A Tutorial on Thermodynamics' Phase Diagrams and Charts

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Preface

This note follows our earlier online public book, *Engineering Thermodynamics – Concepts and Laws: An Informal Presentation*, shared on ResearchGate.net in July 2026. Here, the focus shifts to explaining phase diagrams in key thermodynamic coordinates—namely P-v, T-v, P-T, T-s and h-s. Mastering these diagrams and learning to use thermodynamic tables are essential steps toward the study of practical applications such as power plants, refrigeration systems, air conditioning and combustion processes. While the main development of our earlier book emphasizes thermodynamic derivations based on the ideal-gas model, students should also develop a clear visual understanding of phase behavior and real-substance property relations. For that reason, this supplementary section on phase diagrams is included to present, in a concise and accessible way, the interpretation of regions such as compressed liquid, saturated mixture, saturated vapor, superheated vapor, and the critical state, together with the use of common thermodynamic charts. Its purpose is not to replace the established textbooks or duplicate worked examples, but to complement them by offering another reference perspective. Since meaningful study in thermodynamics often requires consulting more than one source, this addition is intended to help students build the habit of connecting formal derivation with graphical interpretation and physical insight.

1. Boiling

When we heat a liquid, we increase its molecular kinetic energy. Boiling, considered as vaporization, is a phase transition that requires the liquid to reach the saturation temperature (T_{sat}). However, the process is rarely instantaneous. For the case of boiling water in an open pot, we observe the following:

- **The "False" Boil:** Before the water reaches (T_{sat}), we may see bubbles at 80°C or 90°C. These are not steam; they are dissolved gases (nitrogen and oxygen) expanding due to heat.
- **The "Vapor Re-condensation" Phase:** As the water begins to heat, vapor bubbles form at the heat source (the bottom of the pot). However, as these bubbles rise through the cooler bulk liquid (which is not yet at T_{sat}), they lose their heat and collapse. The vapor condenses back into liquid. This is why we hear the "rattle" of a pot before it fully boils—it is the sound of bubbles forming and collapsing.
- **The "True" Boil:** Boiling only becomes continuous and stable once the bulk of the liquid reaches T_{sat}. Only then can the vapor bubbles survive their journey to the surface without collapsing. Once the entire volume of liquid is at the saturation temperature, the vapor finally escapes freely.

1.1. How Pressure Controls the Beginning of Phase Change

T_{sat} is not a fixed number like 100°C; it is a value that changes based on the surrounding pressure.

To understand how pressure affects the boiling point, we should not imagine placing a heavy piston on top of a pot. A piston introduces mechanical complexities. It physically traps the vapor, prevents its natural escape and creates a closed system that complicates the underlying physics.

Instead, let us imagine the atmospheric pressure itself is rising.

- If we increase the ambient pressure surrounding the pot, we raise the "boiling threshold" without introducing a physical lid that blocks the vapor's movement.
- The molecules now require more energy to "break free" from the liquid into the surrounding environment. This allows us to observe the true thermodynamic relationship between pressure and phase change, without the mechanical interference of a piston.

1.2. How We Actually Test at High or Low Pressure

If we don't use pistons, how do we conduct experiments at different pressures in the lab? We control the pressure of the environment using closed systems with controlled boundaries.

a) Low-Pressure (Below 1 atm)

- The Setup**:** water is placed in a sealed glass chamber connected to a vacuum pump.
- The Control: The vacuum pump extracts air, lowering the pressure inside the chamber.
- The Result**:** At lower pressure, the required (T_{sat}) drops. The water will boil vigorously at room temperature or slightly above, with the vapor rising freely into the spacious headspace of the chamber.

b). High-Pressure (Above 1 atm)

- The Setup: The water is placed in a rigid pressure vessel (a boiler) equipped with a back-pressure regulator (or venting valve).
- The Control: As the water is heated, vapor begins to escape from the liquid. Instead of trapping all the steam (which would cause pressure to spike uncontrollably), the regulator valve is set to open at our target pressure (e.g., 2 bar).
- The Result: The valve releases just enough steam to maintain a constant, steady pressure. The vapor is allowed to escape, and we can measure the exact temperature of the boiling liquid at a stable, elevated pressure.

1.3. Atmospheric boiling (open system)

When water boils in a pot, the vapor bubbles rise and reach the surface. The steam (vapor bubbles) escapes into air, which is mostly nitrogen and oxygen.

Thus, the vapor phase above the liquid is not pure water vapor. It is a mixture of air and water vapor. Nevertheless, boiling occurs when the vapor pressure of water equals the surrounding pressure (about 1 atm). The bubble itself contains essentially water vapor, but once it leaves the surface it mixes with air.

Remarks:

1. If the relative humidity of air is 100%, it is saturated by water vapor and cannot absorb additional vapor molecules. At 100% humidity near the interface molecules continuously leave the liquid and continuously return. This is dynamic equilibrium. So, microscopically there is constant exchange. When the bubble reaches the surface in dry air, vapor diffuses away rapidly. However, in humid air diffusion is slower. At 100% humidity, there is essentially no net evaporation from the surface into air. But the bubble itself can still exist if the water is boiling.
2. If we go to a location where the ambient pressure is equal to 101.3 kPa and measure the temperature of boiling with a very accurate instrument the temperature is not exactly 100.000 for the open pot case. In a real open-pot experiment, even if the ambient pressure is exactly 101.3 kPa, the measured boiling temperature will usually not be exactly 100.000 °C. It will be very close, but small deviations occur. Even excellent thermometers have uncertainty. A typical high-quality lab probe has an accuracy of about $\pm 0.01^{\circ}C$ to $\pm\ 0.05^{\circ}C$.

3. More fundamentally, the pressure at the bubble location is slightly higher than atmospheric. Because of the water depth in the pot the pressure is $P = P_{atm} + \rho g h$. If the bubble forms 5 cm below the surface we will get $\rho g h \approx 490$ Pa That raises the local boiling temperature by roughly $\Delta T \approx 1.36°C$ So, bubbles form slightly hotter than 100 °C and cool slightly as they rise. At 101.3 kPa, we might observe 99.9 °C, 100.02 °C, or 100.1 °C, depending on location and measurement conditions.

1.4. Boiler or controlled experiment (closed vapor space)

In a boiler, pressure vessel, or laboratory boiling apparatus the space above the liquid is not air. It becomes filled with water vapor itself. Thus, the vapor that forms in the liquid rises and enters its own pure phase.

This is a very different thermodynamic picture. The gas above the liquid is nearly pure steam. The pressure in the vessel is therefore the saturation pressure of water. Liquid and vapor are in true equilibrium of the same substance.

The steam tables describe the controlled experiment — a pure water system where liquid and vapor coexist in equilibrium.

Liquid water ↔ pure steam is a clean thermodynamic equilibrium. The kitchen pot where vapor mixes with air is a more complex transport system. Both produce a temperature extremely close to 100 °C, but only the first corresponds exactly to the saturation curve in thermodynamics.

Remark: The Hypsometer

Before modern electronic thermometers, scientists used the boiling point of water as a precision reference. The instrument designed for this is called a Hypsometer.

A classic design has a boiler at the bottom, a vertical chamber above, a thermometer suspended in the steam space and a vent allowing pressure to stay at atmospheric value.

Instead of measuring the temperature of turbulent boiling liquid water directly, the hypsometer measures the temperature of pure saturated steam. Moreover, local overheating exists. Bubbles may disturb contact with the thermometer. Hydrostatic pressure varies with depth even if the depth is small. Also, if any dissolved gases exist, they may interfere.

The boiling point is not fundamentally “about heat.” It is about equilibrium between phases:

$$\mu_l = \mu_v$$

where μ denotes chemical potential.

The hypsometer works because saturated steam naturally enforces this equilibrium very precisely.

A tricky experiment: Imagine a glass of water placed inside a pot of boiling water under atmospheric pressure. The container with the glass of water is sealed. Heat enters through the glass. The system consisting of water in the pot and in the glass reaches a thermal equilibrium. However, the air and water inside expand causing the pressure to increase. The temperature is approximately 100 °C, yet the pressure inside the glass is higher than atmospheric. So, the water inside the glass may not boil even though it is hot. Boiling is not simply reaching a temperature—it is a pressure-dependent phase change.

2. Superheating

Having established how boiling occurs in the bulk fluid, we must now examine what happens when only vapor is under study. Assume we have pure vapor at 101.3 kPa and 100 °C. Adding heat to the vapor as a system at constant pressure increases the vapor temperature. In thermodynamics, this is the transition from a saturated vapor to a superheated vapor.

Note that we cannot superheat a vapor if a single drop of liquid remains in contact with it. Let us imagine a closed container holding both liquid water and steam in equilibrium. If we apply heat to this system, the temperature does not rise. Instead, the energy is absorbed by the liquid molecules, breaking their intermolecular bonds and converting them into vapor.

The liquid acts as a thermal sink. Because evaporation is an endothermic phase change, the system's temperature is pinned (or "clamped") at the saturation temperature (T_{sat}) for that pressure. The transition from saturated vapor to superheated vapor is not gradual; it is a sharp, binary threshold. Only when the very last droplet of liquid has evaporated does the thermodynamic anchor release. Once the liquid phase is entirely gone, any further heat added to the system can no longer go toward phase change. Instead, it increases the kinetic energy of the gas molecules. The temperature finally rises above T_{sat}, entering the superheated region where temperature and pressure are no longer coupled.

3. The T–v Diagram (Figure 1)

Consider heating a substance at constant pressure. As heat is added, the system moves across the T–v diagram from left to right, passing through three distinct regions.

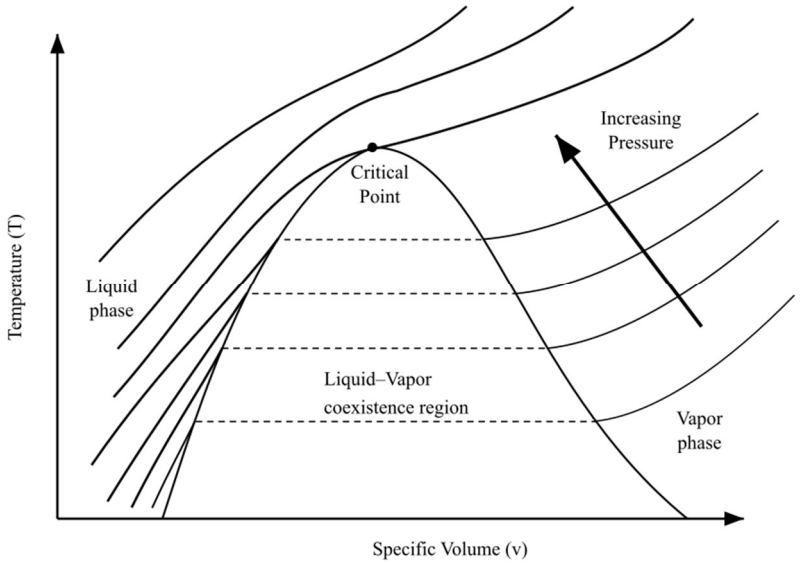

Figure 1: The schematic of T-v diagram

Region 1: Compressed Liquid

This region lies to the left of the saturation dome. Here the substance is entirely liquid. Liquids are nearly incompressible and expand very little when heated. Therefore, a small increase in volume requires a significant increase in temperature. On the diagram, the isobar slopes steeply upward. Physically, this steep slope reflects the fact that liquid volume changes only slightly with heating.

Region 2: Saturated Mixture (Inside the Dome)

Once the process reaches the left boundary of the dome, the liquid begins to boil.

Inside the dome, liquid and vapor coexist. During boiling at constant pressure:

- Temperature remains constant.
- Heat added goes into latent heat of vaporization.
- Liquid gradually converts into vapor.

On the T–v diagram, the isobar inside the dome becomes horizontal. This flat region is called the saturation plateau.

As heat is added:

- the quality (vapor fraction) increases
- the specific volume increases dramatically
- but the temperature does not change

Region 3: Superheated Vapor

After all liquid has evaporated, the process exits the dome and enters the superheated vapor region. Here the substance behaves as a gas. As heating continues at constant pressure, temperature rises and volume increases.

Because gases expand easily, large volume changes occur with relatively small temperature increases. Thus, the isobar slopes upward again, but less steeply than in the liquid region.

Behavior Near the Critical Point

As pressure increases toward the critical pressure, the saturation plateau becomes shorter. At the critical point, the saturated liquid and saturated vapor states merge, the plateau disappears and the isobar becomes a smooth continuous curve (no discontinuity in the derivative of constant pressure curve).

4. The P–v Diagram (Figure 2)

Now consider the P–v diagram. The heating can be explained by isothermal curves. Again, we trace lines across the three regions.

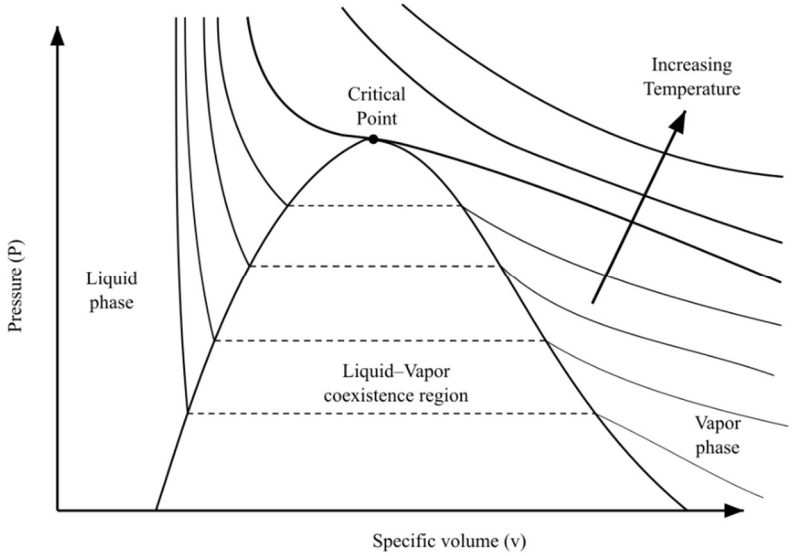

Figure 2: The schematic of P-v diagram

Region 1: Compressed Liquid

In the liquid region molecules are tightly packed and the fluid resists compression. Changing pressure causes very little change in volume. Therefore, on the P–v diagram the isotherm is almost vertical. This reflects the very low compressibility of liquids.

Region 2: Saturated Mixture (Inside the Dome)

When the isotherm enters the dome, the substance begins to change phase. At a fixed temperature the saturation pressure is fixed. Thus, during vaporization at constant temperature:

$$P = P_{sat}(T)$$

The pressure does not change while liquid converts to vapor. On the diagram, the isotherm becomes horizontal. This is analogous to the flat plateau seen in the T–v diagram.

Region 3: Superheated Vapor

Once all liquid disappears, the system enters the superheated vapor region. As volume increases at constant temperature pressure decreases. The isotherm therefore becomes a downward-curving line. This curve gradually flattens at larger volumes as pressure approaches zero. Here the gas follows behavior similar to the ideal gas law:

$$Pv \approx RT$$

The isotherms of an ideal gas on the P-v coordinates are hyperbolic curves.

$$P \approx constant/v$$

5. The Physical Meaning of the Slopes

The slopes change because the molecular structure of the substance changes across regions.

Liquids

Molecules are tightly packed and strong intermolecular forces prevent large volume changes. Therefore, large pressure or temperature changes are needed to alter volume.

Saturated Mixture

Energy added or removed goes into breaking or forming intermolecular bonds rather than raising temperature or pressure. This produces the flat regions in both diagrams.

Vapor

Molecules are far apart and interact weakly. Small changes in pressure or temperature lead to large changes in volume.

6. The Critical Point

As shown in the figures, at the critical point, the distinction between liquid and vapor disappears. Consequently, the two saturation boundaries that separate in the horizontal plateau shrink to zero length.

For water, the critical point occurs at approximately:

- Critical temperature: $374°C$
- Critical pressure: 22 MPa

At the critical point, the P–v isotherm and the T-v isobar develop a point of inflection. Beyond the critical point, the curves become smooth and continuous, since only a single fluid phase exists. The fluid that exists beyond the critical point is called a supercritical fluid.

A supercritical fluid is not a liquid and not a gas in the traditional sense. Instead, it combines properties of both. Typical characteristics of the supercritical state are as follows:

Liquid-like properties such as relatively high density and strong solvent capability. Gas-like properties such as low viscosity, high diffusivity and ability to flow easily and penetrate porous materials. Because there is no liquid–vapor boundary, the fluid simply fills the entire container like a gas while retaining many liquid-like interactions.

Example: Supercritical Carbon Dioxide

Carbon dioxide (CO_2) provides a widely used industrial example.

Its critical point is relatively easy to reach:

- Critical temperature: $31°C$
- Critical pressure: 73.8 bar

Supercritical CO_2 is commonly used to remove caffeine from coffee beans. This works because it penetrates coffee beans easily, like a gas. It also dissolves caffeine effectively, like a liquid solvent.

6.1. Physical interpretation of critical point

The P–v isotherm develops a point of inflection.

$$\left(\frac{\partial P}{\partial v}\right)_T = 0$$

and

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$$

This reflects the enormous compressibility and density fluctuations near the critical point.

There are videos of fluids approaching the critical point on the internet. We see a sharp liquid–vapor interface slowly blurs, shimmers, and finally disappears. The phenomenon is real — but its interpretation requires careful thought.

We can typically observe a sharp meniscus at first, then growing waviness. When fluctuations increase, we see a milky interface and eventual disappearance of the boundary.

Before reaching the critical point, the meniscus is not infinitely thin. It is a region where density changes rapidly several molecular layers thick are subject to thermal fluctuations. So, even in the "clean" regions of the phase diagram, the interface is not a perfect mathematical plane.

As we heat and compress the fluid toward its critical point, the density of the liquid decreases, the density of the vapor increases and eventually their properties converge.

Thus, the interface becomes broader, more diffuse and less sharply defined. It looks like a sudden event. But physically it happens over a small temperature and pressure interval and through continuously increasing fluctuations. Eventually, the interface occupies the entire observation cell. This is what produces the spectacular critical light scattering from large density fluctuations near the critical point.

6.2. Infinite compressibility at critical point

When we say compressibility becomes very large near the critical point, we mean:

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

where κ_T is the isothermal compressibility tends to infinity.

κ_T measures how much the volume changes when pressure changes at constant temperature.

Near the critical point, the substance is neither normal liquid nor normal vapor. Its compressibility becomes much larger than ordinary liquids and even much larger than ordinary gases. So, it is not "liquid-like compressibility" or "vapor-like compressibility." It exceeds both.

Away from the critical point, in normal liquid, molecules are tightly packed and strong intermolecular forces resist compression. Thus, compressibility is very small because volume changes very little when pressure changes. In a normal vapor, molecules are far apart. We can compress it significantly. But the response is still smooth and predictable. Hence, compressibility is moderate.

At the critical point, liquid density becomes nearly equal to vapor density. The distinction between phases disappears. Surface tension tends to zero. The restoring force between dense and less dense regions weakens. The fluid spontaneously forms into temporary dense regions (liquid-like) and temporary less-dense regions (vapor-like). These regions appear and disappear continuously.

The fluid becomes extremely sensitive to pressure. A tiny pressure change can grow or shrink these density fluctuations, causing a large change in average volume.

So:

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

becomes extremely large (theoretically infinite).

Above the critical temperature $T > T_c$, there is no longer a liquid–vapor transition. The fluid becomes a single supercritical phase. There is no latent heat, no phase boundary and density changes smoothly with pressure and temperature. Because of this, the instability that produced huge density fluctuations disappears. So, compressibility becomes finite again, and the fluid behaves smoothly like a dense gas.

7. The Pressure–Temperature Phase Diagram (Figure 3)

Vertical axis is Pressure **(P)** and Horizontal axis is Temperature **(T).**

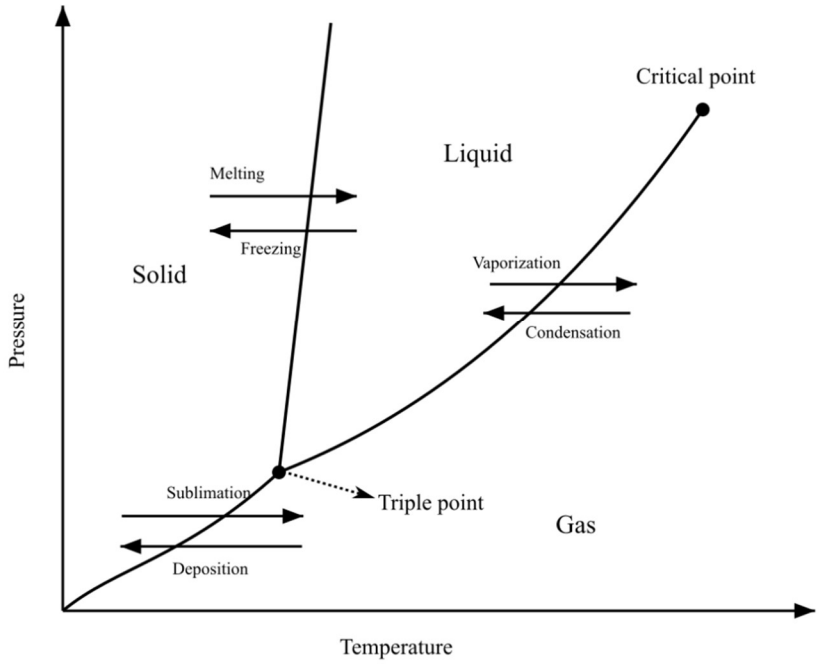

Figure 3: the schematic of P-T diagram

Each point on this graph represents a specific combination of pressure and temperature. Depending on where the point lies, the substance will exist as a solid, liquid, or vapor.

The diagram is divided into regions by three important curves, each representing equilibrium between two phases.

7.1. The Vaporization Curve (Liquid ↔ Vapor)

This curve represents the familiar boiling relationship between liquid and vapor.

At every point on this curve liquid and vapor coexist in equilibrium.

The curve begins at the triple point, where all three phases meet. It ends at the critical point, where the distinction between liquid and vapor disappears.

Beyond the critical point there is no phase boundary, because liquid and vapor merge into a single supercritical fluid. So, the vaporization curve is unique because it has two definite endpoints.

7.2. The Melting Curve (Solid ↔ Liquid)

This curve separates the solid region from the liquid region. At every point along it, solid and liquid are in equilibrium. It begins at the triple point and extends toward higher pressures and temperatures.

Unlike the vaporization curve, the melting curve does not terminate at a critical point. Solid and liquid remain fundamentally different phases even at extremely high pressures. In practical engineering conditions, the melting curve can be considered to continue towards higher pressure and temperature region.

7.3. The Sublimation Curve (Solid ↔ Vapor)

The third curve separates the solid phase from the vapor phase. Along this curve solid and vapor coexist in equilibrium. This direct solid-to-vapor transition is called sublimation.

The substance changes directly between solid and vapor without passing through the liquid phase. Examples include snow disappearing on very cold, dry days without melting.

The curve starts at the triple point and extends toward lower pressures and lower temperatures. Like the melting curve, the sublimation curve has no critical endpoint in the range of practical engineering pressures and temperatures.

7.4. The Triple Point

All three curves intersect at a single unique condition called the triple point. At this exact pressure and temperature, all three phases can coexist simultaneously in equilibrium.

For water, the triple point occurs at:

- Temperature: 0.01 °C
- Pressure: 0.006116 bar (about 611 Pa)

At this precise condition, ice, liquid water, and water vapor can exist together.

No other combination of pressure and temperature allows all three phases to coexist.

Remark: The Special Behavior of Water

Water is unusual compared with most substances. Several of its properties differ from the typical patterns seen in phase diagrams. For most materials, the melting curve slopes upward to the right. Increasing pressure increases the melting temperature. Water behaves differently. For water, the melting curve slopes upward to the left. Increasing pressure lowers the melting temperature. This

occurs because ice is less dense than liquid water. When pressure increases, the system favors the denser phase, which is liquid water. As a result, pressure encourages melting.

This phenomenon explains why ice floats on water.

Under high pressures, water forms many different crystalline structures. In total, more than 17 solid phases of ice are known. Each of these structures has its own equilibrium boundaries and can meet other phases at additional triple points.

8. The T–s Diagram (Figure 4)

The T–s diagram uses temperature and entropy as coordinates.

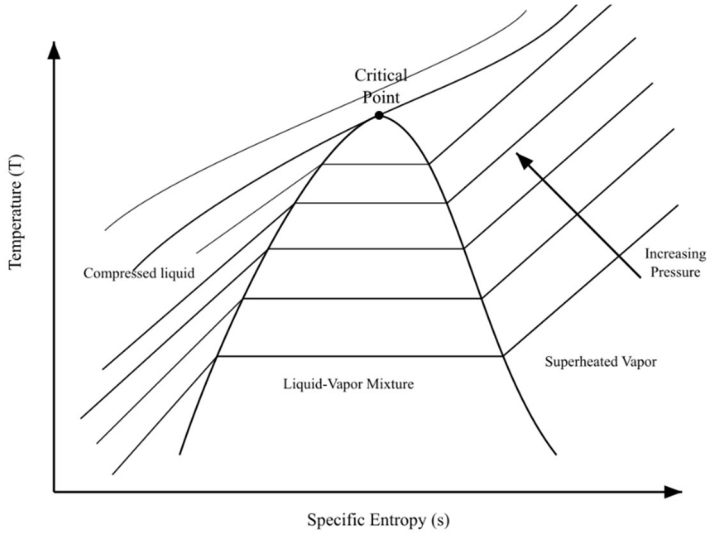

Figure 4: The schematic of T-s diagram

This diagram is extremely important for heat transfer, efficiency analysis and power cycles.

For a reversible process:

$$\delta q_{rev} = T\, ds$$

Therefore, the area under a curve on a T–s diagram denotes the heat transfer. This makes the T–s diagram especially useful for thermal-cycle analysis.

Inside the saturation dome isotherms are horizontal, because phase change occurs at constant temperature. Outside the dome, isobars curve upward in the superheated region.

9. The h–s Diagram (Mollier Diagram-Figure5)

The h–s diagram uses enthalpy and entropy as coordinates. This diagram is widely used for turbines, and nozzles.

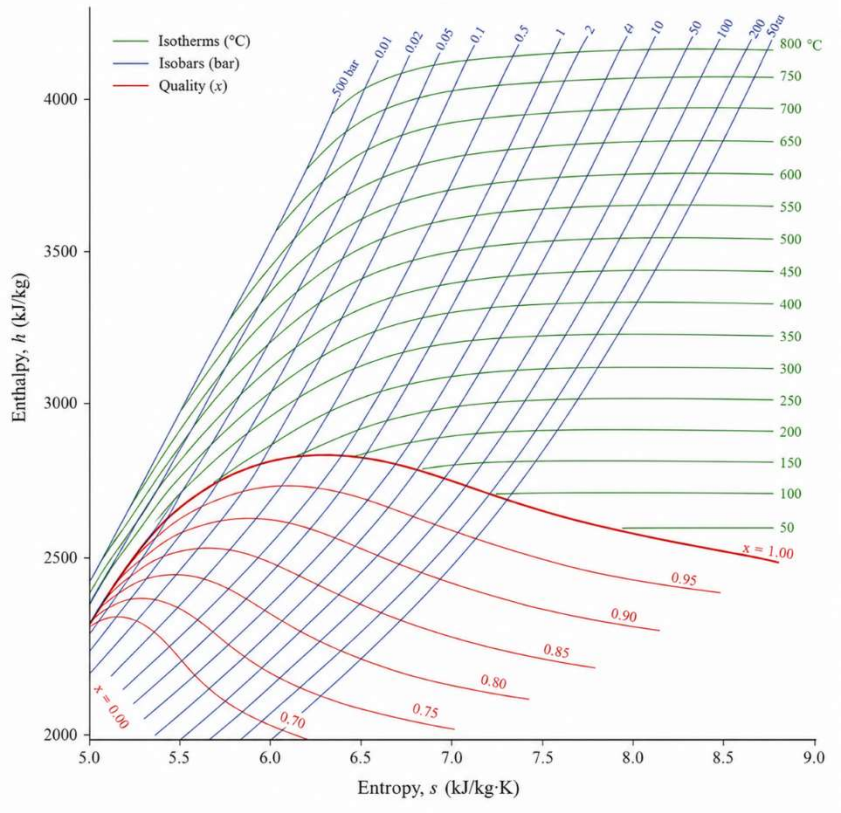

Figure 5: The h-s (Mollier) diagram for water

Turbine work output is related to enthalpy drop. The process of steam flowing in turbine blades (e.g. converging, diverging and converging diverging nozzles or diffusers) is related to enthalpy drop.

10. Slopes of Constant Volume and Constant Pressure Lines for Ideal Gas on T-s Diagram

For an ideal gas, the entropy relationships are derived from the First and Second Laws of Thermodynamics:

$$ds = c_p \frac{dT}{T} - R\frac{dP}{P}$$

$$ds = c_v \frac{dT}{T} + R\frac{dv}{v}$$

a) Constant Volume (Isochoric) Process

For constant volume (v = constant), dv = 0:

$$ds = c_v \frac{dT}{T}$$
$$(\frac{\partial T}{\partial s})_v = \frac{T}{c_v}$$

Slope $\frac{T}{c_v}$ is always positive. Increasing direction is upward and to the right. Curves are relatively steep because c_v is relatively small. Slope of constant volume curves increases linearly with temperature.

At constant volume, adding heat increases both temperature and entropy. The slope represents how much temperature rises per unit entropy increase at a fixed volume. Since $c_v$is constant for monoatomic ideal gas, the slope increases proportionally with T.

b) Constant Pressure (Isobaric) Process

For constant pressure (P = constant), dP = 0:

$$ds = c_p \frac{dT}{T}$$
$$(\frac{\partial T}{\partial s})_p = \frac{T}{c_p}$$

Slope is $\frac{T}{c_p}$ and always positive. Increasing direction is upward and to the right. Curves of isobars are less steep than constant volume lines because $c_p > c_v$. Slope of isochors and isobars increase linearly with temperature.

c) Direction of Increasing Properties

For constant volume Lines:

- Higher specific volume lines are located to the right of lower specific volume lines. At fixed temperature, higher specific volume corresponds to higher specific entropy (since $s = c_v \ln T + R \ln v + \text{const}$, so $(\partial s / \partial v)_T = R/v > 0$). Thus, isochors shift rightward as specific volume increases.
- Moving upward along a constant volume line increases temperature and pressure.

For constant pressure Lines:

- Higher pressure lines are located above and to the right

- Lower pressure lines are located below and to the left
- Moving upward along a constant pressure line increases temperature and volume

Remark:

The ratio of slopes of isochors and isobars is constant: $\frac{(\partial T/\partial s)_v}{(\partial T/\partial s)_p} = \frac{c_p}{c_v} = \gamma$. Lines never cross - each constant volume or constant pressure line is unique.

11. Behavior of Constant Pressure and Constant Volume Curves in the Superheated Steam Region on T-s Diagram

11.1. Non-Ideal Gas Behavior of Steam

Steam in the superheated region exhibits significant deviations from ideal gas behavior due to:

- Intermolecular forces (van der Waals forces, hydrogen bonding)
- Molecular volume effects - water molecules have significant size and association
- Variable specific heats that change with both temperature and pressure
- Complex molecular structure

11.2. Constant Pressure Lines (Isobars) in Superheated Steam Region

- Constant pressure lines curve upward and to the right but with varying slopes
- Near the saturation line, isobars have steeper slopes than ideal gas
- As temperature increases the slopes gradually approach ideal gas behavior
- Higher pressure isobars are located higher on the diagram

For ideal gases, the slope is given by:

$$(\frac{\partial T}{\partial s})_P = \frac{T}{c_p}$$

However, for steam, c_p is not constant - it varies significantly with temperature and pressure. Near saturation c_p can be 2-3 times higher than the ideal gas value. At high temperatures, c_p approaches the ideal gas limit.

Near the saturation line, additional energy goes into overcoming residual molecular attraction. This requires more energy per temperature rise, resulting in higher c_p and flatter slopes initially. As temperature increases, molecular interactions weaken, and steam behaves more ideally.

11.3. Constant Volume Lines (Isochors) in Superheated Steam Region

Constant volume lines also curve upward and to the right. Constant volume lines are steeper than constant pressure lines, similar to ideal gas. Higher specific volume lines are located to the right (higher entropy).

We have:

$$(\frac{\partial T}{\partial s})_v = \frac{T}{c_v}$$

For steam, c_v also varies with temperature and pressure, but less dramatically than c_p. The ratio c_p/c_v (γ) is not constant for steam. γ also varies with both temperature and pressure. For ideal gas γ varies only with the temperature.

As pressure decreases (< 1 bar), constant pressure lines become nearly straight with constant slope T/c_p. Constant volume lines maintain steeper slopes than isobars. The ratio of slopes approaches the constant value of γ. Specific heats approach their ideal gas values.

12.Why Different Diagrams Exist

Each diagram emphasizes a different aspect of thermodynamics.

a) P–v diagram

The pressure–specific volume (P–v) diagram is a cornerstone of classical thermodynamics, particularly invaluable for analyzing quasi-static mechanical processes—such as compression and expansion—in closed systems and intake exhaust processes in open systems. In this domain, the area beneath a given process of a closed system's curve directly represents the magnitude of boundary work per unit mass ($w = \int P\, dv$), with the path direction dictating the sign (expansion yields positive work output; compression requires work input).

The diagram's geometric features are highly informative. Isotherms appear as rectangular hyperbolae ($P \propto 1/v$). For an ideal gas, these curves also denote states of constant internal energy and enthalpy, since both properties depend solely on temperature. Meanwhile, constant-entropy (isentropic) lines, while often omitted in basic implementations to reduce clutter, are critical for real-process comparisons. For an ideal gas, the slopes of these curves are:

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{P}{v} \text{ and } \left(\frac{\partial P}{\partial v}\right)_s = -\gamma\frac{P}{v},$$

where $\gamma = c_p/c_v > 1$. Thus, the magnitude of the isentropic slope is γ times greater than that of the isotherm, making isentropic compression/expansion curves significantly steeper on the diagram.

Beyond simple work calculations, the P–v diagram serves as an indispensable visual and analytical tool in several advanced contexts:

Cycle performance and network output: In cyclic processes (e.g., Otto, Diesel, Brayton, and Rankine cycles), the net specific work is directly equal to the enclosed area of the cycle loop. This allows for rapid qualitative assessments of cycle efficiency and mechanical power density without detailed numerical integration.

Multi-stage compression with intercooling: The diagram clearly illustrates the thermodynamic benefit of intercooling between compression stages. By plotting the isothermal and isentropic paths, designers can visually identify the minimum work requirement (approached by isothermal compression) and optimize intercooler pressures to reduce total input work.

Polytropic process identification: Real expansion and compression often follow polytropic paths ($Pv^n = $ constant). By plotting the curve on logarithmic axes, or by observing its slope relative to the isobars ($n = 0$), isotherms ($n = 1$), isentropes ($n = \gamma$), and isochores ($n = \infty$), engineers can empirically determine the polytropic exponent n and infer heat transfer characteristics.

Phase-change and saturation analysis: For pure substances, the P–v diagram maps the entire saturation dome, clearly demarcating compressed liquid, saturated liquid–vapor mixture, and superheated vapor regions. This enables direct visualization of quality (vapor fraction) and the critical point, which is invaluable for sizing vapor-compression refrigeration systems and steam power plants.

Remarks:

- While the classical P–v diagram is formally derived for a closed control mass (where $W = \int P\,dV$ applies to the fixed gas inside the piston-cylinder), engineers routinely use the measured in-cylinder pressure versus swept volume—known as the indicator diagram—to analyze open control volumes in positive-displacement machinery. In these cases, the piston–cylinder assembly is treated as a transient control volume that exchanges both mass and energy with its surroundings. Intake stroke of a reciprocating compressor: During the suction stroke, the inlet valve opens while the piston recedes. The cylinder is no longer a closed system; fresh gas flows in from the supply manifold. On the indicator diagram, the intake curve appears as a near-horizontal line lying slightly below the supply pressure due to throttling and flow-path pressure drops. Crucially, the area under this intake

segment does not represent boundary work on a fixed mass. Instead, it quantifies the flow work (Pv) and the pumping work required to draw the charge into the control volume against the resisting pressure. When integrated over the full four-stroke cycle (intake → compression → expansion → exhaust), the total net indicated work is the algebraic sum of the positive power loop (compression + expansion) and the negative pumping loop (intake + exhaust).

- The ideal air-standard Otto cycle conveniently omits the intake and exhaust strokes, modelling only the compression and power strokes as a closed loop. However, a real spark-ignition engine's measured indicator diagram includes all four strokes. The intake and exhaust paths together form a distinct pumping loop, which is typically clockwise (negative work) at part throttle and narrows to near-zero at wide-open throttle. The area of this loop directly represents the pumping losses consumed by the engine to expel burnt gases and induct a fresh mixture. Subtracting this negative area from the gross positive area of the compression–expansion loop yields the net indicated mean effective pressure (IMEP)—the single most critical metric for brake-specific fuel consumption and mechanical output.

By integrating these applications, the P–v diagram transcends a simple plot of state variables, evolving into a dynamic decision-making framework for both thermodynamic analysis and system engineering.

b) T–s diagram

The temperature–entropy (T–s) diagram is the preferred domain for analyzing thermal interactions and evaluating thermodynamic cycle efficiencies. For any internally reversible (quasi-static) process, the area beneath the path curve represents the heat transfer per unit mass, $q = \int T\, ds$. Consequently, the enclosed area of a closed cycle on the T–s diagram corresponds to the net heat exchanged over the cycle; by the first law of thermodynamics, this enclosed area is numerically equal to the net work output (or input) for that cycle, making the diagram equally powerful for assessing both heat addition and mechanical performance.

For an ideal gas, where both internal energy and enthalpy depend solely on temperature, the isotherms conveniently coincide graphically with both constant-internal-energy and constant-enthalpy (isenthalpic) lines. In contrast, for real gases or two-phase liquid–vapor mixtures, isenthalpic lines are not flat. For an ideal gas, isenthalpic lines coincide with isotherms on the T–s plane, so $(\partial T/\partial s)_h = 0$. For real fluids, the slope $(\partial T/\partial s)_h$ depends on the equation of state and thermodynamic state; it may be positive, negative, or zero depending on whether the operating point is above or below the Joule–Thomson inversion curve.

c) h–s diagram

The enthalpy–entropy (h–s) chart, widely known as the Mollier diagram, is the preferred graphical tool for analyzing steady-flow adiabatic devices—particularly turbines and nozzles. On this diagram, vertical lines represent isentropic (constant-entropy) processes, providing an immediate visual measure of the ideal (reversible) work output or kinetic-energy generation against which actual (irreversible) performance is benchmarked.

The Mollier diagram typically omits the liquid phase, focusing instead on the superheated and wet-vapor regions—a deliberate choice, as liquid behavior is better captured by property tables. In the two-phase saturation zone, constant-pressure (isobaric) and constant-temperature (isothermal) lines coincide and appear as a flat curve with positive slope. This is because, within the saturated mixture, pressure and temperature are directly dependent ($T = T_{\text{sat}}(P)$); moving horizontally along these overlapping lines simply changes the vapor quality (dryness fraction) at constant pressure and temperature. Constant-quality lines are explicitly plotted because the moisture content in the wet region is critical for turbomachinery (e.g. excessive liquid droplets entrained in the flow during the latter turbine stages cause mechanical erosion, corrosion, and diminished stage efficiency).

A notable asymptotic feature emerges at very low pressures where the working fluid approaches the ideal-gas limit and enthalpy becomes exclusively a function of temperature ($h = h(T)$). Consequently, the isotherms gradually flatten out, and their slopes approach zero—becoming perfectly horizontal lines. At this limit, isotherms merge seamlessly with isenthalpic lines, serving as a useful physical checkpoint for low-pressure superheated steam.

13.Mollier Diagrams, Steam Tables, and Software

Thermodynamics has always relied on tools for determining the properties of working fluids such as steam and refrigerants.

Over time, engineers have used three main approaches:

1. Graphical methods — thermodynamic diagrams
2. Numerical methods — steam tables and interpolation
3. Computational methods — software and property libraries

Each method has strengths and weaknesses. More importantly, each method teaches a different kind of understanding. The challenge in engineering education is not simply obtaining accurate numbers. It is learning how to connect numbers to physical reality.

Before modern computers became common, engineers relied heavily on the h–s diagram, also called the Mollier diagram. An engineer would determine a thermodynamic state by locating the pressure line, locating the temperature line, finding their intersection, then reading properties directly from the chart.

From the Mollier diagram, one could estimate enthalpy, entropy, pressure, quality and degree of superheat. Processes could also be traced visually. The great strength of the diagram was not numerical precision. It was visualization. The engineer could trace the path of the working fluid, understand the sequence of processes, recognize when phase changes occurred, identify superheated or wet regions instantly. The diagram connects mathematics to physical intuition. The weakness of graphical methods was limited accuracy. Values could only be read approximately as interpolation was visual, reading depended on chart resolution and precision was limited to a few significant figures. Thus, the Mollier diagrams are excellent for insight but weaker for exact calculations.

Modern thermodynamics education shifted toward steam tables. These tables provide thermodynamic properties numerically. Students learn to use saturated water, superheated steam and compressed liquid tables.

Steam tables teach numerical discipline. To use them correctly, the student must determine the thermodynamic region, choose the correct table, interpret saturation conditions, perform interpolation carefully and verify consistency among properties. This task develops engineering judgment. The student learns not merely to obtain numbers, but to evaluate whether the numbers make physical sense.

The disadvantage is that tables can become tedious. Interpolation is time-consuming.

The student using only tables may know the value of enthalpy as given in the exercise, but fail to visualize whether the fluid is wet steam, dry saturated vapor, superheated vapor, or compressed liquid. Thus, precision can come at the expense of intuition.

Today most thermodynamic calculations are performed using software. Examples include EES (Engineering Equation Solver), Python thermodynamic packages, online calculators. A user simply enters a pair of properties and the software instantly returns other properties.

Software offers enormous benefits. Complex calculations are completed instantly. No graphical reading or interpolation errors occur. Large thermodynamic systems and cycles can be analyzed rapidly. Engineers can vary operating conditions and optimize performance efficiently. Modern engineering would be nearly impossible without computational tools.

Despite its power, software introduces a serious educational danger. A student may obtain a numerical answer without understanding the physical state.

For example:

$$h = 2800 \text{ kJ/kg}$$

by itself means almost nothing.

That value could correspond to:

- saturated vapor,
- superheated vapor,
- high-pressure steam,
- low-pressure steam,
- or another entirely different condition.

Without understanding the thermodynamic region, the number is meaningless.

Software will calculate properties correctly — but it will not automatically teach the user how to interpret them.