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Adiabatic Processes

Introduction

Adiabatic processes are those processes during which no heat enters or leaves the system, so that with $q = 0$ the First Law[1]

$$\Delta U = q + w \qquad [3.10]$$

shows that any energy change in the system will be entirely due to work, either positive or negative. The amount of PV work done by a system (that is, w negative) in any process (adiabatic or not) can vary from zero (e.g., a gas expanding into a vacuum) to a maximum for a process which proceeds reversibly (see the discussion in Chapter 3). The path followed by a system changing from one equilibrium state to another is capable of virtually infinite variation, but of special interest are the three limiting cases of isentropic ($\Delta S = 0$), isenthalpic ($\Delta H = 0$) and iso-energetic ($\Delta U = 0$) processes.

Isentropic Constant entropy (isentropic) processes were dismissed in brief fashion (§6.2.2) because, being reversible (in the sense of continuous equilibrium), they are completely hypothetical. In fact, however, some natural and mechanical processes, although not of course having $\Delta S = 0$ exactly, are *modeled* as occurring at constant entropy, because they are believed to be sufficiently fast relative to the rate of heat exchange that $q = 0$ is a reasonable approximation, and that entropy-producing processes within the system such as phase changes, turbulence, mixing and so on are also negligible. In subjects such as meteorology and mechanical engineering, where the processes in question are directly observable, both these conditions are in many cases reasonable. In geology, where the processes take place in the crust or deep mantle and are much less understood, they are more problematic and controversial. One reason isentropic expansions are of interest is that being both adiabatic and reversible they provide the *maximum* amount of work available from fluid expansion.

Isenthalpic Constant enthalpy (isenthalpic) processes were then discussed (§6.2.3) using the irreversible Joule-Thompson expansion and the example of a hydrothermal fluid rising in a fissure and boiling due to the decreasing pressure (Figure 6.5, page 156). In the discussion it is briefly noted that if the pressure change is due to a change in depth in the Earth the Joule-Thompson cooling effect is different from that in the usual "porous plug" or constricted flow example.

Iso-energetic Processes Iso-energetic processes, those in which $\Delta U = 0$, are not discussed in the text, and are useful more as a limiting case rather than in any kind of application.

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[1] Equations with numbers in square brackets refer to equations in the book.

	T °C	P bar	V $\mathrm{cm^3\,mol^{-1}}$	U $\mathrm{J\,mol^{-1}}$	H $\mathrm{J\,mol^{-1}}$	S $\mathrm{J\,mol^{-1}\,K^{-1}}$	γ $= C_P/C_V$
state 1	700	5000	24.007	42705	54709	83.187	1.4285
state 2h	489.34	300	150.04	50208	54709	103.28	1.9699
state 2s	403.59	300	58.023	38768	40508	83.187	7.6535
state 2u	416.84	300	83.838	42705	45220	90.089	4.538

Table 1: Data for water from REFPROP (Lemmon et al, 2007). See Figure 1.

Both isentropic and isenthalpic processes have been used as models of natural events to a greater extent than I indicated in the text. In this article I discuss some of these applications of thermodynamic theory, and expand on the effect of gravity on Joule-Thompson cooling. To better understand these processes, data for supercritical water from program REFPROP (Lemmon et al., 2007)[2] are used in examples of fluid expansions.

Work in Adiabatic Processes

To illustrate the nature of these processes, we consider the expansion of supercritical water from state 1 at $T_1 = 700$°C, $P_1 = 5000$ bar to state 2 at a pressure $P_2 = 300$ bar. The temperature in state 2 will depend on what kind of expansion takes place. The three limiting paths mentioned above ($\Delta S = 0$; $\Delta U = 0$; $\Delta H = 0$) are shown in the schematic Mollier or H-S diagram, Figure 1 (as well as in the normal Mollier diagram as shown in engineering texts in Figure 2), and the data for water in the beginning and ending states for these paths are shown in Table 1. It is instructive to consider the work and heat involved in each of these fluid expansions for both the reversible and irreversible cases, and to inquire as to why the isentropic case is always considered to be reversible, while the other two are always considered to be irreversible, when in fact all three can be reversible or irreversible, at least in theory.

Isentropic *PV* Work

The Reversible Case

In normal usage, isentropic always means "reversible isentropic". This means that the system entropy is unchanging *during* the process or reaction, and this implies that the process is reversible in the sense of continuous equilibrium. Reversible isentropic processes are by definition adiabatic by virtue of the relation

$$q_{\mathrm{rev}} = T\,\Delta S \qquad [4.5]$$

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[2] In Table 1 and in the following calculations we follow the common engineering practice of using H and U instead of ΔH and ΔU. Nevertheless, if a number is attached to U or any quantity containing U (e.g., $H = 54709\,\mathrm{J\,mol^{-1}}$) it is understood that this is a difference from some reference state. In program REFPROP, the default reference state for water is defined as having zero entropy and internal energy for the saturated liquid at the triple point. Then because the pressure and volume at the triple point are absolute quantities, this defines the scale for enthalpy, Helmholtz and Gibbs energies (see pp. 387-388 in the book).

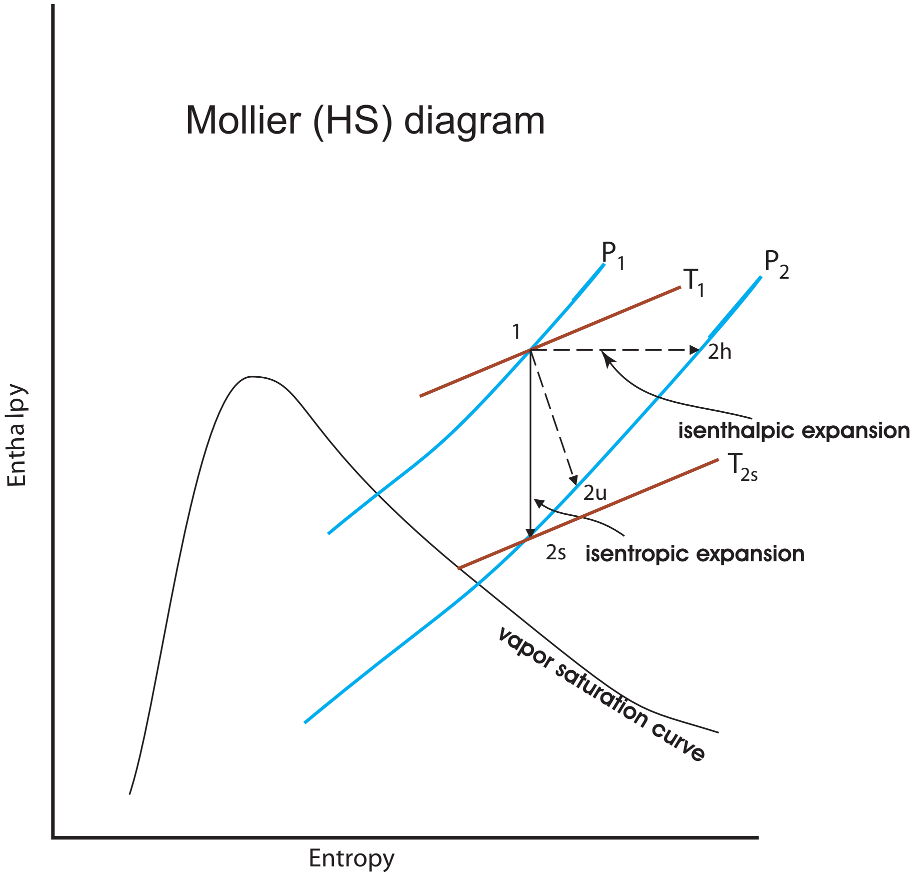

Figure 1: Schematic Mollier or *H*-*S* diagram of the type commonly shown in engineering texts (e.g. Moran and Shapiro (2008), Chapter 6). Isobars are blue, isotherms are red. State 1 is $T_1 = 700°\mathrm{C}$, $P_1 = 5000\,\mathrm{bar}$. P_2 is 300 bar. Data for states 1, 2s, 2u, and 2h are shown in Table 1. The change from state 1 to state 2h is isenthalpic and irreversible, a Joule-Thompson expansion. The change from state 1 to state 2s is isentropic and reversible. States 1 and 2u have the same internal energy, so 1→2u represents an irreversible Joule expansion. The dashed lines 1→2h and 1→2u represent disequilibrium states which cannot be represented on the diagram. Isotherms through points 2u and 2h are not shown for clarity, but the temperatures of all isotherms are shown in Table 1.

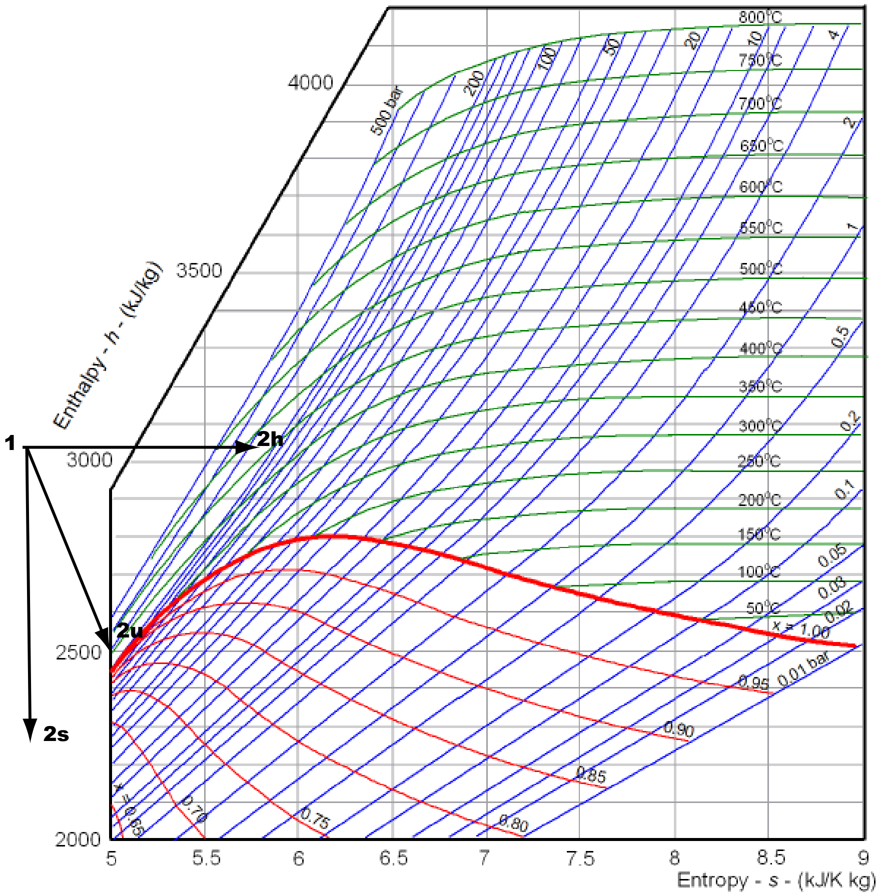

Figure 2: The Mollier diagram for water as shown in most engineering texts. The heavy red line is the vapor saturation curve. The approximate positions of the points in Table 1 have been added. They were chosen originally to represent possible fluid conditions in the Earth's crust, and are clearly outside the range of most engineering applications. Note that the units are specific (per kg) rather than molar as in Table 1.

so that if $\Delta S = 0$, then $q_{rev} = 0$. An *irreversible* isentropic process is simply one having the same entropy at the beginning and the end of the process, whatever non-equilibrium states happen in between, and in such cases q is not zero but negative (since $q_{\mathrm{irrev}} < T\,\Delta S$), and will share the energy transfer process with w, so maximum work is not achieved. Such processes are rarely of much practical interest, but it is nevertheless instructive to consider such a case.

Isentropic expansions are commonly discussed using ideal gas as an example. Ideal gas has the equation of state $PV^{\gamma} = K$, where $\gamma = C_P/C_V$ and K is a constant (Moran and Shapiro, 2008, p. 42), so

$$w = -\int_{V_1}^{V_2} P\,dV \tag{3.3}$$

$$= -K\int_{V_1}^{V_2} \frac{1}{V^{\gamma}}dV \tag{1}$$

With γ constant, which is not the case for real gases, this becomes

$$w = -K\frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma} \tag{2}$$

and because $K = P_1V_1^{\gamma} = P_2V_2^{\gamma}$,

$$w = -\frac{P_2V_2 - P_1V_1}{1-\gamma} \quad \text{(ideal gas)} \tag{3}$$

This result is not very useful for aqueous fluids. The isentropic path 1→2s is shown in Figure 3 as well as Figure 1.

Adiabatic processes have $q = 0$ by definition, so that by the First Law, the work done is

$$w = \Delta U \tag{4}$$

which for the change 1→2s is

$$w = 38768 - 42705$$

$$= -3937\,\mathrm{J\,mol^{-1}} \tag{5}$$

which is the maximum work available from this expansion.

To look at the same problem in a different way, PVT data were obtained from REFPROP for a number of points having the same entropy between states 1 and 2s. These are shown in Figures 4 and 5.

A reasonably good fit to the PV points in Figure 5 is given by

$$P = 97646\,V^{-3.4869} \tag{6}$$

The work done is the area under the curve, given by the integral

$$w = -97646\int_{V_1}^{V_2} \frac{dV}{V^{3.4869}} \tag{7}$$

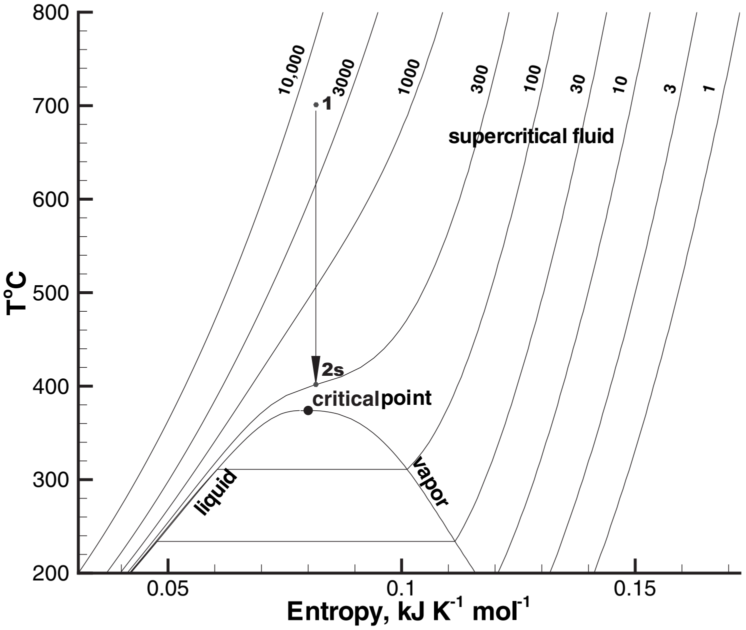

Figure 3: states 1 and 2s in *T*-*S* space. Modified from Figure 4.11 in the book.

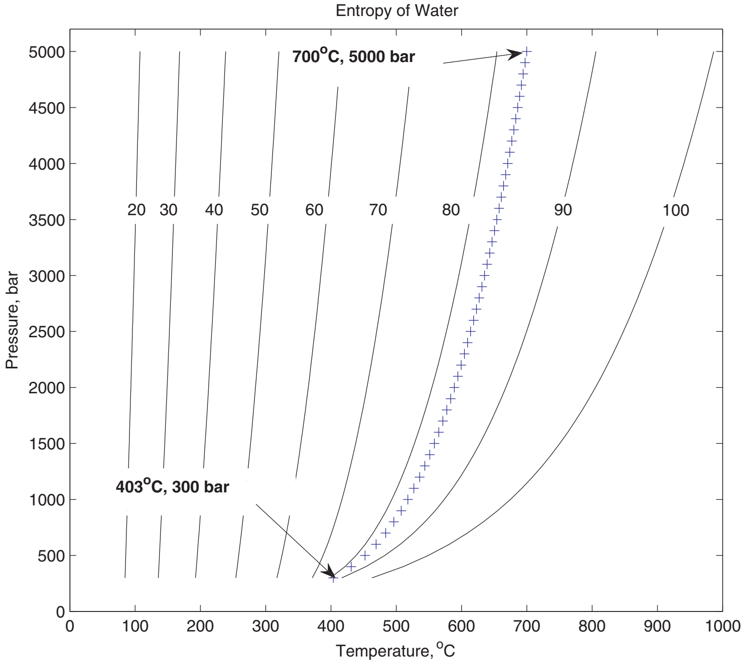

Figure 4: The entropy of supercritical water as a function of P and V from program REFPROP. Isentropic equilibrium states from state 1 to state 2s are shown in blue.

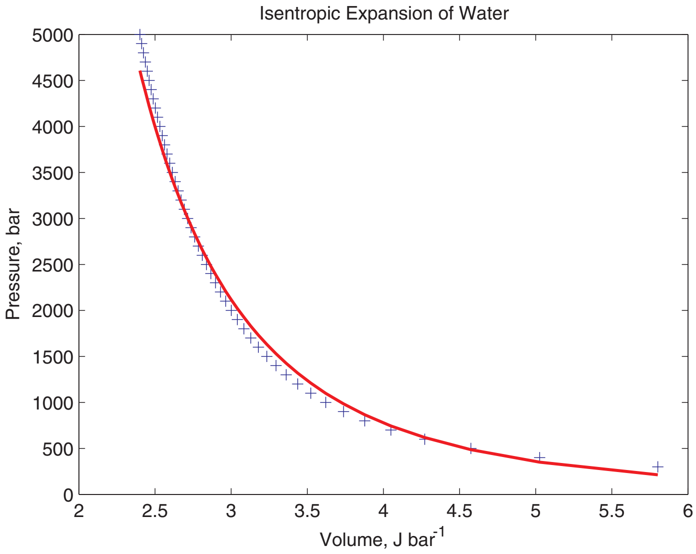

Figure 5: The isentropic equilibrium states from Figure 4 shown in PV space. The red line is the function $P = 97646V^{-3.4869}$ (equation (6)).

which, using equation (2) with $V_1 = 2.4007\,\mathrm{J\,bar^{-1}\,mol^{-1}}$, $V_2 = 5.8023\,\mathrm{J\,bar^{-1}\,mol^{-1}}$ and $\gamma = 3.4869$ evaluates to

$$w = -3952\,\mathrm{J\,mol^{-1}} \tag{8}$$

not unexpectedly slightly different from the exact figure, $-3937\,\mathrm{J\,mol^{-1}}$ (equation (5)) A slightly more accurate result is given by a numerical integration using function TRAPZ in MATLAB, which evaluates the area as the sum of the small trapezoidal $P\Delta V$ areas between adjacent points, giving $w = -3946\,\mathrm{J\,mol^{-1}}$. The point is that ΔU is indeed equal to the area under the isentropic PV curve.

The Irreversible Case

As mentioned above, an irreversible expansion having $\Delta S = 0$ is not usually of any interest, so examples are not often considered. A possible example using data in Table 1 would be the adiabatic irreversible expansion from state 1 to state 2u (a Joule expansion), followed by reversible compression and cooling from state 2u to state 2s. The Joule expansion has $q = 0$ and $w = 0$ (see the discussion of this process below), so we need only consider the change from state 2u to state 2s. The work done by the compression process, because pressure is constant at 300 bar, is

$$\begin{aligned} w &= -P \times (V_{2\mathrm{s}} - V_{2\mathrm{u}}) \\ &= -300 \times (5.8023 - 8.3838) \\ &= 775\,\mathrm{J\,mol^{-1}} \end{aligned}$$

so instead of obtaining $-3937\,\mathrm{J\,mol^{-1}}$ as work from the system, we add $775\,\mathrm{J\,mol^{-1}}$ as work to the system.

During this reversible compression the temperature cools from 416.84 to 403.59°C and the entropy changes from 90.089 to 83.187 $\mathrm{J\,mol^{-1}\,K^{-1}}$. In Figure 6 the heat transferred is determined by fitting the T-S data along this path at 300 bar with a polynomial and integrating,

$$\begin{aligned} q &= \int_{S_{2\mathrm{u}}}^{S_{2\mathrm{s}}} T\,dS \\ &= \int_{90.091}^{83.187} (0.08863\,S^2 - 13.453\,S + 1182.6)\,dS \\ &= -4712\,\mathrm{J\,mol^{-1}} \end{aligned}$$

so $4712\,\mathrm{J\,mol^{-1}}$ is lost from the system as heat. The net energy transfer for this irreversible process is thus $775 - 4712 = -3937\,\mathrm{J\,mol^{-1}}$, which is of course the same as (from Table 1)

$$\begin{aligned} U_{2\mathrm{s}} - U_1 &= 38768 - 42705 \\ &= -3937\,\mathrm{J\,mol^{-1}} \end{aligned}$$

The point of this exercise is to show that there are a lot of ways to perform a $\Delta S = 0$ expansion, but only the reversible expansion will provide the maximum amount of work, and *only the reversible expansion is adiabatic.*

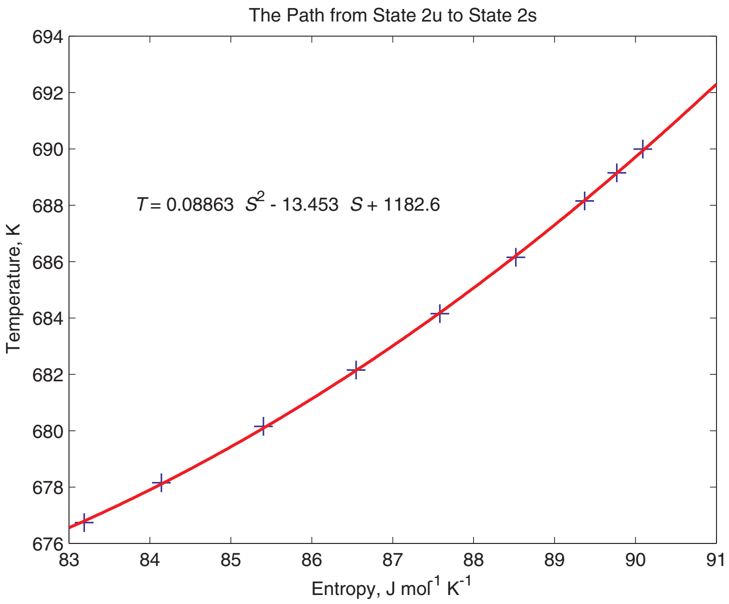

Figure 6: Temperature-entropy data for the path from state 2u to state 2s. The red line is the polynomial best fit function shown.

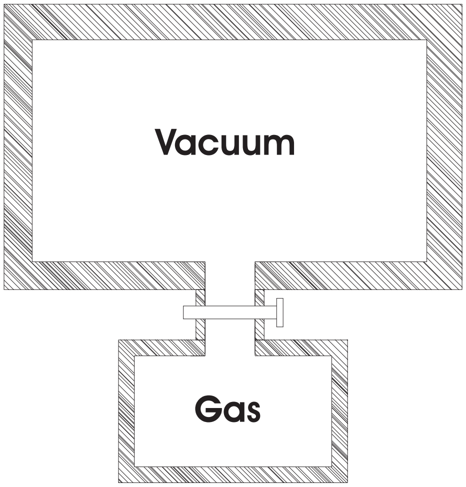

Figure 7: A Joule Expansion consists of a gas escaping adiabatically into a vacuum. With $q = 0$ and $w = 0$, the gas has the same internal energy before and after the expansion.

Iso-Energetic Processes

The Irreversible Case

The classic example of an iso-energetic process is the Joule experiment, in which a gas expands adiabatically and irreversibly into a vacuum, as illustrated in Figure 7. As there is no heat transfer ($q = 0$) and no work is done ($w = 0$), the gas must have the same internal energy before and after the expansion ($\Delta U = 0$). If the "gas" consists of water at 700°C and 5000 bars, and the volumes of the two chambers are such that before expansion the molar volume is 24.007 $\text{cm}^3\,\text{mol}^{-1}$ and after expansion it is 83.838 $\text{cm}^3\,\text{mol}^{-1}$, then the water will have cooled to 416.84°C and the pressure will be 300 bars (data in Table 1). This expansion is represented by the path 1→2u in Figure 1.

There are many other irreversible paths which would also result in $\Delta U = 0$, but only the adiabatic Joule expansion has $w = 0$. For example, a path from state 1 to state 2h (isenthalpic), followed by a reversible compression and cooling from state 2h to state 2u (see Table 1), would also have an overall $\Delta U = 0$, but in this path (and in fact in any path having $\Delta U = 0$ other than the Joule expansion) w is not zero, and by equation [3.10] neither is q. Therefore *only the irreversible expansion can be adiabatic.*

The Reversible Case

Any path having $\Delta U = 0$ other than the Joule expansion will have $w \neq 0$ and $q = -w$, and will not be adiabatic. One such path is the reversible expansion. Reversible PV paths for all three limiting cases are shown in Figure 8, and being reversible, the area under each curve is the work done in that PV expansion.

The value of w as given by the area under the $\Delta U = 0$ curve in Figure 8 (using

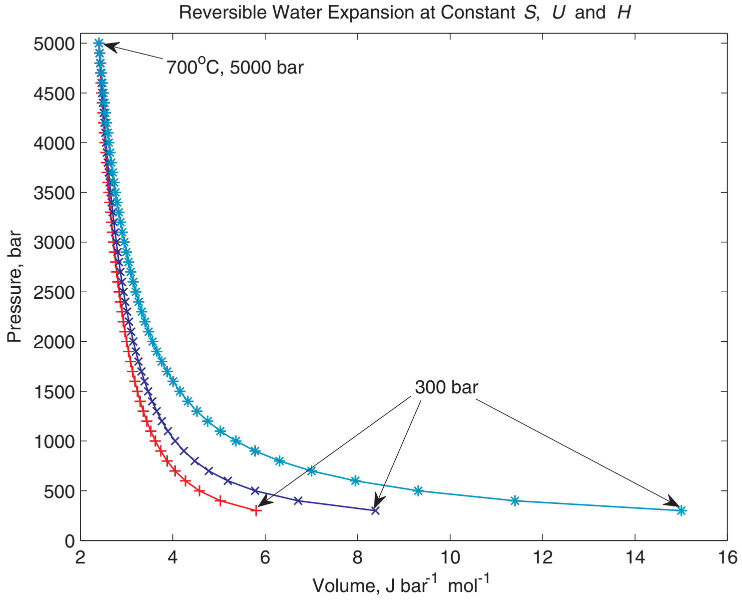

Figure 8: The three limiting cases of reversible expansion of water from 5000 bar, 700°C, to 300 bar. The area under each curve gives the maximum work available from that process, but only the constant *S* expansion is adiabatic. Red–constant *S* (isentropic); Blue–constant *U*; Cyan–constant *H* (isenthalpic).

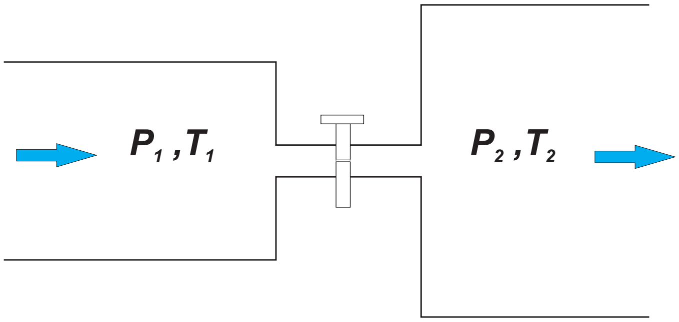

Figure 9: A Joule-Thompson expansion. A steady-state, continuous fluid flow from one equilibrium state to another, traditionally but not necessarily (see Figure 10) separated by a throttle (originally a "porous plug") or valve. Adapted from Pippard (1966) Figure 13.

numerical integration in MATLAB as before) is $-5834\,\mathrm{J\,mol^{-1}}$, and fitting TS data for this change from REFPROP with a polynomial as before,

$$
\begin{aligned}
q &= \int_{S_1}^{S_{2u}} T\,dS \\
&= \int_{83.187}^{90.089} (-1.8983\,S^2 + 285.91\,S - 9671.4)\,dS \\
&= 5817\,\mathrm{J\,mol^{-1}}
\end{aligned}
$$

which is close enough to show that indeed $q = -w$ for the reversible $\Delta U = 0$ expansion.

Isenthalpic *PV* Work

The Irreversible Case

Isenthalpic expansions are traditionally discussed in terms of the classical irreversible Joule-Thompson experiment (Figure 9) in which a steady-state continuous fluid flow passes adiabatically and irreversibly from one equilibrium state to another at a lower pressure. The result is that the two states have the same enthalpy. The most convenient method of doing this experimentally is to have the fluid pass through a valve or throttle, providing a sudden, irreversible expansion.

Pippard (1966, pp. 68–72) points out that an isenthalpic expansion need not have a throttle, but could take place for example in a tube in which the entropy-producing effect of the throttle is replaced by viscous drag along the walls, or possibly by other entropy-producing processes such as turbulence, chemical reactions, and so on. In other words, the essential element of a Joule-Thompson expansion is not the presence of a throttle; it can be any adiabatic irreversible change between two equilibrium states having the same enthalpy. It is one example of *stationary flow*, in which a constant temperature and pressure distribution is maintained, which results in the existence of

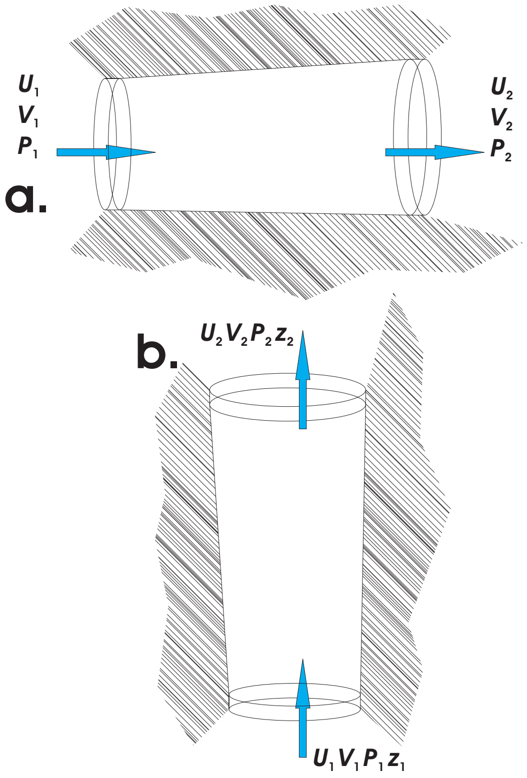

Figure 10: (a.) Modified from Figure 14 in Pippard (1966) to show increasing volume and hence Joule-Thompson effect in the direction of flow. The shaded area represents a perfectly insulating enclosure, so that the flow is adiabatic. (b.) Rotated 90°, adding the effect of elevation (z) and the work against gravity.

the two equilibrium states and, with the additional adiabatic condition, the enthalpy equivalence.

Figure 10a is slightly modified from Pippard (1966) Figure 14 (p. 71), by having the tube increase rather than decrease in volume in the direction of flow. The shaded areas represent a perfectly insulating environment, resulting in adiabatic fluid flow in the tube. We consider an elementary volume at each end of the tube to contain the same mass of fluid. Because the flow is steady state, the mass, volume and energy of the fluid in the tube is constant, so if there are no other energy sources (such as kinetic energy; heat flow in or out) we can write

$$\begin{aligned} U_1 - U_2 + P_1V_1 - P_1V_2 = 0 \quad \text{or} \\ H_1 = H_2 \end{aligned} \tag{9}$$

where H is molar enthalpy. The irreversible isenthalpic path 1→2h is shown in Figure 11 as well as Figure 1.

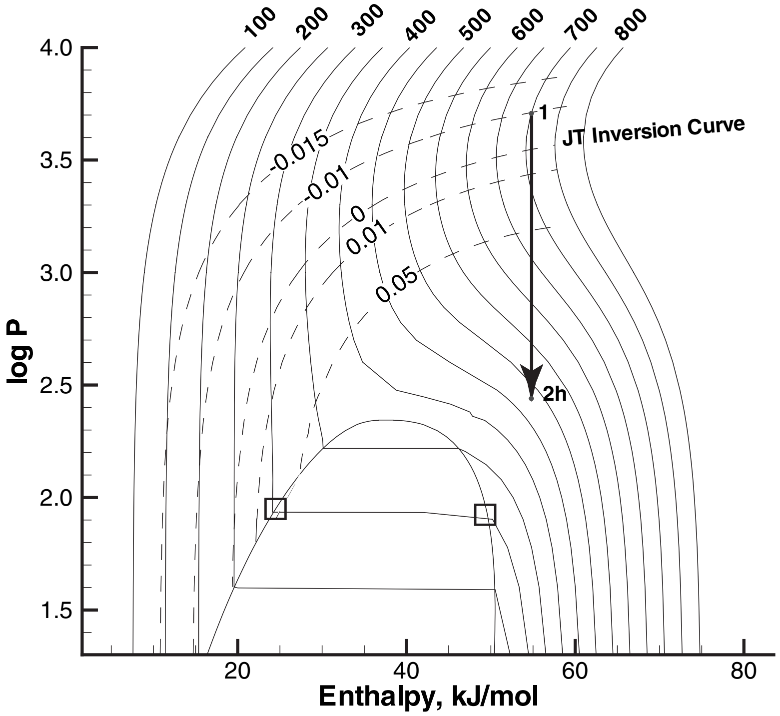

Figure 11: states 1 and 2h in $\log P$ vs. H space. Modified from Figure 6.4 in the book.

It is of interest to verify that $H = U + PV$ for states 1 and 2h.

$$\begin{aligned} U_1 + P_1 V_1 &= 42705 + 5000 \times 2.4007 \\ &= 54709\,\mathrm{J\,mol^{-1}} \\ U_{2\mathrm{h}} + P_{2\mathrm{h}} V_{2\mathrm{h}} &= 50208 + 300 \times 15.004 \\ &= 54709\,\mathrm{J\,mol^{-1}} \end{aligned}$$

which is the value for H in states 1 and 2h in Table 1.

The adiabatic relation equation (4) also holds in this case, so the work done in the irreversible Joule-Thompson expansion 1→2h is

$$w = \Delta U$$

and in this case

$$\begin{aligned} w &= 50208 - 42705 \\ &= 7503\,\mathrm{J\,mol^{-1}} \end{aligned} \tag{10}$$

This quantity can also be calculated a different way, in this case a bit more easily. Thus the work done is

$$\begin{aligned} w &= -(P_{2\mathrm{h}} V_{2\mathrm{h}} - P_1 V_1) \\ &= -(300 \times 15.004 - 5000 \times 2.4007) \\ &= 7502\,\mathrm{J\,mol^{-1}} \end{aligned}$$

The positive sign of this result means that in a Joule-Thompson expansion, more work is done pushing the gas than is recovered as the gas expands.

The Reversible Case

The value of w as given by the area under the $\Delta H = 0$ curve in Figure 8 (using MATLAB as before) is $-11035\,\mathrm{J\,mol^{-1}}$, and the value of q is (fitting TS data for this change from REFPROP with a polynomial as before)

$$\begin{aligned} q &= \int_{S_1}^{S_{2\mathrm{h}}} T\,dS \\ &= \int_{83.187}^{103.28} (-0.8618\,S^2 + 150.03\,S - 5546.2)\,dS \\ &= 18515\,\mathrm{J\,mol^{-1}} \end{aligned}$$

so that the net energy change is $-11035 + 18515 = 7480\,\mathrm{J\,mol^{-1}}$, reasonably close to the true value, $7503\,\mathrm{J\,mol^{-1}}$ (equation (10)). *The reversible isenthalpic process is not adiabatic.*

Joule-Thompson Expansion in a Gravity Field

In Figure 10b the tube is vertical so that the energy balance now includes the change in gravitational potential,

$$H_1 + gz_1 = H_2 + gz_2 \tag{11}$$

showing that, as Ramberg (1971) first pointed out, what is constant is no longer enthalpy H, but $H + gz$. The definition of enthalpy ($H = U + PV$) is not changed (although you might choose to include gz in the definition of H or of U), so *vertical adiabatic flow cannot be isenthalpic*. It is iso-($H + gz$)-ic.

Ramberg (1971) equation (5) is

$$\left(\frac{dT}{dP}\right)_H = \frac{\left(T\alpha + \frac{dP^*}{dP} - 1\right)V}{C_P} \tag{12}$$

where P^* is the pressure at lithostatic equilibrium. We can also write this in terms of depth z, where P is the actual pressure in the fluid, P^* as just mentioned is the lithostatic pressure at the same depth, and P_0 is the amount of overpressure in the fluid, which is the additional pressure required to cause the fluid to move against whatever friction or viscous drag is caused by the walls. The relationship between these pressure terms is $P = P^* + P_0$, or

$$\frac{dP}{dz} = \frac{dP^*}{dz} + \frac{dP_0}{dz} \tag{13}$$

Multiplying both sides of this by dz/dP gives

$$1 = \frac{dP^*}{dP} + \frac{dP_0}{dP} \tag{14}$$

Substituting for dP^*/dP, changing V to $1/\rho$ and multiplying both sides by dP/dz in equation (12), gives

$$\left(\frac{dT}{dz}\right)_{h+gz} = \frac{1}{\rho C_P}\left(T\alpha\frac{dP}{dz} - \frac{dP_0}{dz}\right) \tag{15}$$

the thermal gradient in the vertical tube in Figure 10b.

If we assume that flow is sufficiently slow that the pressure is negligibly different from the lithostatic gradient, or that the walls are frictionless so that $P_0 = 0$ and $dP_0/dz = 0$ so $dP/dz = dP^*/dz$,

$$\left(\frac{dT}{dz}\right)_{h+gz} = \left(\frac{T\alpha}{\rho C_P}\right)\frac{dP^*}{dz} \tag{16}$$

Also, rearranging (16),

$$\left(\frac{dT}{dP^*}\right)_{h+gz} = \frac{T\alpha}{\rho C_P} \quad \text{and because } \alpha = (1/V)(dV/dT) \tag{17}$$

$$= \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P \tag{18}$$

$$= \left(\frac{dT}{dP}\right)_S \tag{19}$$

which is Pippard (1971), equation (6.16), p. 63, the equation for isentropic pressure change. Comparing equations (15), (16) and (17) we see that the departure from isentropic conditions is the "overpressure" term in equation (15), which is in turn caused by the viscous drag along the walls. Equation (15) is equivalent to Spera (1981) equation (4), because the middle two terms in his equation drop out and his $dP_h/dz = \rho g$.

Applications

Both isentropic and isenthalpic processes have been widely discussed in the Earth Sciences literature, though being irreversible and thus more likely to be applicable in nature, isenthalpic processes are more commonly considered.

The cooling of hydrothermal fluids by fluid expansion as a means of precipitating ore minerals has long been of interest to economic geologists. Barton and Toulmin (1961) and Toulmin and Clark (1967) conclude that isentropic cooling is unlikely to be important as unreasonably long vertical distances would be needed to effect the pressure change needed for appreciable cooling, even if irreversible processes in the fluid were negligible. Throttling of a fluid by expansion through a constriction in the vein system is however considered rather likely in some areas. Barton and Toulmin (1961) observe that, in the context of an aqueous solution rising in fractures from in or near a magma toward the surface, "Some sort of constriction at some position is necessary or the whole vein would become a steam vent, open to the surface." They provide some calculations for such a case, based on the general pattern interpreted for the Central City district in Colorado. They also observe, in connection with the mixing of hydrothermal fluids and groundwater, the problem is not the theory involved, but "…the problem lies in demonstrating that this action takes place where ore deposits are forming." Helgeson (1964, pp. 97-99) also considers isentropic and isenthalpic expansions as ore precipitation mechanisms, but more from the point of view of their effects on ion pair stabilities. He concludes that "There is little doubt that irreversible adiabatic expansion of a hydrothermal ore solution is capable of precipitating solid phases."

Petrologists are also interested in the thermal effects of fluid movement in the Earth in connection with magma generation, magma emplacement, volcanic eruptions, and even core formation (Samuel and Tackley (2008) conclude that viscous heating is the dominant factor in iron sinking to the core). Kieffer and Delaney (1979) make the case for isentropic flow based on the speed of sound. The sound speed is considered to control the rate of propagation of disturbances, and if the relaxation time is short compared to the propagation time, thermodynamic equilibrium is assumed and entropy is said to be conserved. However the assumptions made are rather restricting-

> …it is assumed that the characteristic times of the problem (t_0) are larger than relaxation times (τ) for material changes (such as phase changes, nucleation and growth processes, etc.), so that flows are 'slow' in terms of departure from thermodynamic equilibrium.…
>
> …Therefore most magma emplacement and flow conditions (to the extent that they can be idealized as single-component, single-phase systems)

> may be approximately isentropic, the most notable exception being emplacement of granitic magmas at low Reynolds numbers.

I doubt that many petrologists would say that magma emplacement can be usefully idealized as single-component, single-phase systems.

Spera and Bergman (1980) and Spera (1981, 1984) discuss the relevant differential equations and reach a variety of conclusions about both volatiles and melts.

McKenzie (1984) considered that deep mantle melting and upwelling is isentropic, where the process is slow and volatiles are not important, an idea taken up later by Asimow et al. (1995, 2001), Asimow (2002) and by Stolper and Asimow (2007). Asimow (2002) presents an "entropy budget". Entropy producing processes in fractional melting (with melt migration) is contrasted with equilibrium melting (no relative movement) in one dimension. This is done numerically using program MELTS. The entropy producing processes are

- Chemical advection by out-of-equilibrium melt.
- Thermal disequilibrium between melt and residue.
- Frictional dissipation of gravitational potential.
- Dissipation by compaction.

His conclusion is that McKenzie (1984) got it right, that melting and upwelling is close to isentropic. Stolper and Asimow (2007) treat the same subject using a graphical method.

Mastin and Ghiorso (2001) attempt to include gas exsolution in the energy budget. They calculate the change in temperature of decompressing gas-melt mixtures under isenthalpic and isentropic conditions, with and without gas exsolution. They assume a gas phase of pure H_2O, and gas-melt equilibrium. They conclude that

1. Most of the cooling in erupting mixtures results from expanding gases rather than from the exsolution process.
2. This conclusion is independent of which model they use.
3. The limiting factor in converting enthalpy to kinetic energy is viscous resistance to flow below fragmentation depth and conduit geometry above it.

Ganguly (2005) is notable as the only(?) one to question the isentropic paradigm for mantle melting, and to revive the isenthalpic option. His conclusion is that IAD (Irreversible Adiabatic Decompression) results in substantially more melting than does the isentropic model, even though he excludes all entropy production (irreversible effects) other than irreversible decompression. This greatly simplifies the problem, probably at the expense of simulating reality.

Several of these attempts at applying the theory of irreversible expansion to geological processes mention the fact that engineers commonly use the isentropic limiting case as a model. In contrast to geologists, engineers almost invariably consider open systems. Modeling of these open systems involves fluid flow in and out of a specified space called a Control Volume (CV), and the flow is usually but not necessarily considered to be steady state, or unchanging with time.[3] A crucial point is that as long as the flow is steady state, the properties of a fluid at the input and output of the CV and at various points within it are measurable and the thermodynamic properties of the fluid determined. So, for example, the entropy of the input and output of a CV can be calculated from measured properties of the fluid, and the entropy change compared to that of an ideal isentropic process. For relatively simple systems such as nozzles and diffusers, which are very close to adiabatic, which have no internal moving parts or chemical reactions, and in which flow may be laminar, this "isentropic efficiency" is found to be not much less than 100%. The isentropic model is therefore appropriate. In turbines and other machines with moving parts the isentropic efficiency is less, but still a useful quantity, and identifying sources of irreversibility is an important part of engineering design. This subject is sufficiently interesting that a separate companion article on this web site is devoted to it ("Isentropic Efficiency in Engineering Thermodynamics").

Comment

The reason that isentropic processes are always treated as reversible while isenthalpic and iso-energetic processes are always treated as irreversible is that (1) the adiabatic condition is thought to be useful in modeling natural processes, namely those in which the rate of heat transfer is much slower than the process in question, and (2) only reversible isentropic and irreversible isenthalpic and iso-energetic processes can be adiabatic. There is no such thing as, e.g., an adiabatic reversible isenthalpic process or an irreversible adiabatic isentropic process.

What is striking about the geological literature on this topic is that it is almost entirely theoretical. There is almost no attempt at analyzing an actual field situation, and little incorporation of field or experimental data (Manga and Kirchner (2004), who discuss warming of groundwater which loses elevation, is an exception). All the equations are "true". The question is how closely they apply to what happens (or happened) in nature. A skeptic might say that iso-whatever assumptions are made because they make calculations simpler, or even possible, never mind if they are realistic.

It is useful to keep in mind that the three cases considered, isentropic, isenthalpic and iso-energetic, are limiting cases, and that in general natural processes will be none of these, and may well be quite far from being iso-anything.

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[3] Note that steady state does not mean only that the rate of flow is constant, but that *all* properties of the fluid remain constant.

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