) - P \tag{G-4}$$

But from the ideal gas law, $\frac{RT}{V} = P$. Therefore:

$$\left(\frac{\partial U}{\partial V}\right)_T = P \tag{G-5}$$

$$-P = 0 \tag{G-6}$$

This mathematical derivation confirms Joule's experimental finding: For a substance that obeys the ideal gas law $PV = RT$, the internal energy is independent of volume and depends only on temperature, $U = U(T)$.

Remark 1: The Maxwell relation does not prove mathematically that internal energy of ideal gas is independent of pressure or volume. It only shows that the state equation of ideal gas is correct when deduced for a gas at very low pressure omitting the intermolecular forces and its internal energy is only a function of temperature. Therefore, the cancellation of volume dependence is a consequence of using a temperature scale consistent with both the second law of thermodynamics and ideal gas equation of state. The reader is urged to study Maxwell equations, presented in standard textbooks, and the deduction of entropy property from the second law of thermodynamics for further understanding.

Remark 2: For real gases, intermolecular forces do exist. This means the internal energy U has both kinetic and potential energy components. The potential energy depends on the average distance between molecules, which is a function of both temperature and specific volume.

Therefore, for a real gas: $U = U(T, v)$

The specific heat c_v is still defined as $\left(\frac{\partial u}{\partial T}\right)_v$, but its value is no longer a simple constant given by $\left(\frac{f}{2}\right)R$. It becomes a function of temperature and pressure, and its value must be determined experimentally or from more complex equations of state.