Notes on Thermodynamics

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Very short set of notes, intended to be concise. Based on the second year Imperial course taught at the time by Vijay Tymms.

Contents

1 Thermodynamic Systems

1.1 The state of a system and its transformations

In order to explain the thermodynamic concept of the state of a system, we first discuss a few examples.

A system composed of a chemically defined homogeneous fluid. We can measure: temperature T, volume V and pressure P. Although the geometry of the system is characterized by both its volume and shape, most thermodynamical properties are independent of shape except for extreme cases where the surface is much larger than the volume.

The temperature, pressure and volume are not independent quantities. In general, they are related by a relationship of the form:

$$f(P, V, T) = 0, \tag{1.1}$$

which is called the *equation of state*. Its form depends on the properties of the substance. Any one of the three quantities can be expressed as a function of the other two by solving equation (1.1) with respect to the given variable. Hence, the state of the system is **completely** determined by any two of the three quantities P, V and T.

We may use a (P, V) plot to represent states of systems, where each point would represent a unique state. The same would be true for any two of the three variables.

A system composed of a chemically defined homogeneous solid. We may introduce, alongside volume and temperature, the pressures acting in different directions. However, often the assumption is made that the solid is subjected to an isotropic pressure so that only one value for pressure can be used.

A system composed of a homogeneous mixture of several chemical compounds. The concentrations of the different chemical compounds should be included as well.

Nonhomogeneous systems. The system must be divided into a number of homogeneous parts. The state of the system is then defined by giving the mass, chemical composition, state of aggregation, pressure, volume and temperature of each homogeneous part.

A system containing moving parts. One must specify the velocities of the various parts of the system.

It is evident from what we have said that the knowledge of the thermodynamical state alone is by no means sufficient for the determination of the dynamical state. Studying the thermodynamical state of a homogeneous fluid of given volume at a given temperature, we observe that there is an infinite number of states of molecular motion that correspond to it. With increasing time, the system exists successively in all these dynamical states that correspond to the given thermodynamical state. From this point of view we may say that a thermodynamical state is the ensemble of all the dynamical states through which, as a result of the molecular motion, the system is rapidly passing.

Thermodynamical states which have the property of not varying with time given that the external conditions are constant are called **states of equilibrium**.

Often we consider *transformations* of a system from an initial state to a final state through a *continuous* succession of intermediate states. This transformation can be represented by a curve on a (P, V) diagram. A transformation is said to be **reversible** if the successive states of the transformation differ by infinitesimals from *equilibrium states.* A reversible transformation can be realized in practice by changing the external conditions so slowly that the system has time to adjust itself gradually to the altered conditions.

During a transformation, the system can perform positive or negative external *work*; that is, the system can do work on its surroundings or the surrounding can do work on the system. Consider a body enclosed in a cylinder having a movable piston of area S at one end (Figure 1.1). If P is the pressure of the body, then PS is the force exerted by the body on the piston.

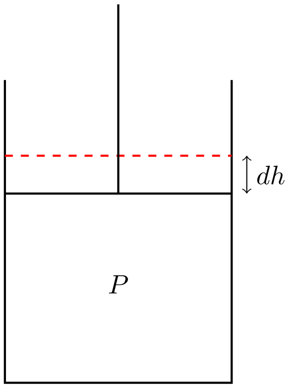

Figure 1.1: Expansion of gas using a piston.

The work is given, for an infinitesimal displacement dh, as

$$dW = PSdh, \tag{1.2}$$

since the displacement is parallel to the force. But Sdh is equal to the increase, dV, in the volume of the system. Thus, we may write

$$dW = PdV. \tag{1.3}$$

For a finite transformation, the work done by the system is obtained by integration (1.3):

$$W = \int_A^B PdV, \tag{1.4}$$

where the integral is taken over the entire transformation.

Aside: (1.3) is generally valid no matter the shape of the container. Let $d\sigma$ be the surface element of the container, and let dn be the displacement of this element in the direction normal to the surface. The total amount of work performed during the infinitesimal transformation is obtained by integrating over the surface element σ:

$$dW = P\int_\Omega d\sigma dn.$$

The change in the volume, dV of the container is given by the surface integral,

$$dV = \int_\Omega d\sigma dn.$$

Comparing these two equation, we obtain (1.3).

The work done during a transformation has a geometrical representation on a (V, P) diagram. The transformation will be represented by a curve connecting A and B the shape of which depends on the transformation. The work done is given by the integral

$$W = \int_{V_A}^{V_B} PdV, \tag{1.5}$$

where V_A and V_B are the volumes corresponding to the states A and B. This integral can be represented geometrically by the area under the curve in Figure 1.2.

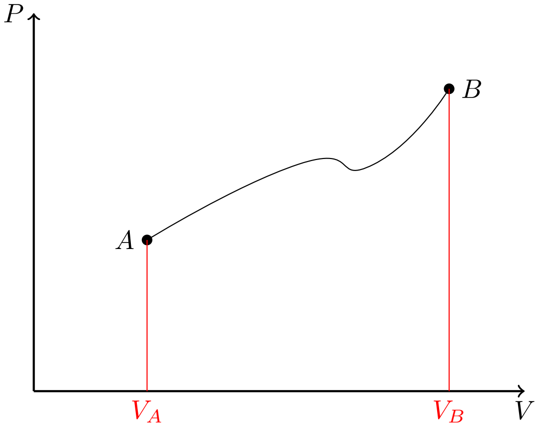

Figure 1.2: Transformation on (P, V) diagram.

Transformations which are especially important are those for which the initial and final states are the same. These are called *cyclical transformations* or *cycles.* A cycle, therefore, is a transformation which brings the system back to its initial state.

A transformation during which the system performs no external work is called an *isochore transformation.* If we assume that the work dW done is given according to equation (1.3), by PdV, we find that $dV = 0$ hence the volume is constant. It should be noticed, however, that the concept of isochore transformation is more general, since it requires that $dW = 0$ for the given transformation, even when the work dW cannot be represented by equation (1.3). Transformations during which the pressure or the temperature of the system remains constant are called isobaric and isothermal transformations, respectively.

1.2 Ideal or perfect gases

Absolute Temperature (Empirical): The equation of state of a system composed of a certain quantity of gas occupying a volume V at the temperature T and pressure P can be approximately expressed by a very simple analytical law. We obtain the equation of state of a gas in its simplest form by changing to a new temperature scale. We shall later see that it is possible to define this same scale of temperature T by more general thermodynamic considerations independent of the special properties of gases. The temperature T is called the *absolute temperature.*

The equation of state of a system composed of N gas molecules is given by

$$PV = Nk_BT, \tag{1.6}$$

where $k_B \approx 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$ is the Boltzmann constant. Equation (1.6) is called *the equation of state of an ideal or perfect gas.*

For an isothermal transformation of an ideal gas, we have:

$$PV = \text{constant}.$$

Isothermal transformations are therefore represented by equilateral hyperbolas having the axes as asymptotes on a (P, V) diagram.

The work performed by the gas during an isothermal expansion from an initial volume V_1 to a final volume V_2 is given (making use of (1.5) and (1.6)) by:

$$W = \int_{V_1}^{V_2} PdV = Nk_BT \log\left(\frac{V_2}{V_1}\right). \tag{1.7}$$

2 The First Law of Thermodynamics

2.1 The statement of the first law

The first law is a statement of conservation of energy. For an isolated system, the amount of work required to change the system's state is independent of how the work is performed. This suggests that there exists another state function $E(P, V)$, and for an isolated system the change in energy is $\Delta E = W$, no matter how the work is performed.

However, for systems that are not isolated, the change in energy is not equal to the amount of work done. We can place two systems that are not in thermal equilibrium in thermal contact. The energies of the systems change without any work being done. Hence, we write

$$\Delta E = Q + W \tag{2.1}$$

where Q is the amount of energy that was transferred to the system that can't be accounted for by the work done. This transfer of energy arises due to temperature differences and is called *heat.*

Heat is *not* a type of energy. It is a process. There is no sense in which we can divide up the energy $E(P, V)$ of the system into heat and work. Neither Q nor W are functions of state.

2.1.1 Quasi-static processes

The first law as expressed in (2.1) refers only to the energy at the beginning and the end - there is no need for the system to be in equilibrium during the process.

From now on, we will add or subtract energy to the system very slowly, so that at every stage of the process the system is effectively in equilibrium and can be described by the state variables. Such a process is called *quasi-static.*

We can now write (2.1) in infinitesimal form:

$$dE = đQ + đW, \tag{2.2}$$

where we show that heat and work are not state variables (hence not exact differentials) by using $đ$.

2.2 The application of the first law to systems with state variables pressure and volume

We now apply the first law to systems whose state can be defined in terms of any two of the three variables V, P and T. Any function of the state, for example its energy U, will then be a function of the two variables which have been chosen to represent the state.

By choosing different state variables to represent the system, we can obtain expressions for some of the properties of the system. An example of this is the *heat capacity.* It is defined to be the ratio of the infinitesimal amount of heat, $đQ$, absorbed by the body to the infinitesimal increase in the temperature dT produced by this heat. In general, the heat capacity will depend on the process during which the heat is supplied. Hence, we would obtain two different expressions for heat capacities at constant volume and constant pressure.

Since, for our system $đW$ is given by (1.3), we write:

$$dU + PdV = đQ. \tag{2.3}$$

If we choose V and T as our independent variables, U becomes a function of these variables, so that

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV,$$

and (2.3) becomes:

$$\left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV = đQ. \tag{2.4}$$

An expression for the constant volume heat capacity, C_V, can be obtained from (2.4). For an infinitesimal transformation at constant volume, $dV = 0$; hence,

$$C_V \coloneqq \left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V. \tag{2.5}$$

Similarly, taking T and P as independent variables, we can express U and V as $U = U(T, P)$ and $V = V(T, P)$. Hence, we get

$$\left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP = đQ \tag{2.6}$$

Using (2.6) we obtain an expression for the constant pressure heat capacity C_P as follows:

$$C_P \coloneqq \left(\frac{đQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P. \tag{2.7}$$

The second term on the right-hand side represents the effect of work done on the heat capacity.

2.3 The application of the first law to gases

It is an empirical observation that *the energy of an ideal gas is a function of the temperature only and not of the volume or pressure.* We may therefore write for the energy of an ideal gas:

$$U = U(T). \tag{2.8}$$

We assume the constant volume heat capacity of an ideal gas to remain constant. Since U is a function of temperature only, we may rewrite (2.5) as

$$C_V = \frac{dU}{dT}. \tag{2.9}$$

The first law now takes the form

$$C_V dT + P dV = đQ, \tag{2.10}$$

and by using the equation of state for an ideal gas (1.6), we get

$$(C_V + Nk_B)\, dT - V dP = đQ.$$

Since $dP = 0$ for a constant pressure process, this leads to

$$C_P = C_V + Nk_B. \tag{2.11}$$

It can be shown from kinetic theory that

$$C_V = \frac{3}{2}Nk_B \quad \text{for a monatomic gas, and}$$
$$C_V = \frac{5}{2}Nk_B \quad \text{for a diatomic gas.}$$

We can then deduce that

$$C_P = \frac{5}{2}Nk_B \quad \text{for a monatomic gas, and}$$
$$C_P = \frac{7}{2}Nk_B \quad \text{for a diatomic gas.}$$

We can then define a quantity γ of the form

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{Nk_B}{C_V}. \tag{2.12}$$

2.4 Adiabatic transformation of a gas

A process is said to be *adiabatic* if the system is thermally insulated so that no heat exchange occurs between it and its surroundings.

We can obtain a quantitative relationship between the change in temperature and the change in volume using equation (2.10), noting that $đQ = 0$;

$$C_V dT + P dV = 0.$$

Using the equation of state, we can eliminate P and obtain:

$$C_V dT + \frac{N k_B T}{V} dV = 0.$$

Integrating the expression yields

$$T V^{\gamma - 1} = \text{constant}. \tag{2.13}$$

Using the equation of state, we can put (2.13) in the form

$$P V^{\gamma} = \text{constant}. \tag{2.14}$$

3 The Second Law of Thermodynamics

The essence of the second law is that there is a preferred direction of time. There are many macroscopic processes in nature which cannot be reversed. The second law summarises this in a single statement about the motion of heat.

3.1 Reversible processes

These are a special type of quasi-static processes that can be run backwards. There is the further requirement that no friction be involved.

If a *cycle* is reversible, then we have from the first law,

$$\oint dE = \oint đW + \oint đQ = 0. \tag{3.1}$$

Hence, for an ideal gas

$$\oint P dV = \oint đQ. \tag{3.2}$$

3.2 The statement of the second law

The second law is usually stated in two forms:

Kelvin: No process is possible whose sole effect is to extract heat from a hot reservoir and convert this entirely into work.

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

It can be shown that these statements are equivalent. We will show how these statements allow us to define a quantity called “entropy”.

3.3 The Carnot cycle

Equation (3.2) suggests we can convert heat into work with a reversible cycle without any limitations. Why does this not contradict Kelvin's statement?

The key to understanding this is to realise that a reversible cycle, by necessity, deposits some heat elsewhere. The energy available for work is the difference between the heat extracted and the heat lost. To illustrate this, it's very useful to consider a particular kind of reversible cycle called a *Carnot engine*. This is series of reversible processes, running in a cycle, operating between two temperatures T_H and T_C. It takes place in four stages:

- Isothermal expansion at T_H. The system absorbs heat Q_H.
- Adiabatic expansion from T_H to T_C.
- Isothermal compression at T_C. Work is done on the system, which is released as heat Q_C.
- Adiabatic compression from T_C to T_H.

The net heat absorbed is $\Delta Q = Q_H - Q_C$, which equals the work performed. We define the *efficiency*, η of an engine to be the ratio of the work done to the heat absorbed from the hot reservoir:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}. \tag{3.3}$$

We see now why a reversible cycle doesn't violate Kelvin's statement: some heat Q_C must be released to the get back to the initial state.

3.3.1 Carnot's theorem

Of *all* engines operating between two heat reservoirs, a reversible engine is the most efficient. As a corollary, all reversible engines have the same efficiency which depends only on the temperatures of the reservoirs.

Proof: Consider a second engine - called Tong - operating between T_H and T_C. The two engines perform the same amount of work, W. However, Tong is not reversible. Let Q'_H and Q'_C be the heat absorbed and deposited by Tong. Then, we can couple the two engines, with Carnot running in reverse.

The net effect of the two engines is to extract $Q'_H - Q_H$ from the hot reservoir and deposit the same amount $Q'_C - Q_C = Q'_H - Q_H$ into the cold. Clausius' statement tells us that $Q'_H \geq Q_H$. Hence, we get:

$$\eta_{tong} = 1 - \frac{Q'_C}{Q'_H} = \frac{Q_H - Q_C}{Q'_H} \leq \frac{Q_H - Q_C}{Q_H} = \eta_{carnot} \tag{3.4}$$

This yields the result we wanted, namely $\eta_{tong} \leq \eta_{carnot}$. The corollary simple to prove. Suppose now that Tong is reversible. Then, we can form the same argument to show that $\eta_{tong} \geq \eta_{carnot}$; hence we conclude $\eta_{tong} = \eta_{carnot}$. This means that all reversible engines operating between two temperatures have the same efficiency. Moreover, this efficiency must be a function of temperature only, so that $\eta = \eta(T_H, T_C)$ simply because they are the only variables. □

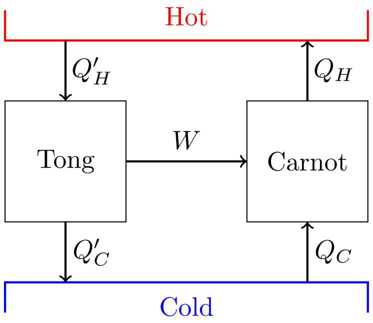

Figure 3.1: Irreversible engine coupled with a reversible engine running backwards.

3.4 Thermodynamic temperature scale and the ideal gas

Since the efficiency of a Carnot engine depends only on the temperatures T_H and T_C, we can define a temperature scale that is independent of any specific system.

We start by noting that the ratio of the heat absorbed to the heat deposited can be written as *some* function of the temperatures:

$$\frac{Q_C}{Q_H} = f(T_C, T_H). \tag{3.5}$$

This follows from the fact that the efficiency of a reversible engine is a function of the temperatures.

Now, consider two reversible engines A and B. A operates between temperatures $T_1 > T_2$, B between $T_2 > T_3$. We set the engines such that the heat absorbed by B, denoted Q_2, equals the heat deposited by A. It follows from (3.5) that

$$\frac{Q_2}{Q_1} = f(T_2, T_1), \qquad \frac{Q_3}{Q_2} = f(T_3, T_2). \tag{3.6}$$

However, as the heat deposited from A equals the heat absorbed by B, the two engines can be thought of as a single engine operating between $T_1 > T_2$. Therefore, we have

$$\frac{Q_3}{Q_1} = f(T_3, T_2). \tag{3.7}$$

Combining (3.6) with (3.7) yields

$$f(T_3, T_2) = f(T_2, T_1) f(T_3, T_2). \tag{3.8}$$

The right hand side of (3.8) implies that the function f has the following form:

$$f(T_2, T_1) = \frac{\theta(T_2)}{\theta(T_1)} \tag{3.9}$$

for some function θ. Now, we use the ambiguity in the definition of temperature to pick $\theta(T) = T$. Hence, we *define* the thermodynamic temperature such that the efficiency of a reversible engine is given by

$$\eta = 1 - \frac{T_C}{T_H}. \tag{3.10}$$

Now, we consider a Carnot cycle for an ideal gas, and show the equivalence of the two temperature cycles (one defined from reversible cycles, the other from the ideal gas law). We start by considering the isothermal expansion and compression. As the energy is a function of the temperature only, $dT = 0$ implies $dE = 0$. For an expansion from volume V_A to V_B, we then have

$$Q_H = \int_A^B \text{đ}Q = -\int_A^B \text{đ}W = N k_B T_H \log\left(\frac{V_B}{V_A}\right),$$

and similarly for a compression from V_C to V_D,

$$Q_C = \int_C^D \text{đ}Q = -\int_A^B \text{đ}W = N k_B T_C \log\left(\frac{V_C}{V_D}\right).$$

Now, we consider the adiabatic processes. Using (2.13), it can be shown that

$$\frac{V_A}{V_B} = \frac{V_D}{V_C},$$

which leads us to the expected expression for the efficiency of a reversible engine for an ideal gas:

$$\eta_{reversible} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}. \tag{3.11}$$

Hence, the two expressions for the temperature are consistent.

4 The Entropy

4.1 Some properties of cycles

Consider a system S that undergoes a cyclic transformation. We suppose the system exchanges heat $Q_1, Q_2, \ldots, Q_n$ with a set of sources at temperatures $T_1, T_2, \ldots, T_n$. Take $Q_i > 0$ for heat absorbed, and $Q_i \leq 0$ otherwise.

We now prove that

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0, \tag{4.1}$$

where the equality sign holds only for reversible cycles.

Consider n Carnot engines, $C_1, C_2, \ldots, C_n$ operating between some arbitrary temperature T_0 and T_i. The engines are set such that the heat exchanged between T_i and C_i is $-Q_i$. The i^{th} section of the system can be represented as follows:

$$\boxed{T_0} \xrightarrow{Q_{i,0}} \boxed{C_i} \xrightarrow{Q_i} \boxed{T_i} \xrightarrow{Q_i} \boxed{S}$$

Now, consider a whole cycle through S and each of the C_i. This can be thought of as a single cycle of a more complex system. We note that the heat exchanged between each source T_i is identically zero because of the Carnot cycles. Hence, the net effect of the cycle is an exchange of heat between all C_i and T_0. This can be expressed as

$$\Delta Q = \sum_{i=1}^{n} Q_{i,0}. \tag{4.2}$$

From the properties of Carnot cycles, we have:

$$\frac{Q_{i,0}}{Q_i} = \frac{T_0}{T_i} \implies Q_{i,0} = T_0 \frac{Q_i}{T_i}.$$

Hence, we can rewrite (4.2) as

$$\sum_{i=1}^{n} Q_{i,0} = T_0 \sum_{i=1}^{n} \frac{Q_i}{T_i}.$$

Now, we note that the heat is exchanged only between our complex system and the source at temperature T_0, i.e. no heat was dumped to another reservoir. From the first law, we know that the heat must have been converted to work. Then, Kelvin's statement tells us that the work cannot be positive, hence we have

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0. \tag{4.3}$$

If, on the other hand, the original cycle S is reversible, we can run it backwards in which case we form the identical argument above with the sign of Q_i changed and we have

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} \geq 0. \tag{4.4}$$

The only way equations (4.3) and (4.4) are both satisfied is if

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} = 0 \tag{4.5}$$

for a reversible cycle. This completes the proof of (4.1). $\square$

So far, we have assumed that the system exchanges heat with a finite number of sources at temperatures T_i. However, the relations so far proven can be extended for heat exchange with a continuous distribution of sources. In that case, the sum in (4.1) is replaced with an integral over the cycle and the heat transfer Q_i becomes $đQ$. Hence we have

$$\oint \frac{đQ}{T} \leq 0 \tag{4.6}$$

which is valid for *all* cycles and

$$\oint \frac{đQ}{T} = 0 \tag{4.7}$$

which is only valid for *reversible* cycles.

4.2 The entropy

Equation (4.7) suggests that for *any reversible* transformation from state A to state B, the quantity $\int_A^B đQ/T$ is path independent. This enables us to define a new function of state called the entropy as follows:

$$S(A) = \int_O^A \frac{đQ}{T}, \tag{4.8}$$

where O is an arbitrary reference state called the *standard state*.

It can be shown that for a reversible transformation from A to B, we have

$$\int_A^B \frac{đQ}{T} = S(B) - S(A). \tag{4.9}$$

Finally, if we choose a different standard state O', we would get

$$S'(A) = \int_{O'}^A \frac{đQ}{T} = S(A) - S(O').$$

The entropy is therefore defined except for an additive constant.

From (4.9), it follows that for an infinitesimal variation in the entropy we have

$$dS = \frac{đQ}{T}. \tag{4.10}$$

4.3 Some further properties of the entropy

We now prove that for *any* transformation from A to B,

$$S(B) - S(A) \geq \int_A^B \frac{đQ}{T}. \tag{4.11}$$

Consider a cycle of the following form: an irreversible transformation from A to B followed by a reversible transformation from B to A. Using (4.6), we get

$$\oint \frac{đQ}{T} = \left(\int_A^B \frac{đQ}{T}\right)_I + \left(\int_B^A \frac{đQ}{T}\right)_R \leq 0,$$

where R and I denote reversible and irreversible respectively. It follows from the definition of the entropy that

$$\left(\int_A^B \frac{đQ}{T}\right)_I - [S(B) - S(A)] \leq 0$$

$$\implies S(B) - S(A) \geq \left(\int_A^B \frac{đQ}{T}\right)_I$$

For an isolated system, (4.11) takes a simple form since $đQ = 0$:

$$S(B) \geq S(A); \tag{4.12}$$

that is *for any transformation occurring in an isolated system, the entropy of the final state can never be less than that of the initial state.* If the transformation is reversible, the equality sign holds in (4.12), and the system suffers no change in entropy.

When an isolated system reaches a state of maximum entropy, it cannot undergo any further transformation as any transformation would decrease the entropy. Hence, *the state of maximum entropy is the most stable state for an isolated system.*

4.4 The entropy of systems with state variables pressure and volume

We represent the system in terms of T and V, and we have from (2.4):

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV.$$

Combining this with (4.10) we get

$$dS = \frac{đQ}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV. \tag{4.13}$$

Since we have already stated that the entropy is a state variable, there exists a function $S = S(T, V)$ of the state of the system. Hence, we conclude the differential on the left hand side of (4.13) is an *exact differential.* One of the properties of exact differential expressions is the following: let df be an exact differential such that there exists a function $f : \mathbb{R}^2 \to \mathbb{R}$ which satisfies

$$df(x, y) = X(x, y)dx + Y(x, y)dy.$$

Then, we must have

$$\frac{\partial X(x, y)}{\partial y} = \frac{\partial Y(x, y)}{\partial x}. \tag{4.14}$$

Applying the condition (4.14) to the expression for dS, (4.13) yields

$$\frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial V} + P\right)\right].$$

Performing the differentiation we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{4.15}$$

We can obtain similar expressions by choosing different state variables to represent dS in. If we take T and P, we get

$$\left(\frac{\partial U}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T - T\left(\frac{\partial V}{\partial T}\right)_P, \tag{4.16}$$

and similarly taking P and V yields

$$T = \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right]\left(\frac{\partial T}{\partial P}\right)_V - \left(\frac{\partial U}{\partial P}\right)_V\left(\frac{\partial T}{\partial V}\right)_P. \tag{4.17}$$

4.5 The Clapeyron equation

work in progress

4.6 The Van der Waals equation

work in progress

5 Thermodynamic Potentials

5.1 Legendre transformation

This section will not provide a rigorous explanation of Legendre transforms. Namely, we present how they can be used to change the variables of a function of two variables.

Let $f : \mathbb{R}^2 \to \mathbb{R}$ be a function such that

$$df(x, y) = u(x, y)dx + v(x, y)dy,$$

where u and v are simply f_x and f_y respectively. We can define a new function g such that it is a function of u instead of x, as follows:

$$g = -ux + f.$$

Taking the differential, we obtain

$$dg = -udx - xdu + udx + vdy = -xdu + vdy,$$

where $x(u, y) = g_u$. This method can be used on the expression for internal energy to obtain three more functions of the state variables T, V, P and S.

5.2 Potentials

We have established a set of state variables: pressure, volume, temperature, entropy, energy. Any given system can be described in terms of two state variables. We can *define* some useful functions of these variables by taking the Legendre transform with respect to different variables. In this section, we will look at the following thermodynamic potentials: internal energy, enthalpy, Helmholtz function and Gibbs function.

5.2.1 Internal energy

The internal energy is most naturally expressed in terms of volume and entropy, due to the form of the first law:

$$dU = TdS - PdV.$$

Its physical definition is the total energy shared among the constituents of a given system.

5.2.2 Helmholtz function (free energy)

Helmholtz function $F = F(T, V)$ is defined as follows:

$$F = U - TS, \tag{5.1}$$

which is the Legendre transform of internal energy. It is a function of temperature and volume. It can be interpreted as a limit to the useful work a system can do during a isothermal process. Consider dF, given by

$$dF = -SdT - PdV. \tag{5.2}$$

From Clausius' inequality, we have for any process

$$\int_A^B \frac{đQ}{T} \leq S(B) - S(A),$$

if the process is isothermal, we have

$$\Delta Q \leq TS(B) - TS(A), \tag{5.3}$$

where ΔQ is the *heat supplied to the system.* From the first law, we have

$$\Delta Q = \Delta U + \Delta W,$$

where ΔW is the *work done by the system.* Therefore, equation (5.3) becomes

$$\Delta U + \Delta W \leq T\Delta S,$$

so we get

$$\Delta W \leq -\Delta F. \tag{5.4}$$

The equality applies to reversible processes. The physical interpretation of (5.4) is that the amount of work that can be extracted from a system with an isothermal process is less than or equal to the change in the Helmholtz free energy.

If we have an isochoric system, we have $\Delta W = 0$ and hence get

$$\Delta F \leq 0.$$

Hence, for an isothermal isochoric process, the equilibrium is reached when the Helmholtz free energy is minimized.

5.2.3 Gibbs function (free energy)

If we instead wanted a function of temperature and pressure, we define $G = G(T, P)$:

$$G = U - TS + PV = F + PV \tag{5.5}$$

in which case we have

$$dG = -SdT + VdP. \tag{5.6}$$

We now use equation (5.4), considering an isobaric process ($dP = 0$) and rewriting in terms of the Gibbs function yields

$$\Delta F + P\Delta V = \Delta F + \Delta(PV) = \Delta G \leq 0.$$

Hence we conclude that the Gibbs free energy is minimized in an isothermal, isobaric process.

5.2.4 Enthalpy

Finally, we can consider a function in terms of entropy and pressure, $H = H(S, P)$, in which case we take the Legendre transform of energy and define *enthalpy* as

$$H = U + PV$$

which yields

$$dH = TdS + VdP.$$

This is useful for processes involving changes in entropy and pressure. In a reversible adiabatic isobaric process, enthalpy is constant. In an isobaric process, we have $dP = 0$ which implies

$$dH = TdS \equiv đQ.$$

From this, we can obtain an expression for the constant pressure heat capacity C_P:

$$C_P \equiv \frac{đQ}{dT} = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P,$$

where it is implied that $S = S(T, P)$.