Chapter 2
Classical Thermodynamics: The Second Law

Starred sections are supplementary

2 Classical Thermodynamics: 2nd law

This is a substantial chapter, containing many important results and many techniques. There are two common technical difficulties for many students at the beginning: proof of theorems and partial derivatives. We will emphasize the understanding and applications of the theorems and we will do many practices in partial differentiations.

In this Chapter, we start from 2 simple experimental observations: (a) Whereas we can (easily) transform work into heat with 100% efficiency by means which leave the system generating the heat in its original state, the converse is not true; and (b) There is a natural direction to spontaneous processes (e.g., the cooling of a cup of coffee; the mixing of the milk in the coffee; etc.); and from them, derive the existence of a new state variable called **entropy**, S.

In classical thermodynamics, entropy "completes the set" of relevant thermodynamic variables (e.g., for a gas the complete set is (P, V, T, S) - anything else can be put in terms of these). However, the underlying deeper meaning of entropy (which is intrinsically a mysterious, deep and subtle concept) only become clearer when we progress to statistical mechanics.

2.1 Heat engines and refrigerators

Heat engines run in cycles. After one cycle: $\Delta E = 0$ (by definition); an amount of heat $Q_H > 0$ has been absorbed from a hot source (or set of hot sources; e.g., the hot combustion products in a car engine); the engine has done work $w > 0$ on its surroundings; and an amount of heat $Q_C > 0$ has been emitted to a cooler thermal reservoir (or set of cooler reservoirs; e.g., the outside air).
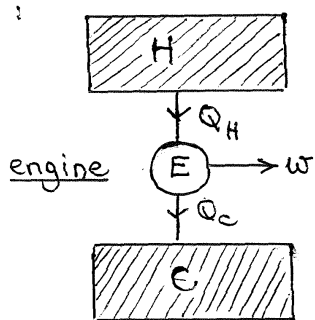

Figure 1

Experimental fact: We can not make $Q_C = 0$, however hard we try, and however desirable, even in the absence of frictional or dissipative processes (i.e., even for a reversible engine $Q_C > 0$). See Figure 1. The first law:

$$w = Q_H - Q_C \tag{1}$$

since $\Delta E = 0$. We define the **efficiency** of heat engine as

$$\eta_E = \frac{w}{Q_H} = 1 - \frac{Q_C}{Q_H} < 1. \tag{2}$$

Example: We have seen one example in Q1 of Example Sheet 3. Lets do another, the air-standard **Otto cycle**: an idealization of a standard gasoline engine in a car.
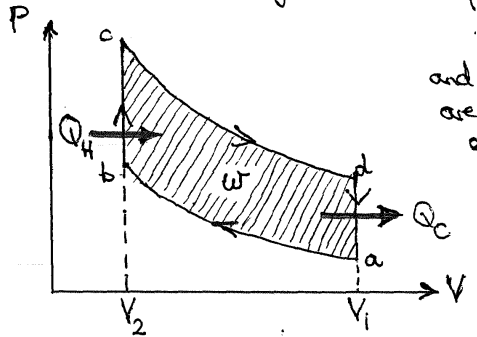

Figure 2

The compression stroke $a \to b$ and the expansion stroke $c \to d$ are adiabatical, so heat enters and leaves only during the constant volume (isochoric) processes $b \to c$ and $d \to a$. It is easy to calculate η_E for this reversible Otto cycle if the working substance is an ideal gas, for which C_V is a constant, independent of temperature, along $b \to c$ and $d \to a$

$$Q_H = \int_{T_b}^{T_c} C_V dT = C_V(T_c - T_b)$$

and

$$Q_C = - \int_{T_d}^{T_a} C_V dT = C_V(T_d - T_a).$$

Thus

$$\eta_E = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_d - T_a}{T_c - T_b}. \tag{3}$$

For an adiabatic process on an ideal gas we have $PV^\gamma = \text{const.}$ (Q1 of Example Sheet 2) and also $PV = nRT$, ideal gas law. There two equations give

$$TV^{\gamma - 1} = \text{const} \tag{4}$$

for adiabatic processes on ideal gas. Thus, the 2 adiabatic processes $c \to d$ and $a \to b$, we have

$$T_d V_1^{\gamma - 1} = T_c V_2^{\gamma - 1}, \quad T_a V_1^{\gamma - 1} = T_b V_2^{\gamma - 1}.$$

After subtraction, we have

$$(T_d - T_a)V_1^{\gamma - 1} = (T_c - T_b)V_2^{\gamma - 1} \tag{5}$$

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Substitute into Eq. (3) we have

$$\eta_E = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma - 1} = 1 - \frac{T_a}{T_b} = 1 - \frac{T_d}{T_c}, \tag{6}$$

where in the last two equations we have used Eq. (4). Note: For the Otto cycle it is easy to see $T_c > T_b > T_a$ and $T_c > T_d > T_a$, hence $\eta_E < 1 - \frac{T_a}{T_c}$, which we will comment on later in correction with the discussion on Cannot engines.

Refrigerators are just heat engine run in reverse, i.e., where we supply work to pump heat from cooler to hotter bodies, i.e. w, Q_H and Q_C all change sign and become W, q_H and q_C, as shown in Figure 3.
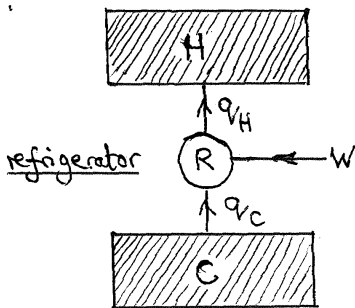

Figure 3

The first law:

$$W = q_H - q_C. \tag{7}$$

Examples of such machines are standard refrigerators, air-conditioners, and heat pumps. These are all essentially the same but have different purposes. Thus, refrigerators and air-conditioners are used for cooling (e.g., the refrigerators cabinet, or room), whereas the heat pump is used to heat (e.g., a room or building). We now tailor the definition of efficiency to the purpose. In general:

$$\eta = \frac{\text{desired output}}{\text{necessary input}}. \tag{8}$$

(Note: Whereas the fact that $Q_C \neq 0$ is an unavoidable nuisance for a heat engine, the fact that $q_C \neq 0$ means that refrigerators and heat pumps actually work!)

- For engines: desired output $= w$; necessary input $= Q_H$, hence

$$\eta_E = \frac{w}{Q_H} = \frac{Q_H - Q_C}{Q_H}. \tag{9}$$

- For refrigerators: desired output $= q_C$; necessary input $= W$, hence

$$\eta_R = \frac{q_C}{W} = \frac{q_C}{q_H - q_C}. \tag{10}$$

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- For heat pump: desired output $= q_H$; necessary input $= W$, hence

$$\eta_P = \frac{q_H}{W} = \frac{q_H}{q_H - q_C}. \tag{11}$$

We note: $\eta_E < 1$ always; η_R may be > 1 or < 0 (usually > 1 in practice); $\eta_P > 1$ always. Real engines are optimised to work in one direction, and are not reversible. However, for idealized reversible engines, only the signs of work and heat will change

$$\eta_P^{rev} = \frac{1}{\eta_E^{rev}}. \tag{12}$$

Most reversible processes require an infinite number of heat reservoirs at infinitesimally close temperatures to keep everything quasistatic. However, a special form of heat engine is one where we have only 2 reservoirs: a hot one at temperature T_H, and a cold one at $T_C < T_H$. Reversible engines with only 2 such reservoirs play a very important role in later developments. We may wonder, e.g., (1) What is the maximum η_E that can be achieved for a given T_H and T_C? (2) What are the characteristics of such maximally efficient engines? (3) Of what effect is the nature of the working substance in such maximally efficient engines? These questions were all answered by Sadi Carnot.

[Refs.: (1) Mandl 5.2, (2) Bowley and Sanches 2.3, (3) Zemansky 6.1-6.5.]

2.2 The second law of thermodynamics

There are 2 different (seemingly) statements, both generalized from everyday experience:

(1) **Kelvin-Planck statement**: It is impossible to construct an engine which, operating in a cycle, produces no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

(2) **Clausius statement**: It is impossible to construct a refrigerator which, operating in a cycle, produced no effect other than the transfer of heat from a cooler body to a hotter one.

Note: (a) The "operating in a cycle" is crucial to the truth of the statements; since this ensures that the engine itself is unchanged by the process. (b) Neither statement is demanded by the 1st law - energy would still be conserved - so this is something genuinely different.

The 2 statements look very different, but in fact each implies the other as we can now easily prove. Consider a hypothetical Kelvin-violating engine $\bar{K}$ and a hypothetical Clausius-violating refrigerator $\bar{C}$ as drawn in Figure 4:
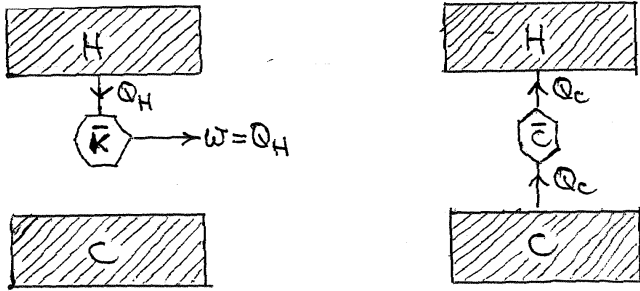
Figure 4

Now hook them up with regular (i.e., legal) engine E or refrigerator R in the 2 ways shown as Figures 5 and 6.
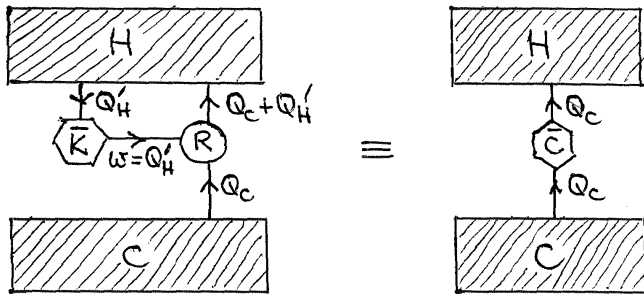
Figure 5

From Figure 5,

$$\bar{K} + R \equiv \bar{C}, \quad \text{i.e.} \quad \bar{K} \Rightarrow \bar{C}. \tag{13}$$

Figure 6

From Figure 6,

$$\bar{C} + E \equiv \bar{K}, \quad \text{i.e.} \quad \bar{C} \Rightarrow \bar{K}. \tag{14}$$

Thus, Eqs. (13-14) show $\bar{C} \Leftrightarrow \bar{K}$, or $\bar{C} \equiv \bar{K}$. But logically,

$$\bar{C} \Leftrightarrow \bar{K} \quad \rightarrow \quad C \Leftrightarrow K$$

or $C \equiv K$.

[Refs.: (1) Mandl 2.1; (2) Bowley and Sanchez 2.2; (3) Zemansky 6.6-6.8]

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2.3   Carnot cycles and Carnot engines

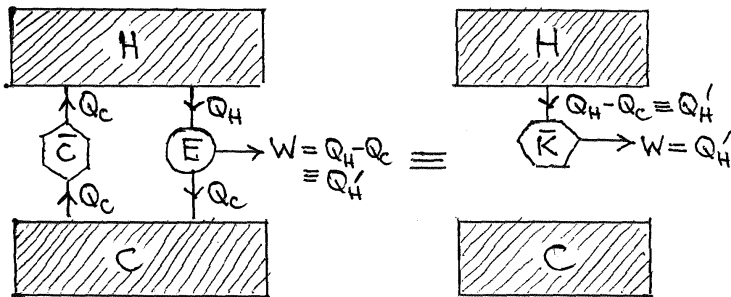Real-life engine running with (even idealized reversible) most standard cycles (e.g., the Otto cycle of Chap. 2.1) are complicated by the fact that they generally need an infinite series of heat reservoirs for the quasistatic processes (e.g., heating at constant volume in the Otto cycle).

By contrast, a **Carnot engine**, by definition is a reversible engine operating between only two heat reservoirs: all processes are either isothermal (i.e., heat transfer at constant temperature) or adiabatic (i.e., no heat transfer). Later, we will see a Carnot cycle for an ideal gas on a P-V diagram. But, first, there are some powerful statements we can make about Carnot engines without any knowledge of the substance.

Carnot's theorem: A reversible engine operating between any 2 given reservoirs (i.e., Carnot engine) is the most efficient that can operate between those reservoirs. (No engine operating between two given temperature is more efficient than Carnot engine.)
Proof: Operate a Carnot engine C and an arbitrary engine X (not necessarily reversible) between two reservoirs at T_H and T_C with $(T_H > T_C)$. By the first law, the work done by the engines

$$w^c = Q^c_H - Q^c_C, \quad \text{and} \quad w^x = Q^x_H - Q^x_C .$$

Let $Q^c_H/Q^x_H = N/M$, where N, M are two integers (can be satisfied to any desired accuracy.). Now operate C engine M cycles in reverse (as Carnot engines are reversible) and X engine N cycles forward. Consider (C+X) as an engine total, then

$$w^{\text{total}} = Nw^x - Mw^c .$$

But

$$
\begin{aligned}
Q^{\text{total}}_H &= NQ^x_H - MQ^c_H = 0 \\
Q^{\text{total}}_C &= NQ^x_C - MQ^c_C
\end{aligned}
$$

hence
$$w^{\text{total}} = Q^{\text{total}}_H - Q^{\text{total}}_C = -Q^{\text{total}}_C = -\left(NQ^x_C - MQ^c_C\right) .$$
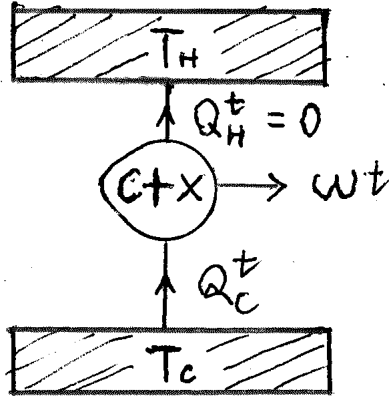
This is shown in Figure a.

Figure a

However, K's statement says we cannot convert heat entirely to work—here we have extracted no heat from T_H. Thus K's statement is broken unless $w^{\text{total}} \leq 0$, or $Q_C^{\text{total}} \geq 0$, i.e.,

$$NQ_C^x - MQ_C^c \geq 0, \quad \text{or} \quad \frac{N}{M} \geq \frac{Q_C^c}{Q_C^x} .$$

Therefore

$$\frac{Q_H^c}{Q_H^x} \geq \frac{Q_C^c}{Q_C^x}, \quad \text{or} \quad \frac{Q_C^c}{Q_H^c} \leq \frac{Q_C^x}{Q_H^x}$$

and

$$\eta_{CE} \left(\equiv 1 - \frac{Q_C^c}{Q_H^c} \right) \geq \eta_X \left(\equiv 1 - \frac{Q_C^x}{Q_H^x} \right) .$$

The equality holds if X engine is also reversible. We therefore have the following corollary.

Corollary: all reversible (i.e., Carnot) engines working between the same 2 heat reservoirs have identical efficiencies.

This is a remarkable (and deep) result. It means for reservoirs at temperatures T_H and T_C, $\eta_C = \eta_C(T_H, T_C)$ only, independent of working substance, e.g., the working substance could be an ideal gas, a real (non-ideal) gas, a paramagnet, etc. We can evaluate for any one, and others will be the same. So we do for an ideal gas.

Efficiency of an ideal gas Carnot cycle. Consider a cycle as shown in Figure 7.

- $a \rightarrow b$: isothermal compression in contact with a reservoir at temperature T_C; heat Q_C emitted

- $b \rightarrow c$: adiabatic compression (no reservoirs; no heat flow)

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- $c \to d$: isothermal expansion in contact with reservoir at temperature T_H; heat Q_H absorbed

- $d \to a$: adiabatic expansion
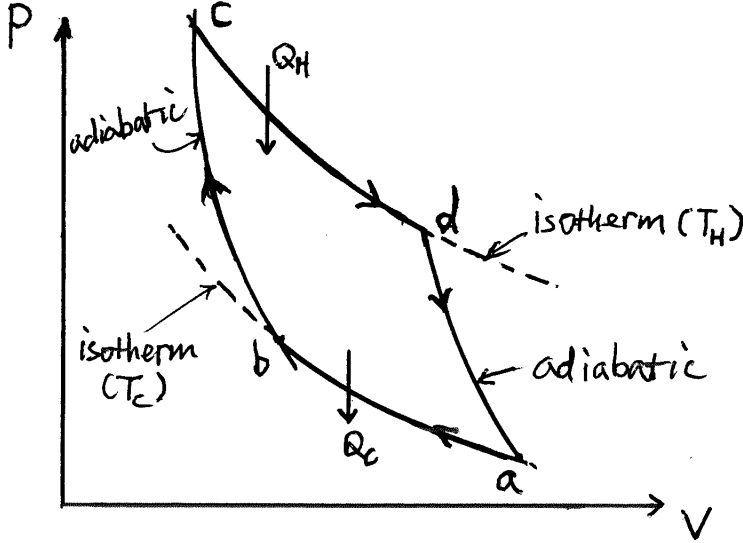
Figure 7

The first law $dQ = dE - dW = dE + PdV$ for reversible process. Also for ideal gas, $E = E(T)$ and $dE = 0$ along an isotherm. Hence $dQ = nRTdV/V$ along an isotherm. Therefore we have

$$Q_C = -\int_a^b nRT\frac{dV}{V} = nRT_C \ln \frac{V_a}{V_b} \tag{15}$$

along $a \to b$ and

$$Q_H = \int_c^d nRT\frac{dV}{V} = nRT_H \ln \frac{V_d}{V_c} \tag{16}$$

along $c \to d$. The efficiency

$$\eta_{CE} \equiv 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}\frac{\ln(V_a/V_b)}{\ln(V_d/V_c)}. \tag{17}$$

Also, from Eq. (4), $TV^{\gamma-1} = \text{const}$ for adiabatic process on ideal gas. Thus for the 2 adiabatic processes $b \to c$ and $d \to a$, we have

$$T_C V_b^{\gamma-1} = T_H V_c^{\gamma-1} \quad \text{and} \quad T_C V_a^{\gamma-1} = T_H V_d^{\gamma-1}.$$

Take a ratio, $(V_a/V_b)^{\gamma-1} = (V_d/V_c)^{\gamma-1}$, or

$$\frac{V_a}{V_b} = \frac{V_d}{V_c}. \tag{18}$$

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Put into Eq. (17), we have

$$\eta_{CE} = 1 - \frac{T_C}{T_H}. \tag{19}$$

From the corollary, although we derived Eq. (19) for an ideal gas Carnot engine, Eq. (19) now holds for **all** Carnot engines. Also from definition of efficiency and Eq. (19), we have an important general relation, **Carnot relation**,

$$\frac{Q_C}{T_C} = \frac{Q_H}{T_H} \tag{20}$$

for Carnot engine. In the followings, we discuss examples involving heat engines.

Example 1: A power station contains a heat engine operating between 2 reservoirs, one comprising steam at 100 °C and the other comprising water at 20 °C. What is the maximum amount of electrical energy which can be produced for every Joule of heat extracted from the steam?

Solution: The maximum w comes from a Carnot engine. We have $Q_H - Q_C = w$ and $Q_H/T_H = Q_C/T_C$. Hence

$$w = Q_H \left(1 - \frac{T_C}{T_H}\right).$$

Insert $Q_H = 1$ J, $T_C = 293$ K, $T_H = 373$ K, $w = 1 \times (1 - 293/373) = 0.21$ J.

Example 2: A refrigerator operating in a room at 20 °C has to extract heat at a rate of 500 W from the cabinet at 4 °C to compensate for the imperfect insulation. How much power must be supplied to the motor if its efficiency is 80% of the maximum possible?

Solution: The minimum $\dot{W}_{min}$ comes from a Carnot refrigerator (Note: all quantities now refer to energy or heat transfer per second). We have [see Eqs. (7) and (20)]

$$\dot{W}_{min} = \dot{q}_H - \dot{q}_C, \quad \text{and} \quad \frac{\dot{q}_H}{T_H} = \frac{\dot{q}_C}{T_C},$$

hence

$$\dot{W}_{min} = \dot{q}_C \left(\frac{T_H}{T_C} - 1\right).$$

Insert $\dot{q}_C = 500$ W, $T_C = 277$ K, $T_H = 293$ K, $\dot{W}_{min} = 500 \times 16/277 = 28.9$ W. But the real refrigerator works at 80% of maximum efficiency, we have $\dot{W}_{real} = \dot{W}_{min}/0.8 = 36.1$ W.

Do you know how a real refrigerator works? What is the common working substance used? Can efficiency of refrigerators as defined in Eq. (10) be greater than 1?

[Refs.: (1) Mandl 5.2; (2) Bowley and Sanchez 2.3; (3) Zemansky 7.1-7.4]

2.4 The thermodynamic temperature scale

Although we have evaluated the efficiency of an ideal gas Carnot engine, one could easily imagine it might be more difficult for other working substances. The whole point, however, is we don't have to! They are all the same (for given T_C, T_H). Indeed, we can now use this fact to define an **absolute** temperature scale, i.e., independent of the working substance. Since all Carnot engines are equivalent the efficiency can dependent on θ_C, θ_H. So we define

$$\frac{Q_C}{Q_H} \equiv f(\theta_C, \theta_H), \quad \text{so} \quad \eta_{CE} = 1 - f(\theta_C, \theta_H) \tag{21}$$

on some, as yet, unspecified temperature scale, where $f(\theta_C, \theta_H)$ is unknown. We will show, by considering Carnot engines working in series what the form of $f(\theta_C, \theta_H)$ must be.

Consider the Carnot engine as shown in Figure 8. Clearly, the 2 engines in series on the left are completely equivalent to the single engine on the right (both the compound engine and the single engine draw Q_H from the hot reservoir at θ_H, and reject Q_C to the cool reservoir at θ_C).

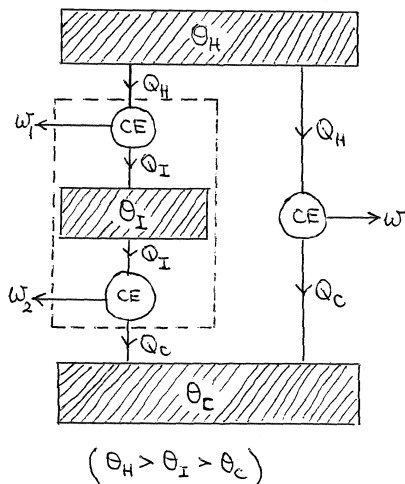$$\left(\theta_H > \theta_I > \theta_C \right)$$

Figure 8

For the compound engine

$$\frac{Q_I}{Q_H} = f(\theta_I, \theta_H); \quad w_1 = Q_H - Q_I = [1 - f(\theta_I, \theta_H)]Q_H$$

and

$$\frac{Q_C}{Q_I} = f(\theta_C, \theta_I); \quad w_2 = Q_I - Q_C = [1 - f(\theta_C, \theta_I)]Q_I = [1 - f(\theta_C, \theta_I)]f(\theta_I, \theta_H)Q_H$$

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Combine 2 equations

$$w_1 + w_2 = [1 - f(\theta_C, \theta_I)f(\theta_I, \theta_H)]Q_H.$$

Hence, the efficiency of the composite engine is

$$\eta_{CE} = \frac{w_1 + w_2}{Q_H} = 1 - f(\theta_C, \theta_I)f(\theta_I, \theta_H)$$

which must be identical to Eq. (21) since $w = w_1 + w_2$. Therefore

$$f(\theta_C, \theta_I)f(\theta_I, \theta_H) = f(\theta_C, \theta_H).$$

But note from Eq. (21), $f(\theta_1, \theta_2) = 1/f(\theta_2, \theta_1)$ by definition, hence

$$f(\theta_C, \theta_H) = \frac{f(\theta_C, \theta_I)}{f(\theta_H, \theta_I)}$$

and the RHS must hence be independent of θ_I since the LHS is. Hence, this can only be true if $f(\theta_1, \theta_2)$ factorizes into a product of functions of θ_1 and θ_2

$$f(\theta_C, \theta_H) = \frac{t(\theta_C)}{t(\theta_H)}$$

where $t(\theta)$ is any function of θ. We have

$$\eta_{CE} = 1 - \frac{t(\theta_C)}{t(\theta_H)} \tag{22}$$

and any function $t(\theta)$ defines a temperature scale (e.g., we could define a linear scale or logarithmic scale, etc.).

The Kelvin absolute scale chooses a linear scale $t(\theta) = \theta$,

$$\text{Kelvin scale:} \quad \eta_{CE} = 1 - \frac{\theta_C}{\theta_H}. \tag{23}$$

Hence θ on this absolute scale is equal, by comparison with Eq. (19), to KT, where T is the ideal gas (absolute) temperature and K is a constant. Clearly $K = 1$ if we define $\theta_{\text{triple}} = T_{\text{triple}} = 273.16$ K.

[Refs.: (1) Bowley and Sanchez 2.3-2.4; (2) Zemansky 7.5]

2.5 Entropy and maximum entropy theorem

The extremely important result which we now prove is the following theorem.

Clausius' Theorem: If a system is taken through a cycle, the algebraic sum of the heat added weighted by the inverse of the temperature at which it is added, can never be greater than zero,

$$\oint \frac{dQ}{T} \leq 0 \ . \tag{24}$$

The equality holds if the process is reversible, i.e.

$$\oint \frac{dQ^{\text{rev}}}{T} = 0 \ . \tag{25}$$

Proof: Consider a system A going through a cycle process. Divide the cycle into n infinitesimal steps, in each of which the temperature can be taken as constant $T_1, T_2, \cdots, T_n$, through contact with a series of heat reservoirs at those temperatures, as shown in Figure b.
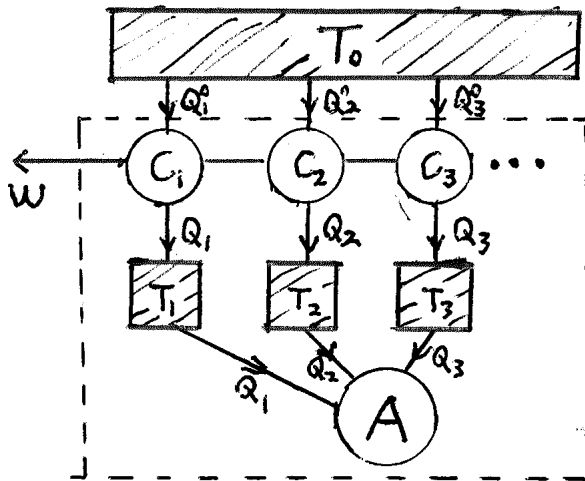
Figure b

Let Q_i be heat absorbed during the ith step, i.e., from reservoir at T_i. We shall prove $\sum_{i=1}^{n} Q_i/T_i \leq 0$ and let then let $n \to \infty$. Construct a set of n Carnot engines, $C_1, C_2, \cdots, C_2$, and let C_i (a) operates between T_i and T_0 (with $T_0 \geq$ all T_i), (b) absorbs heat Q_i^0 from T_0 and rejects heat Q_i to T_i and the total working done by these Carnot engines is $w = \sum_i w_i$. By Eq. (20) for a Carnot engine,

$$\frac{Q_i^0}{Q_i} = \frac{T_0}{T_i} \ .$$

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One complete cycle plus the operation of n Carnot engines (as indicated in the box of dashed lines in Figure b) means that heat $Q_0 = \sum_{i=1}^n Q_i^0$ is absorbed from the reservoir at T_0 and converted entirely into work, none is rejected since the ith engine rejects Q_i to T_i and this is used in the cycle. This violates the 2nd law unless $Q_0 \leq 0$. Since $Q_0 = \sum_{i=1}^n Q_i^0 = T_0 \sum_{i=1}^n Q_i/T_i$, then $\sum_{i=1}^n Q_i/T_i \leq 0$. If the cycle is reversible, reverse it. Then everything is as before except signs of Q_i change, $-\sum_{i=1}^n Q_i/T_i \leq 0$. Combining with above result $\sum_{i=1}^n Q_i/T_i = 0$ for a reversible transformation. QED

Note: This is easily seen to hold true for any Carnot cycle, since for these heat only enters or leaves at one of two temperatures,

$$\oint_{\text{Carnot}} \frac{dQ}{T} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$$

where we have used Eq. (20).

The importance of Eq. (25) is that we can use the fact that only that any quantity whose change vanishes over a cycle must be state variable (or function of state) to write

$$\frac{dQ^{\text{rev}}}{T} = dS \tag{26}$$

such that $\oint dS = 0$. In above equation, S is a new state variable, called entropy. And in general

$$\int_1^2 \frac{dQ^{\text{rev}}}{T} = \int_1^2 dS = S_2 - S_1, \quad \text{independent of path taken } 1 \to 2.$$

Also, from 1st law, $dE = dQ + dW = dQ^{\text{rev}} + dW^{\text{rev}} = dQ^{\text{irrev}} + dW^{\text{irrev}}$ and, by definition of reversibility, for a given change of the system (e.g., given dV for a gas), $dW^{\text{irrev}} > dW^{\text{rev}}$ (to overcome friction, etc.), we have $dQ^{\text{irrev}} < dQ^{\text{rev}}$, or

$$dQ \leq TdS \tag{27}$$

in general. The equality holds for reversible processes. Hence, for an isolated system (for which $dQ \equiv 0$)

$$dS \geq 0 \tag{28}$$

namely, **the entropy of an isolated system never decreases**. This is an alternative statement of 2nd law. Note: Any system plus its surroundings (deliberately called in thermodynamics by the somewhat grandiose title "the universe") forms an isolated system. Hence we have another statement: **the entropy of the universe never decreases**. (i.e., any decrease in the entropy of a system must be at least compensated by an increase in the entropy of its surroundings). Therefore, an isolated system will evolve in the direction of increasing entropy until it reaches a thermal equilibrium state at which entropy is maximum. In summary:

Maximum Entropy Theorem: An isolated system at equilibrium must be in the state of maximum entropy.

In the next section, we will exploit the fact that entropy is a state function (process independent) when we calculate entropy change for an irreversible process by considering a reversible process with the same initial and final states. This is the key idea in most questions on entropy calculation. Understand it and exploit it when you do your exercise questions.

[Refs.: (1) Bowley and Sanchez 2.5,2.7; (2) Zemansky 8.1-8.2, 8.8-8.9]

2.6   Some examples involving entropy changes

We will do various prototypical examples below, which demonstrate (among other thing) that, in general, (a) the entropy of any system increases when it is heated and (b) the entropy of gas increased when it expands at constant temperature. A common theme, and one we will explore in much more detail later is that an increase in entropy means an increase in disorder. We will see that the entropy of the universe always increases during spontaneous changes (typical example are the flow of heat from a hotter to a cooler body and the free expansion of a gas). In these examples the total entropy increases, although that of parts of the system may decrease.

Heat flow from hotter to colder bodies is irreversible, and reversible processes must involve heat flow between bodies at the same temperature or only infinitesimally different. The entropy change of the system

$$dS_{\text{system}} = \frac{dQ^{\text{rev}}}{T}$$

must be exactly balanced by that of the heat bath

$$dS_{\text{reservoir}} = -\frac{dQ^{\text{rev}}}{T}$$

so that $dS_{\text{universe}} = 0$.

For adiabatic process no heat flows $dQ = 0$. Thus, $dS = dQ^{\text{rev}}/T$ and $dS = 0$ for any reversible, adiabatic process. We define **isentropic**= adiabatic and reversible.

In summary,

- $\Delta S_{\text{universe}} > 0$ for spontaneous changes

- $\Delta S_{\text{universe}} = 0$ for reversible changes, during which

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

- Spontaneous changes are always irreversible

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- Isentropic change $\Leftrightarrow$ reversible, adiabatic changes $dS = 0$

Example 1: Two identical blocks of metal, one at 100 °C and the other at 0 °C are put in thermal contact, Derive the total entropy change when equilibrium is re-established. (You may assume that the heat capacity, C, of each block is constant over this temperature range, and neglect volume changes.)

Solutions: Clearly heat will flow from hotter to cooler body until they attain the same temperature. By conservation of energy this will be 50 °C. The heat transfer occurs so as to maximise that entropy. So, if dQ is transferred from the hot body at T_H to the cold one at T_C

$$dS_C > \frac{dQ}{T_C}, \quad dS_H > -\frac{dQ}{T_H}$$

and

$$dS_{\text{total}} = dS_H + dS_C > \left(\frac{1}{T_C} - \frac{1}{T_H}\right) dQ > 0.$$

Thus, the entropy decrease of the hot block is more than compensated by the entropy increase of the cold block; and the spontaneous heat flow is associated with a net (overall) entropy increase. Namely, the blocks exchange heat to maximise their combined total entropy. In order to calculate ΔS_{total} we use the following technique. Since we can't calculate ΔS for irreversible process we must find a reversible process that takes us from the same initial to the same final end point. Then, since ΔS is **independent** of the actual process, this will suffice. For heating or cooling of the blocks this would involve a quasistatic process of bringing the blocks into contact with an infinite sequence of heat baths at infinitesimally increasing or decreasing temperature, so that the temperature difference between the heat bath and the block is always negligible and the entropy change is zero.

$$\Delta S = \int_1^2 \frac{dQ^{\text{rev}}}{T},$$

where $dQ^{\text{rev}} = CdT$. But if $C =$const,

$$\Delta S = C \int_1^2 \frac{dT}{T} = C \ln \frac{T_2}{T_1}.$$

Thus, in our case of 2 identical blocks

$$\Delta S_{\text{total}} = \Delta S_C + \Delta S_H = C \ln \frac{T_f}{T_c} + C \ln \frac{T_f}{T_H} = C \ln \frac{T_f^2}{T_C T_H}.$$

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Inserting the values $T_H = 373$ K, $T_C = 273$ K, $T_f = 323$ K,

$$\Delta S_{\text{total}} = C \ln \frac{323^2}{373 \times 273} = 0.024C$$

Note: $\Delta S_{\text{total}} > 0$, as required; and that the unit of entropy = unit of heat capacity = J K^{-1}.

Example 2: Two identical blocks of metal, one at 100 °C and the other at 0 °C are brought into thermal contact. What is the maximum amount of work w that can be extracted from the hot block in the absence of other heat sinks, expressed as a fraction of the total heat loss Q_H of the hot block?

Solution: Clearly, we can't just extract heat from the hot block an turn it all into work, since $\Delta S_H < 0$. We need to add at least enough heat Q_C to the cold block so that $\Delta S_C > 0$ just balances ΔS_H, i.e. we can make $\Delta S_C + \Delta S_H = 0$. Note the work extracted can always be used to do things which lead to zero entropy change (e.g., raising a weight). Once the 2 blocks come to the same final temperature T_f no further work can be extracted. From Example 1,

$$\Delta S_{\text{total}} = \Delta S_H + \Delta S_C = C \ln \left(\frac{T_f^2}{T_H T_C} \right) \geq 0.$$

The maximum work possible corresponds to the lowest possible T_f (see equation for work w below). The lowest possible T_f is that for which $\Delta S_{\text{total}} = 0$, viz.

$$T_f = \sqrt{T_H T_C} \approx 319.1\text{K} = 46.1\,°\text{C}$$

(If T_f were any lower $\Delta S_{\text{total}} < 0$ and this isn't allowed by the 2nd law). Now

$$Q_H = C(T_H - T_f), \quad Q_C = C(T_f - T_C).$$

Hence, by energy conservation, the work extracted

$$w = Q_H - Q_C = C(T_H + T_C - 2T_f) = C(T_H + T_C - 2\sqrt{T_H T_C}).$$

The efficiency

$$
\begin{aligned}
\eta &= \frac{w}{Q_H} = \frac{T_H + T_C - 2\sqrt{T_H T_C}}{T_H - \sqrt{T_H T_C}} \\
&= \frac{(\sqrt{T_H} - \sqrt{T_C})^2}{\sqrt{T_H}(\sqrt{T_H} - \sqrt{T_C})} \\
&= = 1 - \sqrt{\frac{T_C}{T_H}}.
\end{aligned}
$$

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Inserting the values $T_H = 373$ K, $T_C = 273$ K

$$w = \left(1 - \sqrt{\frac{T_H}{T_C}}\right) Q_H = 0.144 Q_H.$$

i.e., only 14.4% of the heat lost by the initially hot block was available to do work. Note, too, that this maximum efficiency is obtained from a reversible process. [Compare with the corresponding efficiency $\eta = 1 - T_C/T_H = 26.8\%$ for a Carnot engine working between two (infinite) reservoirs at fixed temperatures $T_H = 373$ K, $T_C = 273$ K.]

Example 3: [Heat engines revisited] From the law of non-decrease of entropy, show that the maximum efficiency of a heat engine operating between 2 (infinite) reservoirs at fixed temperatures T_H and T_C occurs when the engine is reversible.
Solution: This is now the converse of our previous discussion. The change in entropy of the total engine

$$\Delta S_{\text{total}} = \Delta S_C + \Delta S_H = \frac{Q_C}{T_C} - \frac{Q_H}{T_H} \geq 0.$$

Hence

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H},$$

with equality for $\Delta S = 0$, i.e. for a reversible process. The efficiency

$$\eta = \frac{w}{Q_H} = 1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H}$$

maximum for equality (i.e., for reversible engine).

Example 4: A quantity of n moles of an ideal gas at temperature T_0 are initially confined to half the volume of an insulated container by an insulated partition. The partition is removed without doing any work. What is the ensuing change of entropy?
Solution: The process is adiabatic, $dQ = 0$. However, we recall, this does not implied $dS = 0$ since this is not a reversible process. Once again, we need to find, however, a reversible process to go from same initial to same final point. As we saw earlier (and see, e.g. Q1(b) on Example Sheet 1), this could be an isothermal expansion done reversibly. In such an expansion

$$Q^{\text{rev}} = -W^{\text{rev}} = \int_1^2 P dV = \int_{V_1}^{V_2} \frac{nRT_0}{V} dV = nRT_0 \ln \frac{V_2}{V_1}$$

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Put $V_2 = 2V_1$ as in this problem

$$\Delta S = \frac{Q^{\text{rev}}}{T_0} = nR\ln 2.$$

Note: The logic here is quite subtle - do make absolutely sure you understand the difference between the actual process (with $Q = W = 0$) and the reversible process for which we could calculate ΔS (with $Q^{\text{rev}} = -W^{\text{rev}} \neq 0$).

Example 5a: A box of gas is joined by an identical box of the same gas. What is the change in total entropy?
Solution: This is a reversible process (as nothing changes when removing the partition and putting it back). Total entropy change is therefore zero, $\Delta S_{\text{total}} = 0$, where $S_{\text{total}} = S_1 + S_2 = 2S_1$. The following example is an irreversible process (How?) and the total entropy must increase.

Example 5: An insulated container is originally divided in half by a partition, and each half is occupied by n moles of a **different** ideal gas at temperature T_0. What is the total change in entropy when the partition is removed without doing any work?
Solution: Since both gases are ideal, they don't interact, each species is oblivious of the other, and ΔS for each is exactly as in Ex. 4 above. Thus

$$\Delta S_{\text{total}} = 2nR\ln 2.$$

Note: the total mixing - which we know will happen eventually - is precisely the change that now maximises the entropy, i.e., clear hint that entropy means disorder. It is obvious that the process is an irreversible one as the situation is quite different from the initial state when putting back the partition after mixing.

[Refs.: (1) Manl 4.3, (2) Bowley and Sanchez 2.8; (3) Zemansky 8.11-8.13]

2.7 The fundamental thermodynamic relation

We have the first law for infinitesimal change

$$dE = đQ + đW$$

or, specifically to reversible change

$$dE = đQ^{\text{rev}} + đW^{\text{rev}}.$$

We have already found expressions for $đW^{\text{rev}}$ for a variety of thermodynamic systems in Sec. 1.6. Now, we also have one for $đQ^{\text{rev}} = TdS$. Therefore

$$dE = TdS - PdV. \qquad (29)$$

This is the fundamental thermodynamic relation (for a fluid). Note:

- Eq. (29) involves only state variables, so it must be for all changes, not just reversible ones.

- For other systems the term $-PdV = dW^{\text{rev}}$ for a fluid is just required by the corresponding expression for that system (e.g., σdA for a surface film, $-\mathbf{m} \cdot d\mathbf{B}$ for a paramagnet, etc., as in Sec. 1.6).

- Eq. (29) will be used over and over again in this course; it is one of the most important equation we will meet (and you must remember it!)

Math note: In general, if Z is a function of two variables (X, Y), we write by convention,

$$Z = Z(X, Y).$$

The small changes in X an Y will result in the change in Z, written as

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY, \tag{30}$$

where $\left(\frac{\partial Z}{\partial X}\right)_Y$ is partial derivative of $Z(X, Y)$ with respect to variable X while keeping the other variable Y as parameter. Comparing Eq. (30) and Eq. (29) of the fundamental relation, we derive that

- internal energy is a a function of (S, V), $E = E(S, V)$; and

- we have two general, useful relations

$$T = \left(\frac{\partial E}{\partial S}\right)_V, \quad -P = \left(\frac{\partial E}{\partial V}\right)_P,$$

  i.e., if the function $E(S, V)$ is known (from statistical mechanics, for example), then temperature and pressure can be defined/calculated by simply taking partial derivatives as above.

- Further relation (Maxwell relation) can be obtained by taking 2nd order derivative,

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$$

  namely,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

  which will be discussed more fully and exploited later.

[Refs.: (1) Mandl 4.1; (2) Bowley and Sanchez 2.5; (3) Zemansky 8.14.]

2.8 Thermodynamic Potentials

So far we have seen two state functions, internal energy E and entropy S. And we know 2nd law can be used to predict the state of a thermodynamic system. For example, if a system in isolation can have several possible states with different values of entropy, we know it must in the state with maximum entropy.

We revisit the fundamental thermodynamic relations of Eq. (29), also known as 1st and 2nd laws of thermodynamics for a hydrodynamic system:

$$dE = TdS - PdV.$$

In this form it suggest that the *natural* variables in which to express E are S and V, i.e., $E = E(S, V)$, as disussed earlier. Hence

$$T = \left(\frac{\partial E}{\partial S}\right)_V ; \quad P = -\left(\frac{\partial E}{\partial V}\right)_S . \tag{31}$$

It is also easy to re-express the fundamental relation as

$$dS = \frac{1}{T}dE + \frac{P}{T}dV \tag{32}$$

where S is a state function, $S = S(E, V)$, and E is a variable. So we have the relations

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V , \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E . \tag{33}$$

From Eq. (29), we conclude that $E = $ const. for process at constant volume and constant entropy. Because these are not exactly the most common experimental condition (S is not directly measurable), it is useful to introduce other state functions, called **thermodynamic potentials**, which are constant when others of variables (such as V, P, T) are held fixed. Note also that a system with constant E, V is usually an isolated system. However, more often than not, we are dealing with a system not in isolation but in thermal contact with its environment. This is another reason that it is more convenient to use other state functions (thermodynamic potentials) to predict its behavior.

(a) Helmholtz Free Energy F:

$$F \equiv E - TS . \tag{34}$$

F is useful for systems at constant temperature.

Theorem: In an isothermal transformation, the change of free energy of a system is less or equal to the work done on the system.

Proof: Let a system undergo an arbitrary isothermal transformation from state A to state B. We have

$$\int_A^B \frac{dQ}{T} \leq S_B - S_A \ .$$

Since T is constant, $\Delta Q \leq T\Delta S$. Using the 1st law, $\Delta E = \Delta Q + \Delta W$, or

$$\Delta W = \Delta E - \Delta Q \geq \Delta E - T\Delta S, \quad \text{or} \quad \Delta W \geq \Delta F$$

The equality holds if the transformation is reversible.

If $\Delta W = 0$, then: for mechanically isolated system at a constant temperature, free energy never increases.

Corollary: In a mechanically isolated system at a constant temperature, the state of equation is the state of minimum free energy, i.e., system evolves until F reaches a minimum.

In an infinitesimal reversible transformation, we have

$$dF = -PdV - SdT \ . \tag{35}$$

Since $F = F(V, T)$ is a state function,

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad S = -\left(\frac{\partial F}{\partial T}\right)_V. \tag{36}$$

Hence, if the function $F = F(V,T)$ is known, P and S can be determined. F is useful for a system under a transformation of constant T and V because $F = F(V,T)$ is constant. F plays an important role in statistical mechanics as we will see later. Taking 2nd order derivatives in Eqs. (36) , since

$$\left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial F}{\partial V}\right)_T = \frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} = \left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial F}{\partial T}\right)_V$$

we have, from Eq. (36)

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{37}$$

which is one of the so called **Maxwell relations**.

Example: Consider a gas in a cylinder at constant T, with a piston dividing the cylinder in two. See Figure. If the piston is released, what is its equilibrium position?
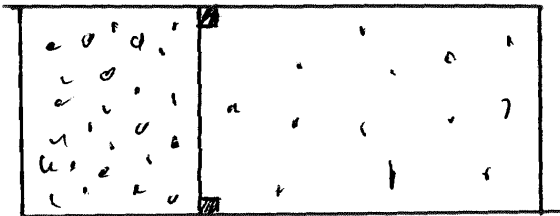

Figure 9

By corollary above, it must be a minimum of F. Consider two parts as our whole system. The total Helmholtz free energy

$$F = F_1(T, V_1) + F_2(T, V_2).$$

Consider a small change from equilibrium (but no work done on the whole), i.e., the piston moves a little, then $\delta F = 0$, since the free energy at the equilibrium is a minimum. We have

$$0 = \delta F = \left(\frac{\partial F_1}{\partial V_1}\right)_T \delta V_1 + \left(\frac{\partial F_2}{\partial V_2}\right)_T \delta V_2 .$$

But $V_1 + V_2 = $ constant, $\delta V_1 = -\delta V_2$,

$$0 = \left[\left(\frac{\partial F}{\partial V_1}\right)_T - \left(\frac{\partial F}{\partial V_2}\right)_T\right] \delta V_1.$$

As δV_1 is an arbitrary change, we must have

$$\left(\frac{\partial F_1}{\partial V_1}\right)_T = \left(\frac{\partial F_2}{\partial V_2}\right)_T , \quad \text{or} \quad P_1 = P_2 ,$$

according to Eq. (36). This is intuitively obvious.

(b) Gibbs free energy:

$$G \equiv F + PV = E - TS + PV . \tag{38}$$

Theorem: In a system kept at constant temperature and pressure, G never increases.
Corollary: For a system kept at constant temperature and pressure, the equilibrium state is the state of minimum Gibbs potential.
Proof: For $T = $ constant, we already have $\Delta W \leq -\Delta F$. If the pressure is kept constant, then $\Delta W = P\Delta V$. Then

$$P\Delta V + \Delta F \leq 0, \quad \text{or} \quad \Delta G \leq 0,$$

i.e., the system can slowly evolve until G is at the minimum.

In an infinitesimal reversible transformation

$$dG = -SdT + VdP, \tag{39}$$

hence G is a function of T, P, $G = G(T, P)$ and

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V = \left(\frac{\partial G}{\partial P}\right)_T . \tag{40}$$

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And we have the second Maxwell relation by taking second order derivative

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \tag{41}$$

Note: The Gibbs free energy G is constant when T and P are fixed - just the conditions for phase transitions (e.g., water boiling or freezing); also relevant to chemical equilibrium (reactions in contact with a heat bath at constant pressure).

(c) Enthalpy H:

$$H \equiv E + PV \tag{42}$$

and correspondingly

$$dH = TdS + VdP \tag{43}$$

hence $H = H(S, P)$ and

$$T = \left(\frac{\partial H}{\partial S}\right)_P, \quad V = \left(\frac{\partial H}{\partial P}\right)_S. \tag{44}$$

And the corresponding Maxwell relation

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \tag{45}$$

Recall Q3 of Example Sheet 1, heat absorbed at constant pressure is equal to the change in enthalpy, $\Delta Q = \Delta H$ at P = constant. At phase transition, this heat is referred to as **laten heat**, a concept you learned in your first year unit "Gases, Liquids and Solids".

In summary:

- $E = E(S, V) \to dE = TdS - PdV$ or $S = S(E, V) \to dS = \frac{1}{T}dE + \frac{P}{T}dV$

- $F = F(T, V) \to dF = -SdT - PdV$

- $G = G(T, P) \to dG = -SdT + VdP$

- $H = H(S, P) \to dH = TdS + VdP$

Question: What is the corresponding Maxwell relation from the fundamental thermodynamic relation $dE = TdS - PdV$?

[Refs.: (1) Mandl 4.4-4.5; (2) Bowley and Sanchez 2.6; (3) Zemansky 10.1-10.3.]

2.9 Open systems and phase equilibrium conditions

Up till now we have mostly deal with **closed systems** (where no matter enters or leaves, i.e., $N = $ const.). Let's generalise to **open systems** (where matter can be exchanged with the surroundings). This situation can also be useful in describing **mixtures of substances** or mixtures of phases of the same substances, as we will see.

We need to extend the fundamental thermodynamic relations of Eq. (29), for a hydrostatic system,

$$dE = TdS - PdV$$

to include the energy change due to adding or subtracting particles, namely

$$dE = TdS - PdV + \mu dN \tag{46}$$

where the new intensive variable μ is referred to as **chemical potential**, the energy required to add a particle to the system. The internal energy is now a function of three variables, $E = E(S, V, N)$ and we have a new thermodynamic relation, in addition to the original two,

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}. \tag{47}$$

By rearranging Eq. (46),

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN, \tag{48}$$

i.e., $S = S(E, V, N)$, and

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}. \tag{49}$$

Similarly, we have the following relations for the other thermodynamic potentials of an open system as

$$dF = -SdT - PdV + \mu dN \tag{50}$$
$$dG = -SdT + VdP + \mu dN \tag{51}$$
$$dH = TdS + VdP + \mu dN, \tag{52}$$

and the new partial derivatives are given by, respectively

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial H}{\partial N}\right)_{S,P}. \tag{53}$$

Theorem: $G = \mu N$. This simple theorem can be easily proved by using the fact that G is extensive, i.e., $G = g(T, P) \cdot N$ together with Eq. (53) for the definition of μ.

We now discuss the conditions for the coexistence of two phases of a given substance. Consider the entropy for each of the phases as a function of its internal energy, volume and particle number, namely $S_1 = S_1(E_1, V_1, N_1)$ for phase 1 and $S_2 = S_2(E_2, V_2, N_2)$ for phase 2. The total entropy of the whole system is the sum of the two

$$S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2),$$

if we ignore the small boundary contributions (involving small numbers of particles of both phases at the phase boundary). Each of the phase is an open system. But the whole system (the two phases together) is an isolated system; its total entropy is maximum at equilibrium. This theorem can be used to show that **all intensive thermodynamic variables of the two phases at equilibrium must be equal respectively**, namely

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2. \tag{54}$$

The proof can be made by considering a small change in the system as whole and using the maximum entropy condition $\delta S = 0$. For details, see Q2 of Example Sheet 7.

So far we have discussed all fundamental physics of thermodynamics systems, including all physical quantities (state variables, state fucntions and thermodynamics potentials) and their relations. In the next few sections we will apply these principles to more specific situations for deeper and better understanding, including some mathematical exercises relating to Maxwell relations.

[Refs.: (1) Mandl 5.3; (2) Bowley and Sánchez 2.5-2.6, E.3; (3) Zemansky and Dittman 10.6, 10.8.]

2.10   The approach to equilibrium

We have seen that for isolated systems $\Delta S \geq 0$. Completely generally if a change can take place that increase the entropy, it will, e.g., 2 gases allowed to mix will do so fully, thereby maximising S. For non-isolated systems, $\Delta S_{\text{universe}} \geq 0$; but it would still be nice to refer only to the system, if possible. There is a way to do this. If T_0, P_0 refer to the temperature and pressure of the surroundings, we define the **availability** as

$$A \equiv E - T_0 S + P_0 V. \tag{55}$$

We find, **for any spontaneous change**

$$\Delta A < 0. \tag{56}$$

The proof is easy. We imagine a system in thermal contact with its surroundings at T_0 and at the pressure P_0 of the surroundings. Imagine a spontaneous change during which heat Q is absorbed by the system, which changed volume by ΔV. $W = -P_0 \Delta V$ is done on the system. The 1st law $Q = \Delta E + P_0 \Delta V$ and

$$\Delta S_{\text{universe}} = \Delta S - \frac{Q}{T_0} = \frac{1}{T_0}(T_0 \Delta S - \Delta E - P_0 \Delta V)$$

and $\Delta S_{\text{universe}} \geq 0$ means
$$\Delta(E - T_0 S + P_0 V) \leq 0.$$

QED.

Now, let S represent any possible variation in a quantity, not necessarily leading to an equilibrium state. Various scenarios:

(a) Processes at constant T, P, $\Delta A = \Delta G$, hence

$$(\Delta G)_{T,P} \leq 0 \quad \text{for all spontaneous changes} \tag{57}$$

$G(T, P)$ is minimum at equilibrium as we have seen earlier.

(b) Processes at constant T, V, $\Delta A = \Delta F$. and

$$(\Delta F)_{T,V} \leq 0 \tag{58}$$

for all spontaneous changes. Hence $F(T, V)$ is minimum at equilibrium as we have seen earlier.

(c) Isolated systems (i.e., const. V, E): $\Delta A = -T_0 \Delta S$

$$(\Delta S)_{E,V} \geq 0 \tag{59}$$

for all spontaneous change, i.e., $S(E, V)$ is maximized at equilibrium (maximum entropy theorem).

[Refs.: Mandl 4.2; (2) Bowley and Sanchez 2.9; Zemansky 15.8.]

2.11   Available work

Let's now consider the maximum amount of work (available work) which can be extracted from a system initially out of equilibrium with its surroundings at temperature T_0 and pressure P_0, as schematically shown in the following diagram.
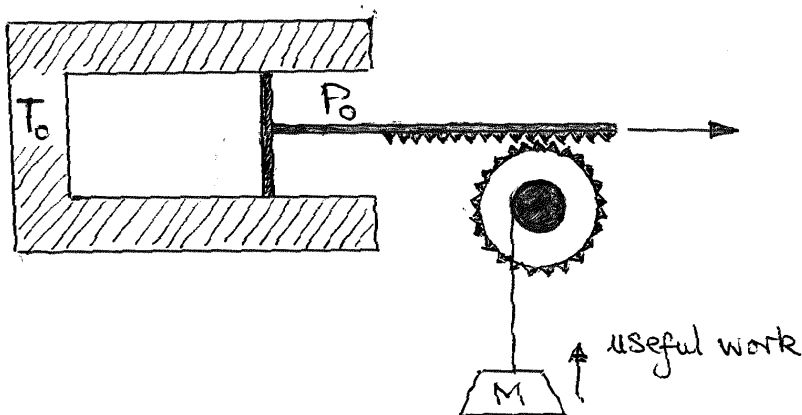
Figure 10

Firstly, if it expands it must do work to push back atmosphere, so $P_0 \Delta V$ is not available. Secondly, if its entropy decreases (as in cooling) it must give heat Q_{out} to the surroundings, where $\Delta S + Q_{\text{out}}/T_0 \geq 0$ or $Q_{\text{out}} \geq -T_0 \Delta S$. All above means that during a change not all of the internal energy change (decrease) ΔE is available to do useful work. We have from 1st law

$$\Delta E = Q_{\text{in}} + W = -Q_{\text{out}} - w,$$

or

$$w = -\Delta E - Q_{\text{out}} \leq -\Delta E + T_0 \Delta S$$

where w is the total work done by the system. Let $w = w_{\text{useful}} + P_0 \Delta V$, so

$$w_{\text{useful}} + P_0 \Delta V \leq -\Delta E + T_0 \Delta S \quad \text{or} \quad w_{\text{useful}} \leq -\Delta(E - T_0 S + P_0 V) = -\Delta A$$

where $A = \textbf{Availability}$ from Eq. (55). Hence

$$w_{\text{useful}} \leq -\Delta A, \tag{60}$$

where equality holds only for reversible process, the maximum useful (available) work. This also explains why A introduced earlier is actually called availability.

Note:

(a) T_0, P_0 are that of the *surroundings, not* those of the system (although, of course, they end up the same)

(b) For all spontaneous changes, as shown in Eq. (56), $\Delta A \leq 0$ and hence $w_{\text{useful}} \leq |\Delta A|$ for all spontaneous changes

(c) For system starting and ending at T_0, P_0: $w_{\text{useful}} \leq -\Delta G$

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(d) For system at constant volume and starting and ending at T_0: $w_{\text{useful}} \leq -\Delta F$

Example: What is the maximum useful work that can be obtained by cooling 1 mole of an ideal gas at constant volume from a temperature T to the temperature T_0 of the surroundings?

Solution: $\Delta V = 0$,

$$w_{\text{max}} = -\Delta E + T_0 \Delta S$$

(Note $\Delta S < 0$ for cooling.) For an ideal gas

$$\Delta E = C_V \Delta T = C_V (T_0 - T) < 0$$

as $C_V = \text{const}$. Also, ΔS will be the same as for a reversible process, $dS = đQ/T = C_V dT/T$ (Ex. 1 in Sec. 2.6),

$$\Delta S = C_V \int_T^{T_0} \frac{dT}{T} = -C_V \ln \frac{T}{T_0} < 0.$$

The maximum work

$$w_{\text{max}} = C_V (T - T_0) - C_V T_0 \ln \frac{T}{T_0}.$$

The rest of the energy is discarded to the surroundings to ensure no overall decrease in entropy. Note: it is not difficult to prove that the above expression for w_{max} is positive for any $T > T_0$. You may care to prove it for yourself.

2.12 Clausius-Clapeyron equation

We now turn our attention to situations where two phases of a given substance co-exist (e.g., ice and water at 0^0C; for which if no heat is exchanged with the surroundings, the mixture will persist indefinitely). In general, different phases have different internal energies, different entropies, different densities, etc. In Section 2.9 (and Q1 of Example Sheet 6) we have proved that temperatures and pressures of the two phases at equilibrium are equal respectively. We wish to find the equation of coexistence curve of the two phases.

We saw above in Section 2.8 that at constant T, P the Gibbs free energy is minimized. Define g_1 and g_2 to be the "specific Gibbs free energy" (i.e., per unit mass) for each phase. If the phases have masses m_1 and m_2,

$$G = m_1 g_1 + m_2 g_2.$$

At equilibrium with T_0, P_0 fixed $\delta G = 0$, we have

$$g_1 \delta m_1 + g_2 \delta m_2 = (g_1 - g_2) \delta m_1 = 0,$$

where in the last equation, we have used the fact that total matter is conserved, $\delta m_1 = -\delta m_2$. Therefore, the condition for 2 phases to co-exist at given T_0, P_0,

$$g_1 = g_2. \tag{61}$$

In fact this is quite general; it also holds for isolated systems. For most choices of T_0, P_0 only one phase will exist (e.g., all the water will freeze at all the ice will melt). A typical coexistence curve on a P-T plot is shown in Figure 11.
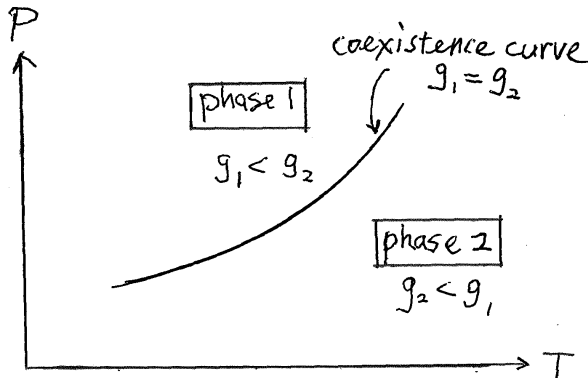

Figure 11

An obvious equation is to ask for the equation of the co-existence line. This is provided by the so-called **Clausius-Clapeyron equation**: Consider 2 infinitesimally close points a and b on the co-existence curve $g_1 = g_2$, as shown in Figure 12.
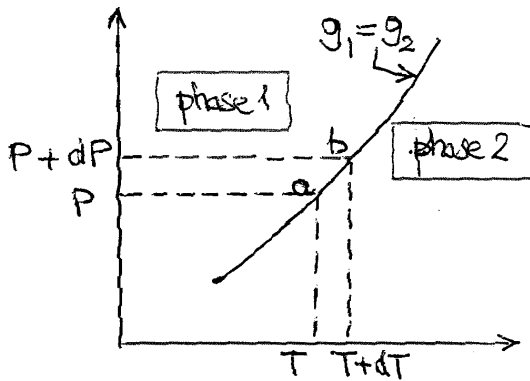

Figure 12

$$g_1^{(a)} = g_2^{(a)}, \quad g_1^{(b)} = g_2^{(b)}.$$

So, if dg is the difference in g_1 between points a and b, it is the same for both phases

$$dg_1 = dg_2.$$

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But, from Eq. (39), $dg = -sdT + vdP$ with $s \equiv S/m, v \equiv V/m$,

$$\begin{aligned} dg_1 &= -s_1 dT + v_1 dP \\ dg_2 &= -s_2 dT + v_2 dP \end{aligned}$$

or $(s_2 - s_1)dT = (v_2 - v_1)dP$. Hence

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{L}{T\Delta v} \tag{62}$$

where we have used $\Delta S = Q/T$ for an isothermal process, and $L = Q$ is simply the **latent heat** (per unit mass) of the substance at given P, T. Eq. (62) the Clausius-Clapeyron equation and it gives the slope the co-existence curve at any point (P, T). We show in Figure 13 the phase diagram for water.
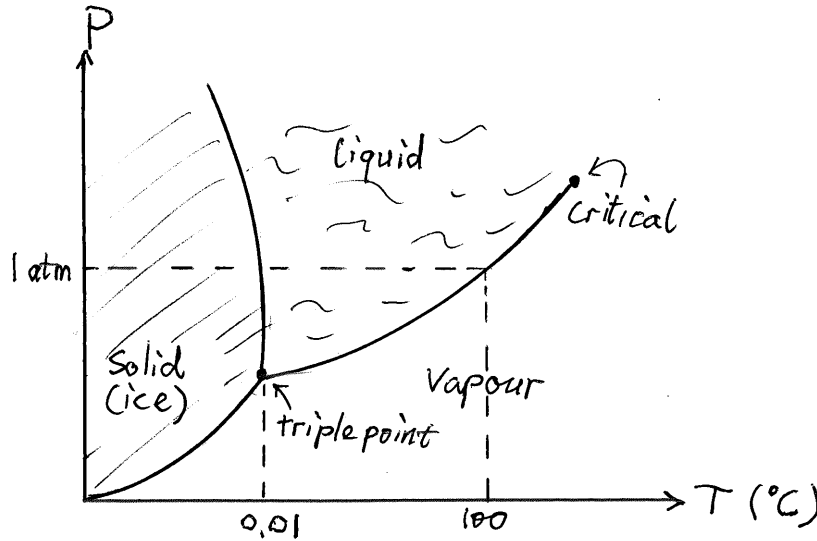

Figure 13

Note: Water is strange in that the solid-liquid coexistence curve has negative slope. This is because ice is less dense than water (putting ice under pressure causes it to melt). Most liquids behave oppositely.

Example: At what temperature does water boil at the top of Mt. Everest? (input data: pressure at top of Everest is 0.36 atm; the density of water vapour at 100 °C is 0.598 kg m^{-3} and the latent heat is 2.257×10^3 J g^{-1}).
Solution: The change is volume of 1 g is well approximated by volume of vapour phase alone (since it is about 10^3 less dense than liquid)

$$\Delta v = v_g - v_l \approx v_g = \frac{1}{\rho_g}.$$

Hence

$$\frac{dP}{dT} = \frac{L}{T\Delta v} \approx \frac{L\rho_g}{T}\bigg|_0 = \frac{2.257 \times 10^6 \text{ J kg}^{-1} \times 0.598 \text{ kg m}^{-3}}{373 \text{ K}} = 3.62 \times 10^3 \text{ Pa K}^{-1}.$$

Hence, by linear extrapolation $\Delta P/\Delta T = 3.62 \times 10^3$ Pa K^{-1}. Use given data $\Delta P = -0.64$ atm and 1 atm $= 1.013 \times 10^5$ Pa,

$$\Delta T \approx -\frac{0.64 \times 1.013 \times 10^5}{3.62 \times 10^3} \text{ K} \approx -17.9 \text{ K},$$

i.e., boiling point at top of Everest is about 355 K or 82 °C. Notice that the difference between the two temperatures 373 and 355 K is small, hence the linear extrapolation made is valid.

[Refs.: (1) Mandl 8.1-8.4; (2) Bowley and Sánchez 11.1,11.4,11.5; (3)Zemansky 11.3-11.5.]

2.13 Maxwell's relations: A review

As should be clear by now, the ability to manipulate partial derivatives is a vital tool in thermodynamics. Since it is so important let's now have a review.

A basic rules are

(1) identify the independent variables, e.g., u and v

(2) If $w = w(u, v)$ is a function of u and v, the partial derivative of w with respect to u with v held fixed is written as $(\partial w/\partial u)_v$

(3) Hence
$$\left(\frac{\partial v}{\partial u}\right)_v = 0 = \left(\frac{\partial u}{\partial v}\right)_u, \quad \left(\frac{\partial u}{\partial u}\right)_v = 1 = \left(\frac{\partial v}{\partial v}\right)_u,$$
etc.

(4) The order doesn't matter if we take more than one partial derivative, i.e.
$$\frac{\partial}{\partial v}\bigg)_u \left(\frac{\partial w}{\partial u}\right)_v = \frac{\partial}{\partial u}\bigg)_v \left(\frac{\partial w}{\partial v}\right)_u, \tag{63}$$
where
$$\frac{\partial}{\partial v}\bigg)_u \left(\frac{\partial w}{\partial u}\right)_v \equiv \left(\frac{\partial}{\partial v}\left(\frac{\partial w}{\partial u}\right)_v\right)_u.$$

(5) If both u and v change infinitesimally, the corresponding change in w is

$$dw = \left(\frac{\partial w}{\partial u}\right)_v du + \left(\frac{\partial w}{\partial v}\right)_u dv. \tag{64}$$

(6) We can just as well take, e.g., v and w to be the independent variables, and from $w = w(u, v)$ solve for $u = u(v, w)$. Now

$$du = \left(\frac{\partial u}{\partial v}\right)_w dv + \left(\frac{\partial u}{\partial w}\right)_v dw. \tag{65}$$

(7) If we compare Eqs. (64-65) with $v = $ Const, i.e. $dv = 0$, we have

$$dw = \left(\frac{\partial w}{\partial u}\right)_v du, \quad du = \left(\frac{\partial u}{\partial w}\right)_v dw$$

hence the **reciprocal theorem**, obviously

$$\left(\frac{\partial w}{\partial u}\right)_v = \frac{1}{\left(\frac{\partial u}{\partial w}\right)_v}. \tag{66}$$

(8) From Eq. (64), if $w = $ const.,

$$\left(\frac{\partial w}{\partial u}\right)_v du = -\left(\frac{\partial w}{\partial v}\right)_u dv.$$

Take $\partial/\partial v)_w$ of both sides

$$\left(\frac{\partial w}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_w = -\left(\frac{\partial w}{\partial v}\right)_u,$$

or, after multiplying both sides by $\left(\frac{\partial u}{\partial w}\right)_v$ and using the reciprocal theorem of Eq. (66)

$$\left(\frac{\partial w}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_w \left(\frac{\partial v}{\partial w}\right)_u = -1 \tag{67}$$

which is not at all obvious. In particular, the factor (-1) is counter-intuitive! Write Eq. (67) using Eq. (66)

$$\left(\frac{\partial u}{\partial v}\right)_w = -\frac{\left(\frac{\partial w}{\partial v}\right)_u}{\left(\frac{\partial w}{\partial u}\right)_v} = -\frac{\left(\frac{\partial u}{\partial w}\right)_v}{\left(\frac{\partial v}{\partial w}\right)_u}. \tag{68}$$

Note: Eqs. (66-68) are out main results. In other contexts we often neglect to specify what is being held constant (i.e., write $\partial f \partial x$ instead of $(\partial f \partial x)_y$ when it is obvious that $f = f(x, y)$. In thermodynamics, where we are often changing variables from one set to another this can be **fatal**: **Always** specify what's held constant. (The only exception is that mostly we deal with a fixed amount of substance, $N = $ no. of molecules = const. and we don't always bother to write, e.g. $(\partial E/\partial S)_{V,N}$ rather than the sloppier $(\partial E/\partial S)_V$ if it is absolutely obvious from context that N is always constant.)

Now return to physics. The fundamental thermodynamic relations of Eq. (29)

$$dE = TdS - PdV$$

suggested $E = E(S, V)$ so that

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV.$$

Comparison shows

$$T = \left(\frac{\partial E}{\partial S}\right)_V, \quad -P = \left(\frac{\partial E}{\partial V}\right)_S$$

as we have seen in Eq. (31). By taking a further derivative as Eq. (63)

$$\left.\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left.\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S,$$

we have the first of 4 Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V. \tag{69}$$

The other three Maxwell relations are derived by other three thermodynamic relations in dF, dG and dH as discussed in Sec. 2.8, namely

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \tag{70}$$

and

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \tag{71}$$

and finally

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \tag{72}$$

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Eqs. (70) and (71) are of particular useful in getting rid of S in favour of experimentally measurable P, V, T.

Note: The forms of the 4 Maxwell relations: the dependent variables are always one of (T, S) and one of (P, V). The independent variables are then the other two [i.e., never get terms like $\partial T/\partial S$ or $\partial P/\partial V$ or $\partial/\partial S)_T$ or $\partial/\partial V)_P$]; we get a minus sign of both S and P occur as variable on the same side of the equation; not otherwise.

[Refs.: (1) Mandl 4.4-4.5; (2) Bowley and Sánchez 2.6, E.1-E.2; (3) Zemanksy 40.5.]

2.14   Heat capacities and calculating entropy

Typically, for a thermodynamic system, we can determine its equation of state and heat capacities by experimental measurements. How do we determine other physical quantities such as entropy from these measurements? We shall demonstrate the Maxwell relations discussed earlier are very useful for this purpose.

By definition, a heat capacity $C \equiv đQ^{\text{rev}}/dT$, depends on the process, since Q^{rev} is not a state variable. We use C for heat capacity and c for specific heat capacity (i.e., per mole or unit mass).

Since $đQ^{\text{rev}} = TdS$ by second law, we have

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P \tag{73}$$

for heat capacity at constant pressure and

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \tag{74}$$

for heat capacity at constant volume.

If we take $S = S(T, V)$,

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV.$$

By Eqs. (74) and Maxwell relation Eq. (70),

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV. \tag{75}$$

Alternatively, use $S = S(T, P)$

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP.$$

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By Eqs. (73) and Maxwell relation Eq. (71),

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP. \tag{76}$$

Integration of equation (75) or (76) will give us entropy.

Example Entropy of an elastic string. Given heat capacity C_l at constant length l and equation of state (a relation between string tension Γ, temperature T and length l) $\Gamma = \Gamma(T, l)$, determine its entropy by using Maxwell relations.
Solution The work done on the string by stretching is

$$đW = \Gamma dl,$$

and the fundamental thermodynamic relation for a string is

$$dE = TdS + \Gamma dl.$$

We need the Maxwell relations involving Helmholtz free energy. We write the free energy $dF = d(E - TS) = -SdT + \Gamma dl$, comparing with the general differential form

$$dF = \left(\frac{\partial F}{\partial T}\right)_l dT + \left(\frac{\partial F}{\partial l}\right)_T dl.$$

we have

$$-S = \left(\frac{\partial F}{\partial T}\right)_l, \quad \Gamma = \left(\frac{\partial F}{\partial l}\right)_T.$$

Take the second order derivative and using the fact that

$$\frac{\partial^2 F}{\partial l \partial T} = \frac{\partial^2 F}{\partial T \partial l}$$

we have the corresponding Maxwell relation,

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial \Gamma}{\partial T}\right)_l.$$

The heat capacity at constant length is, using $đQ = TdS$,

$$C_l = \left(\frac{đQ}{dT}\right)_l = T\left(\frac{\partial S}{\partial T}\right)_l$$

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where we take the entropy $S(l, T)$ as a function of l and T. The differential form of entropy is, in general

$$dS = \left(\frac{\partial S}{\partial T}\right)_l dT + \left(\frac{\partial S}{\partial l}\right)_T dl.$$

Therefore, the differential entropy is given by, using the Maxwell relation and the equation for heat capacity,

$$dS = \frac{C_l}{T} dT - \left(\frac{\partial \Gamma}{\partial T}\right)_l dl.$$

If $\Gamma(l, T)$ and C_l are known, the above equation can be used to determine the entropy. For details, see Q2 of Example Sheet 6.