Energy-balance of experiment: enth

Bas Mannaerts

Ir. S.H.W.M. Mannaerts
(bas.mannaerts.planet.nl),
Eykmanstraat 12,
6706 JW Wageningen is
docent chemie/fysische
transport-verschijnselen

Support is gathered for the position that enthalpy can be considered a form of energy for the case of the throttling process. Ambivalence with respect to enthalpy and volume-work is resolved. Where the throttling process is generally assumed to be isenthalpic, it is shown that this is only true in one specific case, otherwise the enthalpy increases, evidenced by comparing the throttle process with other expansion processes.

Introduction

Theodore et al. (2009) state: "*All forms of energy must be included in an energy balance*".
However, no agreement exists on a definite list of forms of energy (Mannaerts, 2001).
It is commonly taught and believed that 'heat is a form of energy', although this has become incorrect when the concept of heat in this sense was replaced by enthalpy in 1922 (Romer, 2001). Surprisingly, enthalpy is essentially never mentioned as a form of energy, and this aspect is investigated here for gas-expansion in general and the throttle process in particular.
Standard symbols are used, listed in table 1 together with the equations involved. Contrary to tradition, we take a dynamic approach to thermodynamics by using time-derivatives explicitly. Hence q is the instantaneous heat(flow) expressed in watt, Q(J) is its time-integral; w is work(power) in watt and W(J) its time-integral. If the internal energy U is the only form of energy to take into account, the First Law can be formulated as $dU/dt = q+w$, or as $\Delta U = Q+W$, avoiding the use of awkward d's. All q and w terms are positive if the energy is transferred to the system. Note that no equilibrium condition is attached to the validity of the First Law as formulated.

Isochoric transfer: pressure energy

To transfer any system of a given volume V (independent of its content) from an environment with pressure p' (initial state) to an environment with pressure p" (final state), transfer-work W_{pv} needs to be done with $W_{pv} = V(p"-p')$. If $p">p'$, $W_{pv}>0$, meaning this amount of work enters (is added to) the system.
It is unfortunate that this form of energy did not receive a unique name and symbol. There is an array of related concepts, that may or may not be identical. In the literature one finds 'energy of displacement', 'pressure-energy', 'flow energy', 'volume-energy', 'pressure-volume energy' and 'pV-energy'. Since it is sometimes assumed that 'work' can be a form of energy, the list can be extended with 'flow work'.
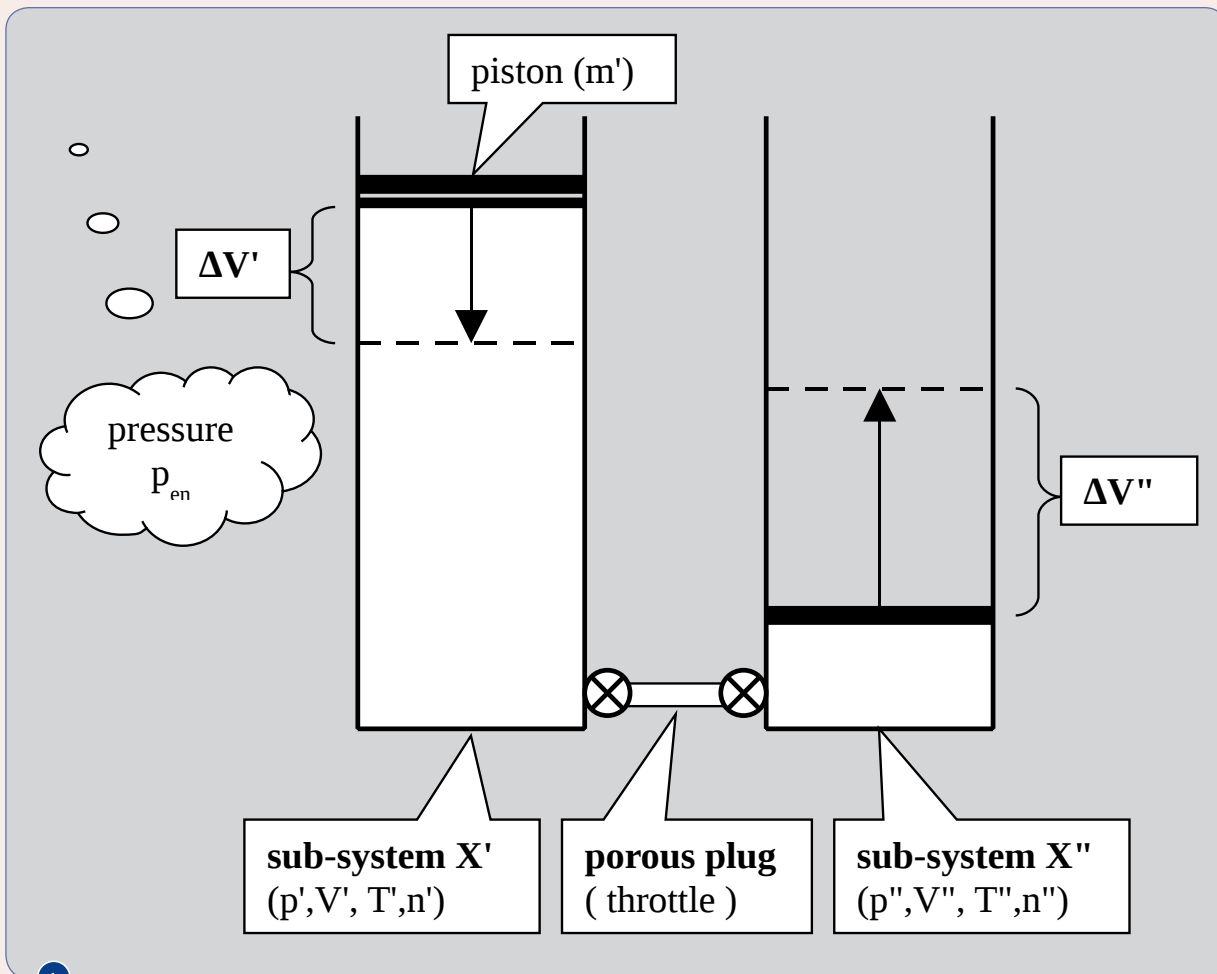A proper name for the form of energy indicated would be 'energy of displacement', in the same sense that 'water-displacement' is used for ships (mass of water displaced), but displacement with a different meaning is used in the definition of work as the product of force and displacement (distance). Hence we will adhere to the choice 'pressure energy' and we postulate that every system of volume V in an environment with pressure p_{en}, has related to it an pressure energy $E_{pv} = p_{en}V$ (J). Several observations are due. First this pressure-energy is well-defined for all systems with a well-defined volume, and obviously systems under constant pressure that change their volume by ΔV, change their pressure energy by $p_{en}\Delta V$. The definition given, makes pressure energy independent of the content of the system, hence independent of internal pressure (if applicable), and independent of the existence of internal or external equilibrium. However, what is to be taken as external pressure, depends on the choice of the boundaries of the system. Thus for a glass of water as a whole, p_{en} equals the atmospheric pressure, but for a 'control volume' inside this glass (eg 1 ml or 1 g) this is the hydrostatic pressure at the level chosen. This applies also to a control-volume of a fluid flowing from high to low pressure. In this case the difference between internal and external pressure is quite subtle, and in engineering pressure energy is indicated as flow energy. Note that the pressure energy extends to 'no-flow' systems.

Decompression

Gaseous systems have both an internal and an external pressure. We will consider 4 pathways for decompression, where these variables are explicitly not equal to each other. Here our main interest goes to the Joule-Thomson experiment, also known as the throttling process. In this adiabatic process the gas is passing through a porous plug or throttle valve from high to low pressure (see figure 1). For ideal gases it is found

f the Joule-Thomson
alpy change at decompression

piston (m')

ΔV'

pressure p_{en}

ΔV"

sub-system X'
(p',V', T',n')

porous plug
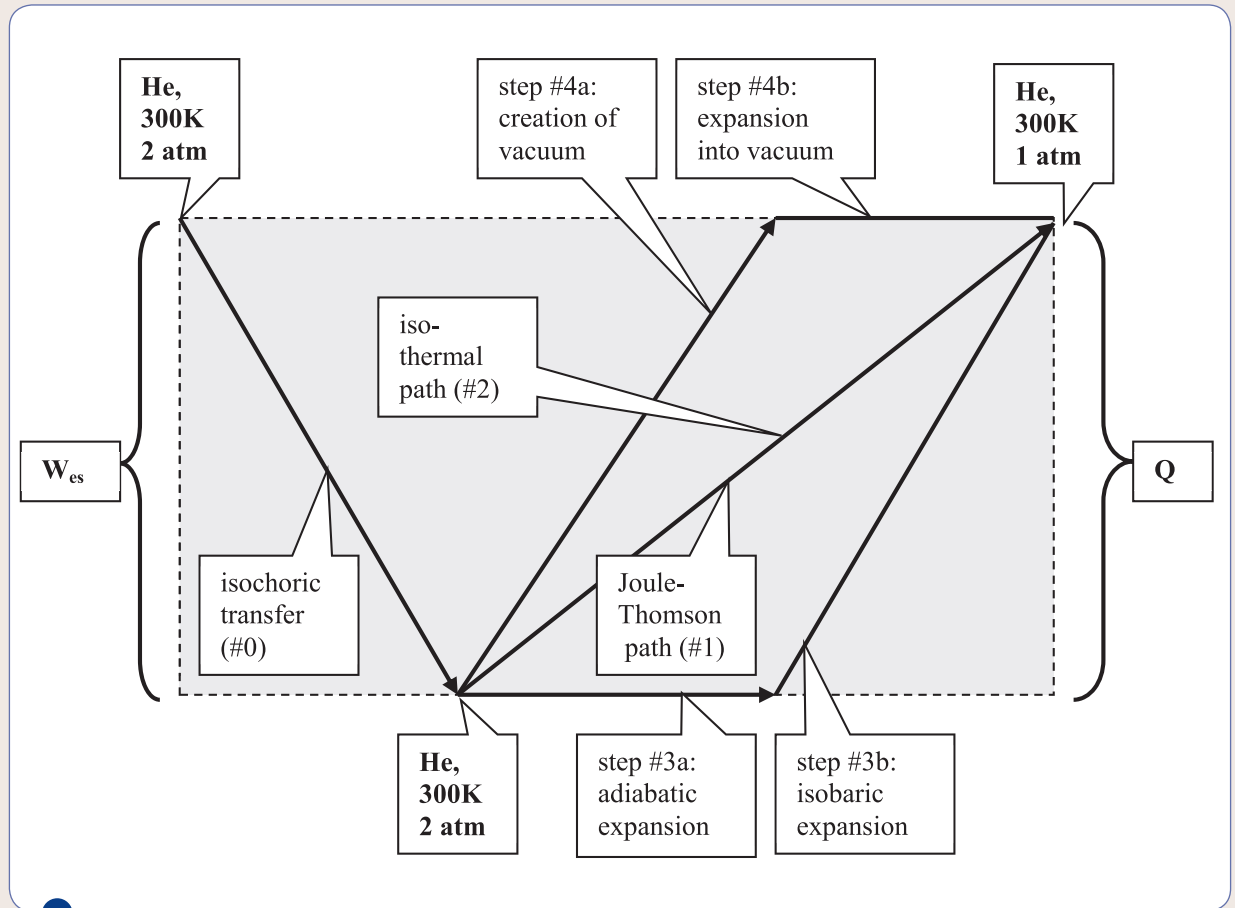(throttle)

sub-system X"
(p",V", T",n")

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Contraption for the performance of the Joule-Thompson experiment

that temperature T, hence the internal energy U, does not change during the passage. For real gasses Joule and Thomson found that the temperature dropped. (For air at 25C, the Joule-Thomson coefficient $= dT/dp = 0.23$ K/atm). It is quite generally assumed that the enthalpy changes neither for an ideal gas nor for real gasses, and for this reason the throttling process is commonly mentioned as an example of a isenthalpic process. If for one path the enthalpy change is zero, it must be zero for all other pathways.

Enthalpy

The McGraw-Hill Dictionary of Engineering defines enthalpy as: "*The sum of the internal energy of a system plus the product of the system's volume multiplied by the pressure exerted on the system by its surroundings*". Along the same line Levenspiel (1996) formulates: "*When you evaluate the energy of an object of volume V, you have to remember that the object had to push the surroundings out of the way to make room for itself. With pressure p on the object, the work required to make a place for itself is pV. This is so with any object or system, and this work may not be negligible. Thus the total energy of a body is its internal energy plus the extra energy it is credited with by having a volume V at pressure p. We call this total energy the enthalpy, H.*" We note that according to this approach enthalpy is the sum of the 'internal energy' and the 'pressure energy'.

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The enthalpy changes for pathways for the expansion of a gas (cf table 2) (pressure indicated is internal, not external)

However many textbooks are not very specific with respect to the meaning of p in H=U+pV. They are satisfied to indicate that p is the pressure, leaving it to the reader and the context to determine whether p is the inside pressure, the outside pressure or both, the latter commonly assumed for the (so-called) reversible processes. Others define p in H=U+pV explicitly as the pressure of the system itself (eg Theodore, 2009), or implicitly so (eg Zemansky, 1981).

Where Levenspiel is clear why pV is to be added to the internal energy U, this becomes less obvious when p is taken to be the internal pressure. Convenience is sometimes stated (eg Moran & Shapiro, p77), but no physical justification is presented. This gives a bias towards the Levenspiel definition of enthalpy.

Volume work and shaft work

The ambivalence with respect to enthalpy, also exists with respect to 'volume-work'. If one considers a gas in a piston-cylinder arrangement (PCA), the work by the piston on the fluid $w_{in} = -p_{in}dV/dt$ [W], the simultaneous work done by the environmental pressure on the piston $w_{en} = -p_{en}dV/dt$. Both terms qualify as 'volume work', but the two work-terms are never equal to each other except for a (quasi-static) isobaric processes. Which of the two work-terms should be entered in the

first law, $dU/dt=q+w$, depends on the choice of the boundaries of the system and on the need or desirability to include work other then volume-work, notably shaft-work, in the balance-equation.

The choice of the boundary is not completely free however, because the boundary chosen for work w must the same as the boundary for the heat-exchange q. For fluids there is always a container involved, most commonly a PCA. The heat transfer from fluid to PCA is not an observable quantity, only the heat transfer from the container (calorimeter) to the surrounding (eg surrounding ice in the case of a ice-calorimeter). Hence, Q as observed quantity is heat transferred to the environment, where the PCA is to be taken as part of the system: a second argument for the Levenspiel approach to enthalpy.

Most pistons in engines are not free, but hooked up to a 'driving shaft' to deliver 'shaft-work' w_{es}. (The shaft-work w_s that is commonly encountered in engineering, is equal to w_{es} but with an opposite sign: $w_s=-w_{es}$). The total (mechanical) work done by the piston|environment $w_e = w_{en} + w_{es}$, and the first law can now be formulated as $dU/dt = q +w_e = q +w_{en} +w_{es}$. In the case that $H=U+p_{en}V$, the first law can now be reformulated as $dH/dt = q +w_{es}$. When $w_{es} =0$, this equation reduces to $dH/dt=q$ or $\Delta H=Q$.

For this derivation we have assumed that the total work done (on the outside of the piston) is the sum of the shaft-work w_{es} and work done on the environment w_{en}. The equation $dH/dt = q + w_{es}$ is an energy-balance equation without any equilibrium assumption.

In the case that $H = U + p_{in}V$, the above derivation is not possible and this is taken as a third indication that enthalpy should be defined as $H = U + p_{en}V$. We will assume such in the following, but to keep an open mind on the subject we will define a quantity $H_{in} = U + p_{in}V$, which might be called 'inthalpy' to prevent further ambivalence. For solids, the internal pressure p_{in} is not an obvious property, so 'inthalpy' may be undefined for solids, a fourth argument in favor of defining enthalpy as a function of the external pressure.

The Joule-Thomson path for a closed system

It will be assumed in the following that the gas involved is one mole of an ideal gas, with an initial (internal) pressure of 200 kPa and a final pressure of 100 kPa, both at 300K.

Instead of the open-system approach that is commonly used to represent the throttling process, we will present the energy-balance of a closed system. Consider the thermally insulated (i.e. adiabatic) system X as given in figure 1. The two subsystems X' and X" are piston-cylinder-arrangements (PCA's) filled with helium-gas, separated and connected by a porous plug. The resistance of the plug is large anough to keep velocity of the gas flow small and its kinetic energy negligible. Subsystem X' is under higher pressure than subsystem X", maintained by the weight of its piston: hence p' > p" and both are constant. We consider a slow adiabatic steady-state process, where a mass (1 mole) ideal gas passes the plug as indicated by the arrows: the left piston is lowered by Δh', while the right piston rises by Δh". The parameters, initial conditions and the calculation of all work-terms and energy changes are presented in table 1.

Where the internal energy of the gas does not change, the enthalpy increases by 1.25 kJ due to the shaft work supplied by the gravitational energy of the left piston. The 'inthalpy' $U + p_{in}V$ is constant.

The Joule-Thomson path for the open system

In the Joule-Thomson path presented above, the process is driven by the gravitational energy of the piston, but does not involve a change in the external pressure. If we have a pressure-bath at 200 kPa available to us, we can use this to lift the piston in subsystem X' to its original level and repeat the process described in the previous paragraph. This can be understood as an isochoric transfer delivering shaft-work (cf figure 2).

Another approach would be to have an open Joule-Thomson system. Now the pressure-energy and the enthalpy of the gas upstream from the porous plug is equal to the same downstream, because the work of expansion is countered by the work of transfer: $p_{en}dV = -Vdp_{en}$, or $d(p_{en}V) = dE_{pv} = 0$. It means that the Joule-Thomson flow process can be split in two steps, transfer and expansion, where in the first the enthalpy decreases

Table 1. Energy-balance for adiabatic passage of 1 mol ideal gas through a porous-plug

symbols	variables & parameters	formula for calculation	system X'	system X"	total X'+X"	units
	parameters					
m	piston mass		100	0		(kg)
A	piston area		0.01	0.01		(m²)
T	temperature		300	300		(K)
p_{en}	pressure environment		100	100		(kPa)
p_p	pressure by piston	$p_p = mg/A$	100	0		(kPa)
p_{in}	gas-pressure	$p_{in} = p_{en} + p_p$	200	100		(kPa)
	initial conditions					
n(0)	initial amnt. of subst.		1.1	0.1	1.2	(mol)
V(0)	initial volume	$V(0) = n(0)RT/p_{in}$	13.7	2.5	16.2	(L)
	variables					
Δn	change amnt. of subst.		-1	+1	0	(mol)
ΔV	volume change	$\Delta V = \Delta nRT/p_{in}$	-12.47	+24.94	+12.47	(L)
w_{en}	work by environment	$w_{en} = -p_{en}\Delta V$	+1.25	-2.49	-1.25	(kJ)
ΔE_{pv}	pressure energy	$\Delta E_{pv} = p_{en}\Delta V$			+1.25	(kJ)
Δh	change piston position	$\Delta h = \Delta V/A$	-1.25	+2.49		(m)
ΔE_g	potential energy piston	$\Delta E_g = mg\Delta h$	-1.25	+0 kJ	-1.25	(kJ)
w_{es}	shaft-work	$w_{es} = -\Delta E_g$	+1.25	+0	+1.25	(kJ)
w_i	work on gas	$w_i = -p_{in}\Delta V$	+2.49	-2.49	+0	(kJ)
ΔU	change internal energy	$\Delta U = 3\Delta nRT/2$	-3.74	+3.74	+0	(kJ)
ΔH_{in}	inthalpy change	$\Delta H_{in} = \Delta U + \Delta(p_{in}V)$			0	(kJ)
ΔH	enthalpy change	$\Delta H = \Delta U + \Delta E_{pv}$			+1.25	(kJ)
ΔH	enthalpy change	$\Delta H = Q + W_{es}$ *)			+1.25	(kJ)
ΔE_t	total energy change	$\Delta E_t = \Delta E_g + \Delta H$			0	(kJ)

*) This equation (with Wes =-Ws) can be found in Denbigh(p65), Smith&VanNess(p33).

Table 2. Energy-balances for 4 different pathways for the expansion of an ideal gas

path	proces	W_{es}	Q	ΔE_{pv}	ΔH	ΔH_{in}
#0	isochoric tranfer	-1.25	0	-1.25	-1.25	0
#1	closed throttle process	+1.25	0	+1.25	+1.25	0
#0+#1	open throttle process	0	0	0	0	0
#2	isothermal expansion	0	+1.25	+1.25	+1.25	0
#3a	adiabatic expansion	0	0	$-\Delta U^{*})$	0	?
#3b	isobaric expansion	0	+1.25	$1.25+\Delta U^{*})$	1.25	?
#3	adiabatic+isobaric expansion	0	+1.25	+1.25	1.25	0
#4a	creation of a vacuum	1.25	0	1.25	1.25	0
#4b	expansion into vacuum	0	0	0	0	0
#4	creation vacuum+expansion	1.25	0	1.25	1.25	0

*) This is the ΔU of the adiabatic step

and in the second increases: the total enthalpy change is zero, as commonly stated for the throttle process. Only in this case the process is properly called isenthalpic. In reality most Joule-Thomson processes are driven by a compression somewhere upstream, for which shaft-work is expended.

The question arises how enthalpy changes in case of the expansion of non-ideal gases. If the temperature drops in an adiabatic process, it means that $\Delta U < 0$ and $W_e < 0$. This means that the real gas expands more then the ideal gas. For the enthalpy in the flow process (open) this does not make a difference because the extra volume-work is compensated by extra transfer-work (or shaft-work). For all other processes it will make a difference.

Other pathways for expansion

The throttle process (#1) can be compared with three other pathways (#2,#3,#4) of decompression as depicted in figure 2. The energy balances for the processes are summarized in table 2, where all data (kJ) apply to an (expansion) process involving 1 mole of an ideal gas for which $\Delta U = 0$ for each pathway, but not necessarily for each step in the pathway. For relations see table 1. All pathway show an increase of enthalpy of 1.25 kJ, except for the isochoric transfer, for which enthalpy decreases by 1.25 kJ. Note that inthalpy ΔH_{in} seems of limited value.

Conclusions

a. It would be useful for sciences that employ energy balances, to recognize 'pressure energy' ($E_{pv} = p_{en}V$) as a separate form of energy, where p_{en} is the environmental pressure of the system with volume V.

b. Enthalpy can be defined as the sum of internal energy and pressure energy, and enthalpy can be listed as a form of energy. This allows for the formulation of the First Law as $\Delta H = Q + W_{es}$.

c. If there is a need to define a quantity ($U + p_{in}V$), it is proposed to call this quantity 'inthalpy' to prevent ambivalence. For the energy-balance of the throttle process this quantity seems not very useful.

d. If the Joule-Thompson experiment is carried out with an ideal gas and the gravitational energy of a pistons providing the shaft-work needed, then the gravitational energy is completely converted into pressure-energy, while the internal energy is constant. Hence the passage across the porous plug is not isenthalpic as is commonly assumed, when the work is supplied externally. If this energy is supplied by a large source of pressure, the process is isenthalpic, even if the gas is not an ideal gas.

e. Since heat Q is not a variable of state, hence not a form of energy, the general mantra that 'heat is a form of energy' should be replaced by 'enthalpy is a form of energy' in line with the replacement of the concept 'total heat' by 'enthalpy' in 1922. ●

For references see *www.npt.nl* at *Inhoudsopgaven*.