Chapter 1

Review of Thermodynamics

Here we will recap the key points of thermodynamics which you have come across in year 1. These we will be useful later to link to the ideas of Statistical Physics, and will enable us to extract experimentally useful quantities.

1.1   Introduction and definitions

Thermodynamics is concerned with the properties of a system containing a large number of components (typically 10^{23} atoms or molecules) that has been left free of external influences. Instead of trying to describe the microscopic details of the system, it focuses on macroscopic properties called *thermodynamic variables*. These thermodynamics variables are measured extremely slowly (much slower than the time for the system to equilibrate), and so can only describe static states, and are averaged over large spatial regions (containing a large number of atoms), so can only describe homogeneous states. These variables can be classified into two types:

- Extensive variables – proportional to system size, and non-local quantities, e.g. Volume V, Internal Energy U, Entropy S, Particle number N, . . .

- Intensive variables – independent of system size, and local quantities e.g. pressure p, Temperature, T, chemical potential μ, . . .

These variables can be put into conjugate pairs containing a generalised force and a response to that force, so that their product has the dimensions of energy. Some examples are given in the table below.

Generalised Force (intensive)	Response (extensive)
Pressure, p	Volume, V
Temperature, T	Entropy, S
Tension, F	Length, L
Surface tension, γ	Area, A
Electric field, $\mathbf{E}$	Dipole moment $\mathbf{p}$
Chemical potential, μ	Particle number N

A *function of state* is a quantity that does not depend on the history of the system, and has a unique value for each state of the system. Directly observable quantities such as volume are clearly functions of state, however other quantities such as entropy, and internal energy are also functions of state.

We will later discuss systems enclosed in a container. The properties of the wall are crucial to determining the state of the system. Walls that do not allow the transmission of heat are called

adiathermal or adiabatic, whilst those that conduct heat are called diathermal. Hence an adiabatic change occurs when no heat is transferred to or from the system.

A system left free of external forces, and allowed to settle down will achieve an *equilibrium state*. These are time-independent states that do not depend on any previously applied forces. There are several different types of equilibrium; stable, neutral, and metastable. The metastable state is the most common of these.

Changing the state of a system in thermodynamics is done extremely carefully, and takes place unlimitedly slowly. This is called a *quasi-static* or *reversible* processes, and the system is in equilibrium at each point during the process. We shall discuss irreversible changes later, but these changes are done in such a way (e.g. too quickly) so that the system is not in equilibrium at each point along the route. Hence it is impossible to label the intermediate states using thermodynamic variables.

1.2   Laws of thermodynamics

***Zeroth law** – If two systems are each in separate thermal equilibrium with a third, they are in thermal equilibrium with each other*

This enables us to define an empirical temperature. For example, if we have three bodies labelled A, B and C, then if A and C are in equilibrium there is some function, F, of the pressures and volumes that is zero.

$$F(p_a, V_a, p_c, V_c) \ = \ 0 \tag{1.1}$$
$$\Rightarrow p_c \ = \ f(p_a, V_a, V_c). \tag{1.2}$$

Similarly if B and C are in equilibrium then we have

$$p_c = f(p_b, V_b, V_c). \tag{1.3}$$

Hence

$$f(p_b, V_b, V_c) = f(p_a, V_a, V_c) \tag{1.4}$$

This expression should not contain information about the third system C, hence

$$f(p_b, V_b) = f(p_a, V_a) = \theta \tag{1.5}$$

where θ is an empirical temperature. This relationship is a thermal equation of state. For an ideal gas we know that $pV = R\theta_g$, where θ_g is the gas temperature scale.

***First law** – Energy is conserved if heat is taken into account*

The internal energy U of a system can be changed by supplying some heat Q to the system, or by doing work W on the system. If we want to move the system between two states of different internal energy, then there are many different ways to achieve this depending on how we divide up the source of the energy. However, even though W and Q depend on the method of energy supply, their sum $W + Q$ is independent of it. We can write this relation for very small changes in differential form as

$$dU = \ dQ + \ dW \tag{1.6}$$

where we have used a cross symbol $đ$ to denote that they are not exact differentials, and hence depend on the method the energy is supplied.

***Second law** – There are many equivalent statements of the second law:

- Carnot's theorem: *Of all heat engines working between two given temperatures, none can be more efficient than a reversible heat engine.*

- Clausius: *No process is possible whose sole result is the transfer of heat from a colder to a hotter body.*

- Kelvin: *No process is possible whose sole result is the complete conversion of heat into work.*

- Ostwald: *It is impossible to construct a perpetual machine of the second kind.*

Not all processes that are allowed by the first law can happen. The second law of thermodynamics allows us to define a direction of temperature, as it states that heat cannot go from cold to hot. You will have studied head engines in some depth last year. A schematic abstraction of a heat engine is shown in Fig. 1.1.
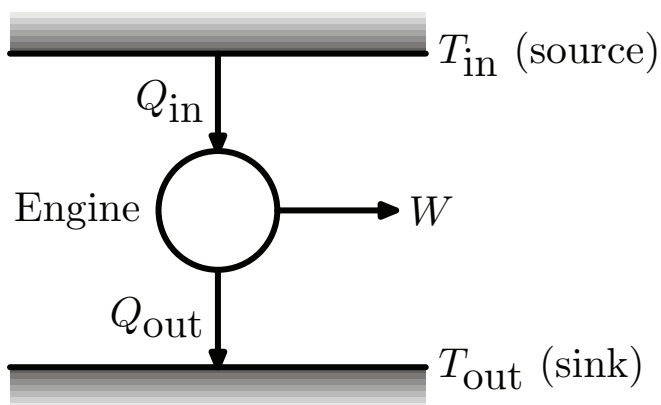

Figure 1.1: An illustration of a heat engine, working between temperatures T_{in} and T_{out}, and producing work output W.

The efficiency of a heat engine is given by

$$\eta = \frac{W}{Q_{\text{in}}} \tag{1.7}$$

where $W = Q_{\text{in}} - Q_{\text{out}}$ by the first law. It can be shown that the most efficient engines, i.e. those that are reversible, have an efficiency of

$$\eta = 1 - \frac{T_{\text{out}}}{T_{\text{in}}} \tag{1.8}$$

Suppose we have a heat engine of efficiency η. We know that

$$1 - \frac{T_{\text{out}}}{T_{\text{in}}} \geq \eta = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} \tag{1.9}$$

where the equality holds for a reversible engine. We can rearrange this equation to read

$$\frac{Q_{\text{in}}}{T_{\text{in}}} \leq \frac{Q_{\text{out}}}{T_{\text{out}}} \tag{1.10}$$

Hence if we define heat input to be positive, and heat output to be negative

$$\sum_{\text{cycle}} \frac{Q_i}{T_i} \leq 0 \tag{1.11}$$

where we have an equality for the reversible case, and an inequality for the remaining (irreversible) cases. For the case of an infinitesimal cycle we have

$$\oint \frac{\dd Q}{T} \leq 0, \tag{1.12}$$

which is Clausius' theorem.

This definition motivates the definition of the entropy change ΔS between two states as

$$\Delta S = \int_A^B \frac{\dd Q}{T}. \tag{1.13}$$

Now let us consider the entropy change in an arbitrary (potentially irreversible) process where the system goes from a state A to B. We form a cycle by taking the system back along a reversible path, hence

$$\int_A^B \frac{\dd Q_{\text{irrev}}}{T} + \int_B^A \frac{\dd Q_{\text{rev}}}{T} \leq 0 \tag{1.14}$$

but since

$$S_B - S_A = \int_A^B \frac{\dd Q_{\text{rev}}}{T} \tag{1.15}$$

we have

$$\int_A^B \frac{\dd Q_{\text{irrev}}}{T} \leq S_B - S_A \tag{1.16}$$

or since this is true for arbitrary A and B we have

$$dS \geq \frac{\dd Q}{T} \tag{1.17}$$

where dS is the entropy change in going from A to B and $\dd Q$ is the heat supplied. If we supply no heat to the system, then $\dd Q = 0$, and we find the statement of the second law:

For an isolated system, the entropy S cannot decrease.

1.3   Differential relations

Using the first law of thermodynamics we can write a differential relation for the internal energy $U(V, N, S, \ldots)$ as follows

$$\begin{aligned} dU &= \quad \dd Q + \dd W \tag{1.18} \\ \Rightarrow dU &= \quad TdS - pdV + \mu dN + \ldots \tag{1.19} \end{aligned}$$

We could have in principle included various other relations e.g. for an electric field in the system. This differential form could also be written as

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial N} dN + \ldots \tag{1.20}$$

and so we can obtain various relations between the internal energy of the system and the intensive variables as follows:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \tag{1.21}$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \tag{1.22}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{1.23}$$

$$\tag{1.24}$$

Alternatively if we rearrange for dS we find that

$$dS = \frac{(dU + pdV - \mu dN)}{T} \tag{1.25}$$

which gives rise in the same way to the following relations

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \tag{1.26}$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \tag{1.27}$$

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{1.28}$$

These relations will prove useful later in our study of statistical physics.

1.4 Heat capacities

The heat capacity is defined as the amount of heat that must be given to the system in order to raise its temperature by one degree. The specific heat capacity is the heat capacity per unit mass or per mole of substance. Various heat capacities can be defined depending on the way in which it is measured. In general

$$C_{\Theta} = \left(\frac{\dj Q}{dT}\right)_{\Theta} = T\left(\frac{\partial S}{\partial T}\right)_{\Theta} \tag{1.29}$$

where Θ denotes any quantities that are held constant when the heat capacity is measured. Typically as temperature rises thermal motions increase, and there is greater microscopic disorder so the entropy increases. Hence heat capacities are associated with a gradual increase in disorder as temperature rises. As we will see later the heat capacity can rise anomalously, indicating that there has been a microscopic change in order. As a result of this measurement of heat capacity is the focus of many experimental papers. An illustration of the heat capacity of He^3 and of a liquid crystal are show in Figure 1.2. The spikes in the heat capacity indicate the phase transitions.

As a further example, consider a fluid which has work $\dj W = -pdV$ done on it, and is supplied with heat $\dj Q$. The heat capacity at constant volume is given by

$$C_V = \left(\frac{\dj Q}{dT}\right)_V \tag{1.30}$$

but since $\dj Q = dU + pdV$ then
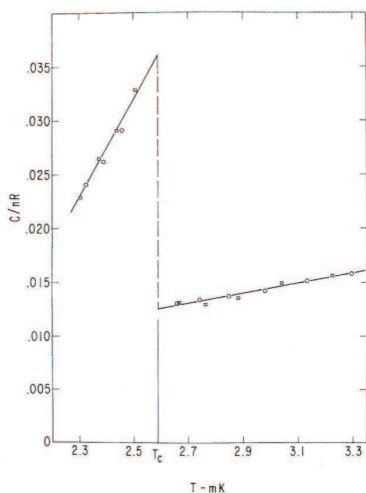
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.31}$$

FIG. 3. Total molar heat capacity as a function of temperature of liquid He^3 at a pressure of 484.5 lb/in.^{2} as deduced from the measurements and a $T*$–T relation discussed in the text.
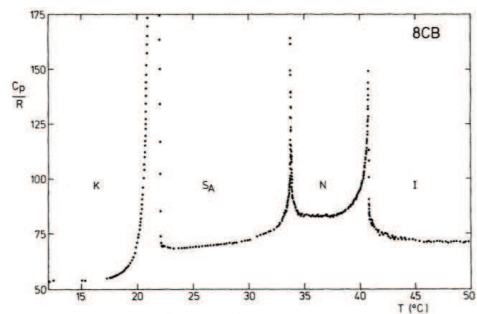
a)

FIG. 2. Reduced heat capacity per mole (R is the gas constant) for octylcyanobiphenyl (8CB) as a function of temperature in the crystalline (K), the smectic-A (S_A), the nematic (N), and the isotropic (I) phases.

b)

Figure 1.2: a) Shows the measured heat capacity of Helium-3 from Webb et al. (Phys. Rev. Lett. 30, 210, 1973). The discontinuity indicates a phase transition. b) Shows the measured heat capacity of a liquid crystal from Thoen et al. (Phys Rev. A 26 2886 1982). There are many phase transitions in this system, one at each of the heat capacity spikes.

whereas the heat capacity at constant pressure is

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p. \tag{1.32}$$

The second term here arises as the fluid now has to push against the atmosphere as its volume changes.

Ideal gas

To make these ideas a bit clearer, we will now look at a specific example of a monatomic ideal gas. Here the internal energy is purely a function of temperature, $U = U(T)$, because there are no internal forces between the molecules. From kinetic theory

$$U = \frac{3nRT}{2} \tag{1.33}$$

where n is the number of moles of gas, and R is the ideal gas constant. Hence a molar heat capacity of $C_V = \frac{3R}{2}$. You will have met this result last year. It can also be derived from the principle of equipartition of energy which states that each quadratic degree of freedom has $\frac{1}{2}RT$ energy associated with it *per mole*, or $\frac{1}{2}k_BT$ per degree of freedom. Here we have 3 directions (hence 3 velocities) in which the particle can move. For molecules we must also include rotational and vibrational degrees of freedom which increase the heat capacity. We will derive the principle of equipartition of energy later in the course, and look again at the heat capacity of a gas.
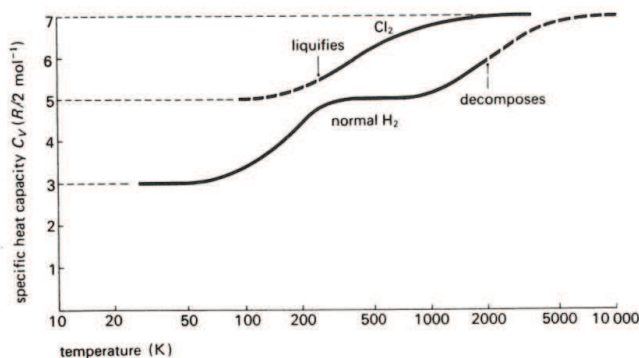
Figure 1.3: The variation of the heat capacity of H_2 and Cl_2 with temperature (from *Gases, Liquids and solids* by D. Tabor)

Using the equation of state for one mole of an ideal gas $pV = RT$ we have that $\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$, hence

$$C_p = \frac{3R}{2} + R = \frac{5R}{2} \tag{1.34}$$

The specific heat capacities are crucial in adiabatic expansions. Here $\bar{d}Q = 0$, hence

$$0 = dU + pdV = C_V dT + pdV. \tag{1.35}$$

By differentiating the ideal gas law, we know that $pdV + Vdp = RdT$. It we combine this with the above expression we obtain

$$-\frac{C_V}{R}Vdp = p\left(\frac{R + C_V}{R}\right)dV \tag{1.36}$$

$$\Rightarrow 0 = \frac{dp}{p} + \gamma\frac{dV}{V} \Rightarrow \text{const} = pV^\gamma \tag{1.37}$$

where $\gamma = \frac{C_p}{C_V}$ is the ratio of heat capacities.

We can calculate the heat capacity of a crystalline solid using classical physics by assuming it is made of N atoms, so has a total of $3N$ degrees of freedom. Each of these is modelled as an oscillator with $k_B T$ of energy, so the heat capacity (both constant volume and constant pressure) is $3R$ per mole. This is appropriate for some monatomic solids and is called the *Du long and Petit Law*. It does break down as the temperature drops. This is illustrated in Fig. 1.3 and is something we will return to later in the course.

1.5 Equilibrium of closed systems

We will now show how the second law can be applied to a closed system. In this case the as nothing is supplied externally we must have that $dS \geq 0$. It is useful to rearrange the differential for the internal energy as follows

$$dS = \frac{(dU + pdV - \mu dN)}{T} \tag{1.38}$$

We will divide our system into two parts labelled 1 and 2. Hence

$$
\begin{align}
U &= U_1 + U_2 \tag{1.39}\\
V &= V_1 + V_2 \tag{1.40}\\
N &= N_1 + N_2 \tag{1.41}
\end{align}
$$

or alternatively if we write these as differentials we have

$$
\begin{align}
dU_1 &= -dU_2 \tag{1.42}\\
dV_1 &= -dV_2 \tag{1.43}\\
dN_1 &= -dN_2 \tag{1.44}
\end{align}
$$

if we insert this into the expression for the differential of the entropy $S = S_1 + S_2$ we find that

$$
dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1 \geq 0 \tag{1.45}
$$

From this expression we can deduce the criteria for equilibrium under various circumstances.

- Fixed V and N – In this case there is a fixed diathermal wall between the two regions, and $\left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 \geq 0$. Hence in thermal equilibrium $T_1 = T_2$, and if $T_2 > T_1$ then $dU_1 > 0$, so energy flows into the colder region 1.

- Fixed N and T – Here $(p_1 - p_2)dV_1 \geq 0$, so mechanical equilibrium occurs when $p_1 = p_2$. If $p_1 > p_2$ then $dV_1 > 0$ so the high pressure region expands.

- Fixed V and T – Here only the particles may cross from one side of the container to the other. $(\mu_1 - \mu_2)dN_1 \leq 0$, hence $\mu_1 = \mu_2$ in equilibrium, and if $\mu_1 > \mu_2$ then $dN_1 < 0$ i.e. particles flow out of region 1.

1.6   Thermodynamic potentials

If instead of a closed system we have a system in contact with a reservoir (i.e. an open system) e.g. a thermal reservoir, or a particle reservoir, then its equilibrium state can be found by using a thermodynamic potential. To see this we apply the first and second laws of thermodynamics as follows. The first law tells us that

$$
dU = \dbar Q + \dbar W \tag{1.46}
$$

If the system is in contact with a heat reservoir, then $\dbar Q$ is the heat supplied from that reservoir. The entropy change of the reservoir is

$$
dS_{\mathrm{res}} = -\frac{\dbar Q}{T} \tag{1.47}
$$

The total entropy change is thus

$$
dS_{\mathrm{tot}} = dS - \frac{\dbar Q}{T} \geq 0 \tag{1.48}
$$

where dS is the entropy change of the system, and the inequality follows from the second law of thermodynamics. Hence we know that $dS \geq \frac{\dbar Q}{T}$. Substituting this into the first law gives

$$
\begin{align}
dU &= \dbar Q + \dbar W \leq T dS - p dV \tag{1.49}\\
\Rightarrow \underbrace{dU - T dS + p dV}_{dA} &\leq 0 \tag{1.50}
\end{align}
$$

where we have defined dA as the change in the quantity A called the availability. Since any change must be less than zero, A must always decrease, and hence be a minimum in equilibrium. Since the reservoir fix p and T we know that

$$A = U - TS + pV. \tag{1.51}$$

If only T is fixed then we remove the term pV in the availability and hence can use the Helmholtz free energy defined below. The other potentials described below depend on whether T, p, μ or some combination of them are fixed by a reservoir. The use of the thermodynamic potential can be though of as a change of coordinates. The internal energy U can be regarded as a function of V, S and N (extensive variables). However, if we wish to change one of these variables for an intensive variable, then we carry out a Legendre transformation. The most common potentials are as follows

- Enthalpy $H = U + pV$ is a function $H(p, S, N)$ so is useful when the system is at constant pressure, rather than constant volume (i.e. in contact with a volume reservoir).

$$dH = TdS + Vdp + \mu dN$$

- Helmholtz free energy $F = U - TS$ is a function $F(T, V, N)$ so is useful when the system is in contact with a heat reservoir at fixed temperature T.

$$dF = -SdT - pdV + \mu dN$$

- Gibbs free energy $G = U - TS + pV$ is a function $G(T, p, N)$ so is useful when the system is in contact with a volume and heat reservoir.

$$dG = -SdT + Vdp + \mu dN$$

- Grand canonical potential $\Phi = U - TS - N\mu$ is a function $\Phi(T, V, \mu)$ so is used when the system is in contact with a reservoir heat and particles.

$$d\Phi = -SdT - PdV - Nd\mu$$

Maxwell relations are derived from the fact that the second partial derivative commutes under most circumstances in physics. Hence if we consider the thermodynamic potentials above (assuming $dN = 0$) then

$$dU \quad = \quad TdS - pdV = \frac{\partial U}{\partial S}dS + \frac{\partial U}{\partial V}dV \tag{1.52}$$

$$\frac{\partial^2 U}{\partial S \partial V} \quad = \quad \frac{\partial^2 U}{\partial V \partial S} \tag{1.53}$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S \quad = \quad -\left(\frac{\partial p}{\partial S}\right)_V \tag{1.54}$$

A similar procedure can be applied to the other thermodynamic potentials.

These relations are useful for example in calculating an expression for the entropy an ideal case in terms of p and T can be calculated from

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT = -\left(\frac{\partial V}{\partial T}\right)_p dp + \left(\frac{\partial S}{\partial T}\right)_p dT \tag{1.55}$$

where we have used the Maxwell relation arising from the Gibbs free energy G. If we substitute in the constitutive equation and the heat capacity we find

$$dS = -\frac{R}{p}dp + \frac{C_p}{T}dT \Rightarrow S = S_0 - R\ln p + C_p \ln T \tag{1.56}$$