

## Displacement-energy and enthalpy as forms of energy: an upgrade.

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**Summary:** In order to formulate proper energy balances and uphold the law of conservation of energy, there is a need to account for all forms of energy for any system. A survey of thermodynamic engineering literature reveals little consensus about the energy forms to be taken into account. This paper intends to advance the case for formal and explicit recognition of 'displacement energy' as a form of energy that is either missing from textbooks, implied by some unspecified potential energy, hiding inside enthalpy, or incorrectly designated as 'flow work' or 'pV-work' as work is not a form of energy. An important implication is that contrary to prevailing views, enthalpy can also be deemed a form of energy, thereby justifying its presence in many energy balances, and thus rendering Hess' law into an energy balance as well. The paper specifies 23 conclusions and recommendations.

**Keywords:** fluid-mechanics, chemistry, thermodynamics, energy balance, forms of energy, displacement, displacement energy, enthalpy, Archimedes principle, Stevin's law of hydrostatics, gravity, potential energy, pressure work, volume work, flow work, vacuum.

### 1. Introduction

Quote: *Conservation of energy can be understood only if we have the formula for all of its forms* (Feynman, 1964, vol I, 4-2). This statement implies that *we* should have identified all forms of energy ('E-forms' in the following), and how they are quantified. The verification of the *conservation of energy* implies an energy-balance equation with an understanding of whether E-forms overlap and when their change can be neglected. It would not be too exacting to have unique names and symbols assigned to all E-forms, preferably across the sciences. The following intends to show a few prevailing shortcomings and an attempt to fix some of them.

The survey of the literature in Section 2 addresses the issue of what E-forms have been identified (see table 1), with an emphasis on engineering thermodynamics and a special interest in the intersection between thermodynamics and fluid mechanics. The E-form hereinafter referred to as 'displacement energy' resides in that intersection. Section 3 is preparation for Section 4, specifying the notation used (3a, Appendix A) and tackling five related issues. Those issues are: the meaning of 'displacement' (3b), the need to make 'ambient parameters' explicit (3c), and its spin-off for work terms (3d). Section 3e addresses the problem of sign conventions, and the energy-balance equation is addressed in Section 3f. In the review of Section 4, 'displacement energy' is properly introduced and it is shown how it fits the prevailing formulations. This includes implications for enthalpy. Conclusions and recommendations are collected in Section 5(a/w).

The word 'body' is taken here to have the same meaning as 'system'. This paper assumes macroscopic systems and bodies without relativistic effects.

### 2. Forms of energy (E-forms) in engineering thermodynamics.

Formulating a proper energy balance with implied conservation of energy requires all forms of energy to be accounted for. For those E-forms that are "not considered" in the process at hand, i.e. E-forms that are not entered in the energy balance, it must be explicitly or implicitly assumed that their change is zero or negligible, or that they are included in one of the forms specified. The energy balance cannot specify quantities that are not E-forms (it must be energy only) and the forms specified cannot share any components: all intersections should be void, i.e. the E-forms should be disjoint. The case can also be made that every E-form must

have a unique name and symbol: without a symbol, the quantity cannot be entered in an equation and for physical quantities, quantification is a must, specially for the one that are considered to be conserved.

Having said that, it may come as a surprise that there is no agreement among textbooks (and presumably scientists) about a definitive list of E-forms. Table 1 shows what are considered to be E-forms in the literature selected: It lists 15 E-forms as encountered in 37 references, sorted by year of publication (1948-2023).

**2a. Literature selected.** The 37 references can be classified mainly as texts on engineering and/or thermodynamics, with a few physics texts and a few internet sources (including chatgpt). The selection is based on an interest in those parts of applied science where energy balance equations are most common. In addition, the accessibility of the text itself (English only) was a factor.

**2b. E-forms listed:** The table lists 15 E-forms, with symbols used as specified in Appendix A. Some E-forms are not included in the table itself, but listed at the bottom of the table, most of them encountered only once or twice. The emphasis is on the more common quantities, notably those that might be encountered in general energy balances. It must be emphasized that the table quotes the E-forms as given, but the assumed exact meaning has not been checked and can differ between the references. This is notably true for 'heat' (see 2e). Nothing is assumed or specified in the table about the mutual independence of the E-forms mentioned, i.e. whether they are disjoint or not. For example, mechanical energy is commonly defined as the sum of kinetic energy and potential energy, so it overlaps with both. To arrange the E-forms, they have been classified as mechanical energy (to the left of enthalpy) or internal energy (to the right). The three quantities at the extreme right (radiation, heat and work) have been included simply because they are mentioned as E-forms (see 2e). The 'displacement energy', to be defined and demarcated in Section 4, appears centrally in the table, in anticipation of its position in the spectrum of E-forms. Note that internal energy (hence enthalpy) encompasses the unquantified E-forms chemical energy and thermal energy.

**2c. Relative occurrences of E-forms:** The literature is quite diverse in terms of the E-forms listed: The number of E-forms mentioned by each reference ranges from 3 to 9 out of the 15, with an average of 6.3. Only 3 out of the 15 E-forms occur 25 times or more: kinetic energy (32|37), electrical energy (27|37), and potential energy (25|37). Two of the listed E-forms occur 6 times or fewer: flow-/pressure energy (6|37) and enthalpy (1|37). Interestingly internal energy is only mentioned by 43% in this survey, gravitational energy by only 38% .

**2d. Potential energy:** When Rankine introduced the concept of 'potential energy' (Rankine, 1853) he also proposed designating kinetic energy as an 'actual energy'. So Rankine defines potential energy as the collection of all non-kinetic energies. Today there is little 'potential' about potential energy (Roche, 2003), but it still encompasses a large number of different E-forms. Trefil (Trefil & Hazen, 2000, p67) specifies: gravitational-, chemical-, elastic- and electromagnetic energy. Lumping these E-forms together does not seem to be helpful. Sometimes potential energy is indicated as the 'energy of position' or 'energy of configuration', which could include spring energy (elastic energy). Others define it as 'energy of position in an external field', which could include electric energy. In thermodynamics, potential energy commonly means gravitational energy when applied in the energy balance and does not include chemical energy, the latter being included in enthalpy. From the above, it is inferred that it would be helpful to abandon potential energy altogether and replace it with

the intended, more precise E-forms. In most cases, potential energy is simply gravitational energy.

**2e. Heat and work:** In 1948 Steiner is clear and writes: *In thermodynamics, heat and work are not considered forms of energy.* Romer (2001) deems it necessary to write: *Heat is not a noun.* In this paper too, heat (Q) and work (W) are not understood as E-forms, but as input variables, the way they are used in energy balance equations. However, Blundell & Blundell (2006, p106) formulate : *Though the idea that heat and work are both forms of energy seems obvious to a modern physicist, the idea took some getting used to. Lavoisier had, in 1789, proposed that heat was a weightless, conserved fluid called caloric.* This *quote* and Table 1 show that there is still a need for the stipulation. However, this being understood, in the following 'flow work' is promoted as 'displacement energy' and 'heat at constant pressure ' as an E-form called 'enthalpy'.

**2f. Conclusions from the survey:** There is no consensus about E-forms among the references listed. The nomenclature, ordering and understanding of the E-forms lack clarity. Work and heat are still listed as E-forms, while 'flow energy' and 'enthalpy' are scarcely recognized as such. Thermal energy and chemical energy are not quantified and do not belong in the list and (in all practical circumstances), both are taken care of as enthalpy. The replacement of potential energy by more specific E-forms is to be recommended. The position of 'displacement energy' and enthalpy needs to be more closely considered, as done in Section 4.

Table 1. Forms of energy (E-forms), listed as such in the literature of science and engineering 1948-2023\*).

		energy forms (E-forms)											not E-form but input			totals		
		electrical energy	magnetic energy	mechanical energy	kinetic energy (motion)	potential energy	gravitational energy	flow, pressure energy	enthalpy (heat content)	internal energy	spring & strain energy	chemical energy	thermal energy	radiation, light	heat	work		
		e-m energy		mechanical energy				enthalpy		internal energy								
		symbols		Em	Ek	Ep	Eg	Ed	H	U	Ey	?	?	Q	Q	W	15	
year	author page																	
1948	Steiner p24	x		x	x	x					x	x	x				7	
1948	Faires p22	x			x	x		x		x		x			x	x	8	
1961	Schaum&al p49,126	x	x		x	x								x	x		6	
1964	Feynman ch4	x			x		x					x		x	x		6	
1966	Joel p59				x	x		x							x	x	5	
1972	Abbott&al p10				x	x				x							3	
1976	James p62	x		x	x	x					x	x			x		7	
1979	Simms p211	x		x	x	x	x	x			x	x			x		9	
1980	Alonso&Finn p241			x	x		x			x		x		x			6	
1991	deNevers p95	x	x		x	x	x			x	x						7	
1994	Smil p2			x	x		x					x	x	x			6	
1996	Warn&Peters p11	x		x								x	x	x			5	
2000	Trefil&Hazen p67	x	x		x	x	x				x	x			x		8	
2001	Dincer&al p120	x	x		x	x	x			x	x	x	x				9	
2001	Darby p108			x	x	x	x	x		x			x		x	x	9	
2003	Earle&Earle p33				x	x		x	?			x			x	x	7	
2004	Hobson p113	x			x		x				x	x	x	x			7	
2005	Felder&al p315				x	x				x							3	
2005	Massoud p3 p96	x		x								x	x	x	x	x	7	
2006	Cengel&Boles p53	x	x	x	x	x						x	x				7	
2006	Moran&Shapiro p43				x		x			x							3	
2007	Rajput p46	x		x	x	x	x			x		x					7	
2009	BorgnakkeSontag p130				x	x				x							3	
2009	Theodore&al p65				x	x				x					x	x	5	
2010	Holbrow &al p47	x	x		x		x	?			x	?			x		6	
2012	Goldemberg p8	x	x	x								x	x				5	
2013	Koretsky p37	x	x		x	x				x							5	
2014	Potter&al p11	x			x	x				x		x					5	
2015	Winterbone&Turan p7	x	x		x	x							x				5	
2016	Kleidon p25	x			x	x		?				x	x	x			6	
2018	Smith&al p25	x	x	x	x	x				x					x	x	8	
2018	eia.gov/kids/energy	x		x	x	x	x					x	x	x	x		9	
2019	Jenkins p6	x			x							x		x	x		5	
2019	NajamAcademy	x		x	x	x						x	x	x			7	
2020	EnglishWiki:	x	x	x			x				x	x	x	x			8	
2023	ChatGPT-Q1(sci)	x			x	x				x		x	x	x			7	
2023	ChatGPT-Q2(eng)	x	x	x				x		x		x	x				7	
		symbols		-	-	Em	Ek	Ep	Eg	Ed	H	U	Ey	?	?	Q	Q	W
37	<b>totals</b>	<b>27</b>	<b>12</b>	<b>16</b>	<b>32</b>	<b>25</b>	<b>14</b>	<b>6</b>	<b>0</b>	<b>16</b>	<b>7</b>	<b>24</b>	<b>17</b>	<b>14</b>	<b>15</b>	<b>7</b>	<b>233</b>	

\*) E-forms encountered but not included in this table are: capillary-, centrifugal-, cohesion-, mass-, nuclear-/atomic-, osmotic-, sonic-/sound-, surface- and ionisation-energy.

### 3. Preliminaries: notations, definitions, demarcations.

**3a. Notation:** The symbols used, both standard and some new, are listed in appendix A. Symbols of quantities in bold ( $\mathbf{V}, \mathbf{m}, \mathbf{g}, \mathbf{W}$ ) have a meaning slightly different from the regular-font symbols ( $V, m, g, W$ ). The rest of Section 3 can be seen as a clarification of appendix A. Except for  $U$  and  $H$ , symbols for E-forms are all of the format 'Ej', e.g.  $E_k$ =kinetic energy. All equations are separated from the embedding text by curly brackets: {equation |<sub>constraint</sub>}, to improve readability and conciseness. In *quotes*, the symbols used in the original have been transcribed to the symbols from appendix A.

**3b. Displacement.** The word 'displacement' has two meanings in physics. First, in the displacement of a body, it is moved from P to Q: it changed position, i.e. is "displaced". This displacement is a vector, expressed in metres. This kind of displacement is referred to hereinafter as a 'change in position' or movement, expressed as  $\Delta x$  (horizontal) and  $\Delta z$  (vertical). In this paper, 'displacement' refers to the fluid volume a body will force aside, in the way a ship at sea displaces the water and a balloon displaces the air: displacement by a body. This displacement is a 'displacing volume', a scalar denoted here as  $\mathbf{V}$  (bold). This displacement volume may be slightly different from the volume enclosed in a container (system) and commonly denoted as  $V$ . In mechanical engineering, 'displacement' is the volume displaced by a piston (as in a pump or an engine) in a single stroke, a usage compatible with the intended meaning, as the volume change will equal the change in displacement  $\{\Delta V = \Delta \mathbf{V}\}$ .

**3c. Ambient parameters:** Approaching the subject of displacement, requires a proper distinction to be made between the system and its surroundings. Properties of the system itself are given without a subscript, or with subscript capital O if warranted. The system and its surroundings are separated by either a piston or other interface: the subscript 'I' (capital i) is used for the interface. In the surroundings, a distinction is made between 'natural surroundings' (subscript A, e.g.  $p_A$ =ambient pressure) and 'artificial surroundings' or load (subscript X,  $p_X$ =pressure exerted by weight and/or engine). When all the contributions from the surroundings are added, the subscript E is used:  $\{p_E = p_A + p_X\}$ . When the system pressure ( $p$ ) is equal to the pressure exerted ( $p_E$ ), then  $\{p = p_E\}$ , but such an external equilibrium is not generally present in working systems and is not assumed in this paper except for control volumes.

**3d. Volume-work versus shaft-work:** Work is taken to be an energetic interaction between the system and its surroundings. Following Guggenheim (1967, p10) this can be reflected in the use of subscripts with the symbol for work:  $W_{IO}$  stands for work done by the interface/piston (I) on the system (O), and  $W_{OI}$  stands for work by the system on the interface/piston, with  $\{W_{IO} = -W_{OI}\}$ . This notation might end most of the enduring confusion with the sign of work terms in energy balances. It also allows for proper distinctions between various work terms.

Most changes in volume involve work done, particularly when a piston is in play. However, it is not always made clear that a moving piston means that at least four forces (and hence four work terms) are involved, and all four classify as volume-work. The first force is the one that the enclosed fluid (system) imposes on the piston, and the related work  $\{W_{IO} = -p\Delta V = -W_{OI}\}$ . The second force comes from the load exerted (weight, engine) with  $\{W_{XI} = -p_X\Delta V\}$ . In the more technically oriented literature, this type of work is indicated as shaft work or technical work. For systems with a free interface, this term is zero. The third force arises from the ambient pressure  $p_A$ , with related work  $\{W_{IA} = p_A\Delta V\}$ . The sum of these

three forces is the fourth force, which determines the movement of the piston:  $\{F_I = \sum(F)\}$  and  $\{W_I = W_{OI} + W_{AI} + W_{XI}\}$ . The most interesting one here is  $W_{IX}$  with  $\{W_{IX} = -W_{XI}\}$ , as it represents 'useful work', hence the upper limit (maximum) of  $W_{IX}$  represents the system's 'capacity to do work' (a.k.a. free energy). Remarkably, its fixed companion ( $W_{AI}$ ) is not always made explicit. Some wrongly consider work on the surrounding atmosphere as 'lost work' (Mayhew, 2020). Note that in a full cycle, the work  $W_{AI}$  is zero, i.e.  $\{W_{AI} = 0\}_{\text{cycle}}$ . The latter condition predicts that  $W_{AI}$  is a 'variable of state'. However, with these in mind, it must be remembered that in a chemical reaction  $\Delta V = \Delta V$  (and hence  $W_{AI}$ ) will often be non-zero and has to be accounted for.

**3e. Sign conventions:** In mechanics, the preferred sign convention would be the one implied by the Cartesian system with coordinates (x,y,z). This assumes forces, velocities and accelerations are vectors, where (in 2D) upward (z) and rightward (x) forces are positive and downward and leftward forces negative. In a homogeneous gravitational field, this convention implies that the gravitational force ( $F_g$ ) and the acceleration of gravity (g) must always be negative and that a buoyant force ( $F_b$ ) always positive. To prevent confusion, we distinguish the positive gravity constant  $\{g = +9.8 \text{ m/s}^2\}$  from the negative one  $\{g = -9.8 \text{ m/s}^2\}$ , with  $\{g = -\mathbf{g}\}$ . Applying Newton's second law gives  $\{F_g = m\mathbf{g}\}$ , where  $F_g$  is negative as required in the Cartesian convention. However, gravitational work is quantified by  $\{W_g = |z', z''| \int F_g \cos(\alpha) dz\}$ , where  $|z', z''|$  represents the integration interval and  $\alpha$  represents the angle between force and change in position, with  $\{\alpha = 0\}$  and  $\{\cos(\alpha) = 1\}$ . The definition of work does not allow for signs to be changed at will. As a consequence, the change in gravitational energy becomes  $\{\Delta E_g = W_g = mg(z'' - z')\}$ , which makes  $W_g$  negative when the movement is upward, i.e.  $\{z'' > z'\}$ . The sign convention in thermodynamics is that negative work means that energy is leaving the system, but in mechanics it is established that the gravitational energy increases with z. This problem might be overcome by considering gravitational energy as an 'external energy': Raising a body increases its gravitational energy, but that energy is seen as belonging to the body. When the body is in free fall, this external energy is converted into kinetic energy, but no energy is added to the body or removed from it during this process. We will show that 'displacement energy', to be introduced below, might also be considered to be external energy.

**3f. Energy balances:** Energy is a conserved extensive quantity. The energy balance equation for a system can be written as  $\{\Delta E = \sum E_i\}$ , where  $\Delta E$  is the change of the total energy of the system, and  $\sum E_i$  represents all inputs ( $E_i > 0$ ) and outputs ( $E_i < 0$ ) without a need to use two separate symbols. The total energy is the sum of all E-forms:  $\{E = \sum E_i\}_{\text{disjoint}}$  with the condition that all  $E_i$  must be mutually disjoint. Forms that are considered to be constant do not need to be included, but this constancy is then a required constraint (condition).

In thermodynamics, the energy balance is commonly first encountered as the First Law:  $\{\Delta U = Q + W\}_{\text{constraints}}$ . There is an implicit requirement that internal energy  $U$  is a form of energy (cf. Section 2c), and there are two constraints: internal energy is the only E-form involved, and the system is closed (energy is only exchanged by heat  $Q$  and work  $W$ ). The equation does not exclude any irreversible process. The system boundaries have to be specified to include, or exclude, the walls and/or pistons, which in turn will determine how  $W$  and  $Q$  are to be specified. Two cases can be distinguished. In the first, more common in engineering, there is an external load and the kinetic energy of the piston is neglected. Here the external load must be specified, otherwise little can be calculated, hence the energy balance is  $\{\Delta U = Q + W_{AI} + W_{XI} \mid E_k(\text{piston}) \approx 0\}$ , with  $\{W_{AI} = -p_A dV\}$ . As  $p_A$  is independent of the state of the system,  $W_{AI}$  is independent of the path. If we define  $(\mathbf{H} = U + p_A V)$  we can write the energy balance equation as  $\{\Delta \mathbf{H} = \Delta U + W_{IA} = Q + W_{XI} \mid E_k(\text{piston}) \approx 0\}$  (cf. Section 4g for enthalpy).

The case that is more common in physical chemistry and calorimetry is the one without a load:  $\{W_{XI}=0\}$ . As pistons are absent or neglected, the energy balance equation becomes  $\{\Delta H=Q\}_{\text{no-load}}$ . Again: irreversibility is not excluded. This is important for calorimetric observations. Many of the processes such as chemical reactions that proceed in the calorimeter are irreversible, and these observations lead to Hess's Law, which is in essence a law of energy conservation.

For an open system with mass transfers  $\Phi(\text{kg})$ , the energy balance is written as  $\{\Delta E=\sum(\Phi.e)+Q+W\}$  where  $e$  the total energy per unit mass  $\{e=ek+eg+h\}$ . The total specific energy  $e(\text{J/kg})$  is taken as the sum of specific kinetic energy ( $ek$ ), specific gravitational energy ( $eg$ ), and specific enthalpy ( $h$ ). For a horizontal steady-state process (reactor), the energy balance simplifies to  $\{\Delta E=\Delta H=\sum(\phi.h)+Q+W_{IX}\}$ , where the maximal (useful) work equals  $\{W_{IX}<0\}$  as the work may be taken out as an electric current.

It can be concluded that in the more common energy balances, enthalpy plays a central role. This suggests that enthalpy should be considered to be a form of energy (cf. Section 4g).

#### 4. Displacement energy.

In the following, the whereabouts of displacement energy is shown for several processes with an indication of the existing approaches to this quantity.

**4a. Moving a solid across a pressure difference:** First, define the system as a rigid, solid cylinder of length  $L$ , cross-section  $A$ , and displacing volume  $V$ , with  $\{V=L.A\}$ . This system is to be moved from an environment with pressure  $p_L$ , to one with pressure  $p_R$ . (see Figure 1; assume horizontal move from left to right). For this transfer, work  $W_{XI}$  needs to be done, with  $\{W_{XI}=V(p_R-p_L)\}$ , to be called 'pressure-work'. If  $\{p_L>p_R\}$ , thus  $W_{XI}>0$ , this work is done on the system and hence is associated with the system, although the system as such (internal energy, gravitational energy) is unaltered if compression can be ignored. We call the energy supplied the 'displacement energy' ( $Ed$ ) with  $\{W_{XI}=\Delta Ed=V(p_R-p_L)\}$ . This is consistent with setting  $\{Ed_R=V.p_R\}$  and  $\{Ed_L=V.p_L\}$ , or in general:  $\{Ed=V.p_A\}$ , where  $p_A$  is the ambient pressure, here equal to the hydrostatic pressure. The displacement energy is independent of the path taken: compare the long path in Figure 1, and consider the energy-changes during a full cycle. If  $\{p_R>p_L\}$  at level  $z$ , the system has 'a capacity to do work' as long as the reservoir with pressure  $p_L$  is accessible. Turbines make use of this property to generate electricity, where the system is a control volume with a composition identical to the reservoir, commonly water.

Note first that here a distinction is made between the 'pressure-work' ( $W=Vdp$ ) and the 'volume work' ( $W=pdV$ ) (cf appendix A). Also note that the displacement energy is completely independent of the composition of the system (parts, chemical make-up, temperature) and hence independent of any inside pressure, i.e. the pressure of an enclosed fluid. If the solid encloses a vacuum (see section **4b** below), this vacuum will contribute to the 'energy of displacement' according to its volume. Also note that if the system stays in place but the pressure of the surroundings changes because the water level in the reservoir has changed, its 'energy of displacement' changes accordingly. The problem with this change is that no work (or heat) is supplied to the system itself: it seems to violate the energy balance for the system. This might be compared to a change of the gravitational energy due to a change in  $g$ . Small changes in  $g$  occur for example, due to a change of the position of the moon relative to the position of the body under consideration. (These changes are small, but large enough to cause the tides).

The question might arise of whether the displacement energy can be called a state variable. If state variables are defined in such a way that they cannot depend on the state of the environment, then  $Ed$  is not a state variable *sec*, but (following Gibbs) it qualifies as a

mixed variable of state, depending on the state of the system (via  $\mathbf{V}$ ) and the state of the medium (via  $p_A$ ). This is not different from the situation for gravitational energy  $E_g$ , where  $g$  is a property of the environment and not of the body.

**4b. Vacuum:** Consider the system as a piston-cylinder arrangement (PCA). In this system, a vacuum is created by starting with an initial internal volume  $V'=0$  and final volume  $V''=V$ . To do so, we have to do work  $\{W_{XA}=p_A(V''-V')=p_AV\}$ , where  $p_A$  is the ambient pressure. The shaft work needed ( $W_{XI}$ ) is used to displace the ambient air from the PCA with volume  $V$ , i.e.  $\{W_{XI}=-W_{AI}\}$ . So the energy input (work) does not end up inside the system but flows into the environment. It might be indicated as 'external energy'. However, this energy is still associated with the volume of the displacement, as is obvious from the fact that the vacuum system has 'a capacity to do work' (a.k.a. free energy) equal to  $p_AV$ . Once again, we define  $\{E_d=p_AV\}$  and call it the 'displacement energy'. The work involved could be called 'volume work of displacement' and has to be distinguished at all times from 'volume work' done by the system itself. Note that in this case, the vacuum itself does no work at all.

**4c. Stevin's law of hydrostatics:** Stevin's law is generally known as the law of hydrostatics and it describes the static pressure  $p$  in a liquid under gravitation as a function of depth, generally formulated as  $\{p=p^\circ+\rho gh\}$  (Homer, 2014, p571) where  $p^\circ$  is the atmospheric pressure,  $\rho$  is the density of the fluid,  $h$  is the depth below water level,  $g=+9.8m/s^2$ . Note: all quantities in the equation are positive.

Now consider a system (control mass) of  $m$  kilograms of water  $\{\rho=m/V\}$  (suspended) in a reservoir with water level  $z^\circ$  and its centre of gravity at position  $z$  with  $\{h=z^\circ-z\}$ . For this control volume,  $\{p=p_A\}$  so there is no need to distinguish  $p$  and  $p_A$ . Now the Stevin equation can be written as:  $\{(p-p^\circ)V=mg(z^\circ-z)\}$  or, if  $\{g=-g\}$ ,  $\{(p-p^\circ)V=mg(z-z^\circ)\}$  or  $\{\Delta pV=mg\Delta z\}$  and  $\{\Delta p/\Delta z=\rho g\}$ . The lower  $z$  (the deeper), the higher the pressure, or  $(\Delta p/dz)$  should be negative, and it is as required as  $\rho g < 0$ . Where the traditional formulation of the gravitational energy is  $\{E_g=mgz\}$ , it can be written as  $\{E_g=-mgz\}$ . This lets us state that in a hydrostatic reservoir, at any depth  $z$  the sum of the gravitational energy and the displacement energy is constant, i.e.  $\{d(E_g+E_d)/dz=0\}$  or  $\{d(-mgz)/dz+d(pV)dz=0\}$ ,  $\{-\rho g+(dp/dz)=0\}$  and  $\{(dp/dz)=\rho g\}$ . This indicates that Stevins' law is a specific formulation of the conservation of energy. A consistent sign convention seems helpful for this conclusion.

It might be possible to claim that the sum of gravitational energy and displacement energy is potential energy, but it is preferable to call this energy the 'Stevin energy'  $E_s$ :  $\{E_s=E_g+E_d\}$ , to distinguish this potential energy from all other potential energies (see 3d). From Cengel & al (2017, p90): *The flow energy at the turbine inlet is equal to the gravitational potential energy at the free surface of the reservoir.* Hence Cengel thinks along the same line. (cf. 4f)

**4d. Bernoulli equation:** Now, the sum of the Stevin energy and the kinetic energy  $E_k$ , which applies in hydrodynamics, can be called 'Bernoulli energy'  $E_b$ :  $\{E_b=E_s+E_k\}$ . The Bernoulli equation then also embodies the conservation of energy under specified circumstances (cf. Homer, 2014, p575). Note that both the Stevin energy and the Bernoulli energy can be classified as mechanical energy and that they are both independent of the internal energy of the system. *Without the consideration of any losses, two points on the same streamline satisfy  $\{p/\rho.g+vv/g+z=constant\}$  where  $p/\rho$  is flow energy,  $vv/2$  is kinetic energy, and  $gz$  as potential energy, all per unit mass. The Bernoulli equation can be viewed as an expression of mechanical energy balance.// Therefore, the mechanical energy of a flowing fluid can be expressed on a unit-mass basis as  $\{e(mech)=p/\rho+vv/2+gz\}$ , where  $p/\rho$  is the flow energy,  $vv/2$  is the kinetic energy, and  $gz$  is the potential energy of the fluid, all per unit*



mass. (quote from: 'Thermo-Fluid Engineering, 2nd semester 2013-14, by S Essalaimeh, Philadelphia University).

**4e. Archimedes' principle:** Archimedes' principle is one of the oldest laws in physics, literally as old as the road to Rome. According to Galileo: *A solid heavier than a fluid will, if placed in it, descend to the bottom of the fluid, and the solid will, when weighed in the fluid, be lighter than its true weight by the weight of the fluid displaced.* (Heath, 1897, p258). Note that Galileo measures buoyancy as a correction to weight. Weight and volume (fluid displaced) are the observables.

Wikipedia (<sup>2020/03/20</sup>) formulates under the 'Archimedes Principle': *the buoyant force that is exerted on a body immersed in a fluid is equal to the weight of the fluid that the body displaces.* In the 'wiki' entry, the word 'force' occurs 69 times. However the words 'work' and 'energy' are not encountered at all. Stated differently: after the concepts force, work and energy are introduced, 'buoyant force' has become a household name, but 'buoyant work' and 'buoyant energy' have not. However, it can be seen from the above that for the 'buoyant force'  $F_b$  (which at equilibrium balances the force of gravity  $F_g$ ), the following holds:  $\{F_b = dE/dz\}$ . In other words, the buoyant force is the (commonly vertical) gradient in the displacement energy.

**4f. Flow energy and flow work:** From Cengel et al. (2017, p64): *A pressure force acting on a fluid through a distance produces work, called flow work, in the amount of  $p/\rho$  per unit mass. Flow work is expressed in terms of fluid properties, and it is convenient to view it as part of the energy of a flowing fluid and call it flow energy. Therefore, the mechanical energy of a flowing fluid can be expressed on a unit mass basis as  $\{e(mech) = (p/\rho + v^2/2 + gz)\}$  (eqn 3.10).* What is called mechanical energy here, is called 'Bernoulli energy' in this paper (Section 4d). Note that mechanical energy is commonly defined as  $(E_k + E_p)$ .

From Cengel et al. (2017, p188): *Others argue that the product  $pV$  represents energy for flowing fluids only and does not represent any form of energy for nonflow (closed) systems. Therefore, it should be treated as work. This controversy is not likely to end, but it is comforting to know that both arguments yield the same result for the energy balance equation.*

The name 'flow energy' suggests that if there is no flow, the flow energy is zero. This is made explicit by Wu (2007, p18): *Flow energy occurs only when there is a mass flow into the system or out from the system.* However, on the next page, Wu writes: *Enthalpy is not a directly measurable property. It is a synthetic combination of the internal energy ( $U$ ) and the flow energy ( $pV$ ) exchanged with the surroundings  $\{H = U + pV\}$ .* The problem then arises that the concept of enthalpy is also applied to closed (no-flow) systems. It is shown above that even closed systems have 'displacement energy' and that the name flow energy for the same quantity leads to confusion.

In the literature, 'work of displacement' is also referred to as 'pV-work', commonly without specifying which pressure is involved. Note that work is not a state variable, but 'displacement energy' is, although it depends on the state of the system ( $\mathbf{V}$ ) and the state of the surroundings ( $p_A$ ).

**4g. Enthalpy:** In thermodynamics, part of both chemical engineering and thermal physics, enthalpy can be seen as a central concept. Firstly, enthalpy is an important intrinsic property of all substances. Secondly, there are enthalpies listed for many processes, including atomization, combustion, dissociation, evaporation, formation, hydration, hydrogenation, hydrolysis, isomerization, solution, sublimation, etc. Thirdly, for most systems, enthalpy is a common element of the energy-balance equation, together with the kinetic energy and the

gravitational energy. Quote: *These equations suggest the usefulness of enthalpy, but its greatest use becomes fully apparent with its appearance in **energy balances for flow processes** as applied to heat exchangers, chemical and biochemical reactors, distillation columns, pumps, compressors, turbines, engines, etc..* (Smith *et al.*, 2018, p40, this author's emphasis).

The collection of enthalpy data started with the invention of the calorimeter and made much progress with the formulation of Hess' law (law of constant heat summation) in 1840. However, the word 'enthalpy' was only introduced in 1922, to replace *what is usually known in England as 'total heat' or 'heat content'*. *I submit that these names are not satisfactory.* (Porter, 1922). The problem at hand was (is?) that the state variable 'total heat' ( $U+pV$ ) was not well distinguished from the input-variable 'heat' ( $Q$ ). This ambiguity is exemplified by the use, even today, by 'heat of evaporation' and 'enthalpy of evaporation' for the same quantity and reinforced by the equation  $\{\Delta H=Q\}_{\text{constraints}}$ , where the equality can be mistaken for an identity because the constraints are not always properly specified. These constraints are twofold: no other work than work against ambient pressure,  $\{W_{IX}=0\}$ , and constant pressure, i.e.  $\{p=p_A=\text{constant}\}$ . Gibbs (1961, p92) calls enthalpy 'heat function for constant pressure'. An historical review can be found in (Howard, 2002).

If a system is under isobaric conditions, this means mathematically  $\{dp=0\}_{\text{isobaric}}$  hence  $\{pdV=d(pV)\}_{\text{isobaric}}$ , but physically (experimentally) it means that system pressure follows the constant ambient pressure closely, hence  $\{p\approx p_A\}_{\text{constant}}$ , where  $\approx$  can be understood as quasi-equal. In equations that apply to isobaric systems and processes,  $p$  could (and should) be eliminated by substituting it with  $p_A$ , but in prevailing equilibrium thermodynamics, the ambient pressure is seldom made explicit, with the tacit assumption  $\{p=p_A\}_{\text{equilibrium}}$ . The convention of writing  $p$  instead of  $p_A$  with  $(p=p_A)$ , leads to confusion and obstructs the conceptualisation of 'enthalpy'. This becomes evident as  $\{dH/dT=C_{|p}\}$  where  $C_{|p}$  is the 'heat capacity at constant pressure'. If the derivative ( $dH/dT$ ) has a constraint (constant  $p$ ) attached, so must the original function ( $H$ ). Note that before 1922, enthalpy was called 'heat at constant pressure' and the importance of  $\{dH/dT=C_{|p}\}$  is obvious from the experimental point of view (calorimetry).

For solids, 'pressure' is neither a state variable nor an observable property: the only pressure around is the ambient pressure  $p_A$ . This pressure does cause stress in the solid, but the related 'strain energy' is not mentioned in most thermodynamic textbooks, and is (tacitly) included in the internal energy. If enthalpy is defined as  $\{H\equiv U+pV\}$  and enthalpy is an intrinsic property of every solid, then this definition raises the questions of what  $p$  in ' $U+pV$ ' stands for. That problem is solved when  $\{H\equiv U+p_A V\}$ .

This paper proposes to understand  $p$  in the definition of enthalpy  $\{H=U+pV\}$  as the ambient pressure, hence  $(H=U+p_A V)$ . This is not something new. Brodkey (1988, p287) formulates: *The [specific] enthalpy  $h$  is related to  $u$  by the defining relation:  $\{h=u+p/\rho\}$  (7.36), where adjustments are made in the transcription to conform to specific quantities. This is a straightforward definition of enthalpy as the sum of internal energy and displacement energy. Brodkey is backed by MIT: *In an open flow system, enthalpy is the amount of energy that is transferred across a system boundary by a moving flow, composed of the internal energy ( $u$ ) and the flow work ( $pv$ ) associated with pushing the mass of fluid across the system boundary.* (MIT>thermo6,<sup>2020/06/21</sup>).*

To these testimonies we can add those of Schroeder (physics) and Fletcher (chemistry):

Schroeder (2000,p33): *To create a rabbit out of nothing and place it on the table the magician must summon up the energy  $U$  off the rabbit, and some additional energy, equal to  $pV$ , to push the atmosphere out of the way. The total energy required is the enthalpy,  $H=U+pV$ .* Fletcher (2012,p68): *Enthalpy: This measures the total energy of a physical system, including the*

*internal energy and the energy needed to accommodate the system by displacement of the surrounding environment*. Fletcher (2012) forgets about (macroscopic) kinetic and potential energy and assumes ( $p=p_A$ ). Elsewhere, support is gathered for the position that enthalpy can be considered a form of energy for the case of the throttling process (Mannaerts, 2010).

Most textbooks define enthalpy not as a form of energy, but as  $\{H \equiv U + pV\}$ , without any physical explanation except that  $H$  must be a state variable because  $U$ ,  $p$  and  $V$  are. This assessment may be comforting, but leaves everybody, including students, in the dark. The mystery is further enhanced when it is assumed that enthalpy is to be understood as the Legendre transform of the internal energy (Alberty, 2001) and (Mander, 2014).

Once enthalpy is accepted as a form of energy, the specific total energy of a system  $e$  can be defined as  $\{e = h + ek + eg\}$ . This is not new, as Urieli writes: *The (total) specific energy  $e$  can include kinetic and potential energy, however, will always include the combination of internal energy and flow work ( $pv$ ), thus we conveniently combine these properties in terms of the property enthalpy:  $\{e = u + pv + ek + ep\}$  or  $\{e = h + ek + ep\}$ .* (Urieli, 2010).

This position is endorsed by Cengel & Boles (2006, p824): *When analyzing control volumes, we find it very convenient to combine internal energy and flow energy of a fluid into one term, enthalpy, defined per unit mass as  $\{h = u + pv\}$ . Whenever  $E_k$  and  $E_p$  of the fluid are negligible,  $H$  represents the total energy of a fluid.*

The defence rests its case.

## 5. Conclusions and recommendations:

Conclusions and recommendations from the survey on E-forms (Section 2):

- a. There is no consensus in the specified literature on a proper list of E-forms (Table 1).
- b. There is a persistent tendency to include heat ( $Q$ ) and work ( $W$ ) as E-forms, while these are energy inputs and they are not state-variables as required (Table 1).
- c. Flow energy/pressure energy is not seen as a form of energy by most references.
- d. Enthalpy is essentially not mentioned as a form of energy, internal energy only by a minority.
- e. The concept of potential energy can be abandoned: while there is very little 'potential' about it, it is a collection of unconnected 'non-kinetic' forms of energy that can be specified separately. In thermodynamics and fluid mechanics, gravitational energy is intended anyway.
- f. Solids do not have a property 'pressure' as a state variable but they can be under 'stress', and this stress is always imposed from the outside. Stress  $\sigma$  ( $N/m^2$ ) is expressed as a strain (change in length) or as a change in volume. In thermodynamics, it is silently assumed that strain energy is a (small) part of the internal energy. This silent assumption might need further corroboration.
- g. While 'mechanical energy' can be defined in outer space as the sum of kinetic and gravitational energy, in the anthroposphere, the mechanical energy balance is disturbed by pressurized surroundings, most commonly the atmosphere but also the hydrosphere. This aspect can be handled by the displacement energy.

Conclusions and recommendations from the preliminaries (Section 3):

- h. It is useful and necessary at all times to distinguish the pressure of the surroundings from the pressure of the system. In the surroundings, the ambient (natural) pressure (commonly the atmospheric pressure) can be distinguished from the auxiliary (artificial) pressure due to loads, commonly weights or engines hooked up to a piston.
- i. Every pressure relates to a force through the surface area, and every force relates to work through the movement of the piston or interface. It is to be recommended that the

notation for different work terms should follow the Guggenheim convention, with an implied sign convention.

j. The energy balance is a *sine qua non* for the check on the conservation of energy.

k. The constraints on the validity of the First Law as  $\{\Delta U=Q+W\}$  are not always properly explained in thermodynamics, notably that E-forms other than  $U$  are constant. The First Law can equally be formulated as  $\{\Delta H=Q+W_{XI}\}$  with the constraint that E-forms other than  $H$  are constant.

l. The most common formulation of the specific total energy of a system is:  $\{e=ek+ep+h\}$ .

m. In most energy balances, enthalpy plays a central role, strongly suggesting that enthalpy should be considered to be a form of energy.

Conclusions and recommendations concerning displacement energy (Section 4):

n. Currently (in texts on engineering thermodynamics), the displacement energy is covered by a list of quantities like 'flow work', 'flow energy',  $pV$ -work,  $pV$  energy, pressure energy, volume energy, ' $pV$  work energy' and 'energy of displacement'.

o. The displacement energy ( $E_d$ ) can be defined as  $\{E_d \equiv p_A \cdot V\}$  where  $p_A$  is the ambient pressure and  $V$  is the displaced volume. In a natural environment,  $p_A$  will be a function of vertical position ( $z$ ). For systems at constant pressure:  $\{p=p_A|_{\text{isobaric}}\}$  hence  $\{E_d = p \cdot V|_{\text{isobaric}}\}$ .

p. The displacement energy is an extensive quantity, i.e. an additive quantity. (Mannaerts, 2014) It is also a state variable, i.e. independent of the path. (cf. Figure 1).

q. Each and every system or body, even a vacuum, that displaces a volume  $V$  in a pressurized environment with pressure  $p_A$  can be assigned a displacement energy ( $E_d$ ) with  $\{E_d \equiv p_A \cdot V\}$ .

r. The displacement energy of can change in three different ways: 1) A system at constant (external) pressure changes its volume for whatever reason:  $\{\Delta E_d = p_E(\Delta V)\}$ ; 2) A system of constant volume moves from an environment at pressure  $p_L$  to one with  $p_R$ :  $\{\Delta E_d = V(p_L - p_R)\}$ ; 3) Any system for which the pressure of the environment changes around a system of constant displacement  $V$  from  $p_A'$  to  $p_A''$ , with  $\{\Delta E_d = V(p_A'' - p_A')\}$ . Note that this change in  $E_d$  does not involve any work related to the system. A common change of this kind is a change in hydrostatic pressure due to the tides, or a change in barometric pressure.

s. A system moving upward in a fluid gains gravitational energy ( $dz > 0$ ) but loses displacement energy ( $dp_A < 0$ ).

t. Enthalpy can be defined as an E-form, as the sum of internal energy and displacement energy.

u. This definition as  $\{H = U + p_A V\}$  is in accordance with the expression 'heat at constant pressure' that was used for the quantity enthalpy before 1922, as constant pressure is attained by setting inside pressure equal to ambient pressure.

v. Granting enthalpy the status of an E-form makes its presence in energy balances self-evident.

w. The first law of thermodynamics can equally be formulated as  $\{\Delta H = Q + W_{XI}\}$ .

This sets  $\{H = Q|_{\text{no tech work}}\}$  i.e. with the condition that no technical work is done, which includes electrical work. This aspect is very useful in science education to explain Hess' law.

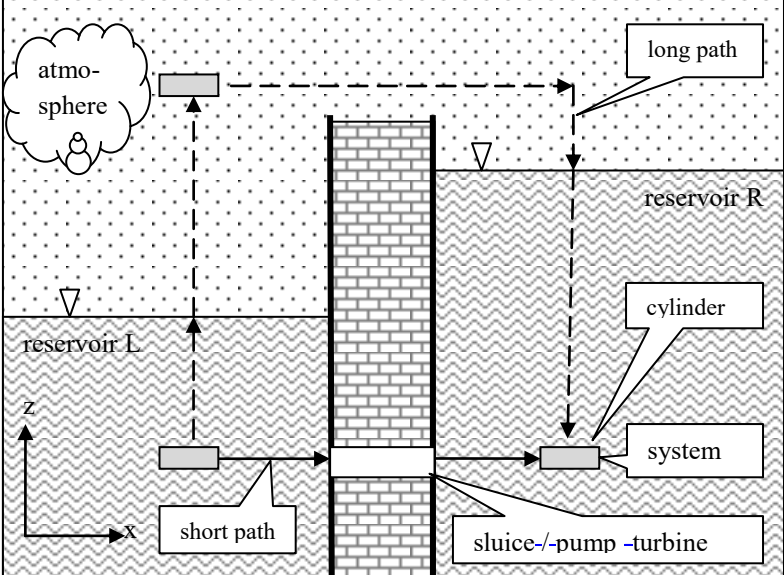
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**Figure 1.** Exchange of a body(system=cylinder) between constant-level reservoirs L and R through either a long path or a short path that together constitute a full cycle.



Appendix A: Symbols for quantities and their relationships (grey: new or deviating quantities).

sym bol	units (SI)	name	relationship	notes
superscripts & Greek				
$y^\circ$	m	y at reservoir-level		used for $p$ , $z_L$ and $z_R$
$y', y''$	~	initial, final values of y	$\Delta y = y'' - y'$	interval of integration $ y', y'' $
$\alpha$	°	angle between force & path	$W = \int F \cdot \cos(\alpha) dx$	nb $\cos(90^\circ) = 0$ , $\cos(180^\circ) = -1$
$\rho$	kg/m <sup>3</sup>	density (ambient fluid)	$\rho = m/V$	hence $V = m/\rho$
$\Phi$	kg	mass transfer (cf. $E^{\leftarrow}$ )	$\dot{\phi} = d\Phi/dt$	applies to open systems
Latin symbols				
A	m <sup>2</sup>	area (cross-sectional, piston)	see V and p	L(m): length, stroke length
E	J	total energy (system)	$E = U + E_b = H + E_m$	sum of all E-forms
$E^{\leftarrow}$	J	any energy input or output	$\sum E^{\leftarrow} = W + Q + \Phi \cdot e$	energy balance eqn: $\Delta E = \sum E^{\leftarrow}$
e	J/kg	specific total energy	$e = E/m$	
$E_b$	J	Bernoulli energy	$E_b = E_d + E_g + E_k$	Bernoulli-eqn: $dE_b = 0$
eb	J/kg	specific mechanical energy	$eb = E_b/m$	(cf. Cengel & al, 2017, p64)
$E_d$	J	displacement energy	$E_d \equiv p_A V$	
ed	J/kg	specific flow energy	$ed = p/\rho = E_d/m$	(cf. Cengel & al, 2017, p64)
$E_g$	J	gravitational energy	$E_g = mgz = -mgz$	$dE_g/dz = F_g = mg = -mg$
$E_k$	J	kinetic energy	$E_k = \frac{1}{2}mv^2$	(here: macroscopic only)
$E_m$	J	mechanical energy	$E_m = E_k + E_g$	(compare to $E_b$ )
$E_p$	J	potential energy	$\sum(\text{non-kinetic } E)$	$E_p$ commonly used for $E_g$
$E_s$	J	Stevin energy (external E)	$E_s = E_g + E_d$	embodies law of hydrostatics
$E_y$	J	strain & spring energy	part of U or $E_m$	y for T. Young (1773-1829)
F	N	force (vector)	$F = m(dv/dt)$	v=velocity
$F_g$	N	force of gravity	$F_g = mg = -mg$	definite negative
$F_b$	N	buoyancy	$F_b = dE_d/dz$	$F_b = V dp_A/dz = V \cdot \rho g$
g	m/s <sup>2</sup>	gravity (acceleration of)	$g = +9.81 = -g$	$g < 0$ : Cartesian convention
H	J	enthalpy (useful function)	$H = U + pV$	applies at constant pressure
<b>H</b>	J	enthalpy (E-form)	<b>H</b> = U + $E_d$	if $p = p_A$ : $E_d = pV$ , hence <b>H</b> = H.
h	m	depth <i>below</i> water level	$h = z^\circ - z$ , $dh = -dz$	nb: height = z in this paper
m	kg	mass (body/system)		
<b>m</b>	kg	mass of displaced fluid	Archimedes law	see $\rho$ and V
p	Pa	pressure (system)	$p = F/A$	$(p - p_A)$ = gauge pressure
$p_A$	Pa	ambient pressure	$(dp_A/dz) = \rho g$	Stevin's law of hydrostatics
$p_E$	Pa	imposed (external) pressure	$p_E = p_A + p_X$	at equilibrium ( $p = p_E$ )
$p_X$	Pa	load-pressure (auxiliary p)	$p_X = F_X/A$	imposed by load/engine
Q	J	heat (transfer)		$q = dQ/dt$ = heat-power (watt)
T	K	temperature (system)	(nb: t=time)	( $T_A$ : ambient temperature)
U	J	internal energy		f(T, composition)
V	m <sup>3</sup>	volume (available, enclosed)		nb: volume under piston
<b>V</b>	m <sup>3</sup>	volume of displaced fluid	<b>V</b> > V, but $\Delta \mathbf{V} = \Delta V$	for cylinder: <b>V</b> = A(m <sup>2</sup> ).L(m)
W	J	work (general)	$W = \int F \cdot \cos(\alpha) dx$	$w = dW/dt$ = work-power (W)
$W_I$	J	work on piston/interface	$W_I = W_{OI} + W_{XI} + W_{AI}$	mech. equilibrium: $W_I = 0$
<b><math>W_{IA}</math></b>	J	(p) work of displacement	<b><math>W_{IA} = V dp_A</math></b>	flow-work, pressure-work
$W_{IA}$	J	(V) work of displacement	$W_{IA} = p_A dV$	expansion-, volume-work
$W_{IO}$	J	work on enclosed gas	$W_{IO} = -pdV$	commonly: gas = system
$W_{IX}$	J	shaft-work	$W_{IX} = V dp_X$	technical work, useful work
$W_g$	J	work of gravitation	$W_g = F_g(z'' - z')$	
x	m	position in x-direction	(centre of gravity)	
z	m	position in z-direction, height	(centre of gravity)	<b>z</b> = position centre buoyancy