

Thermodynamics

1 Introduction

A macroscopic system has many degrees of freedom, only a few of which are measurable. Thermodynamics thus concerns itself with the relation between small number of variables which are sufficient to describe the bulk behavior of the system in question. In the case of a gas or liquid the appropriate variables are the pressure P , volume V , and temperature T . In the case of a magnetic solid the appropriate variables are the magnetic field H , the magnetization M , and the temperature T . In more complicated situations, such as when a liquid is in contact with its vapor, additional variables may be needed: such as the volume of both liquid and gas V_L, V_a , the interfacial area A , and surface tension σ . If the thermodynamic variables are independent of time, the system is said to be in a steady state.

If the thermodynamic variables are independent of time, the system is said to be in a steady state. If, moreover, there are no macroscopic currents in the system, such as a flow of heat or particles through the material, the system is in equilibrium. Any quantity which, in equilibrium, depends only on the thermodynamic variables, rather than on the history of the sample, is called a state function.

In subsequent sections we shall meet a number of such quantities. For a large system, the state variables can normally be taken to be either extensive (i.e., proportional to the size of the system) or intensive (i.e., independent of system size). Examples of extensive variables are the internal energy, the entropy, and the mass of the different constituents or their number, while the pressure, the temperature, and the chemical potentials are intensive.

The postulate that quantities like the internal energy and entropy are extensive and independent of shape is equivalent to an assumption of additivity or of the existence of the thermodynamic limit. In the process of taking the thermodynamic limit, we let the size of the system become infinitely large, with the densities (of mass, energy, magnetic moment, polarization, etc.) remaining constant.

In equilibrium the state variables are not all independent and are connected by equations of state. The role of statistical mechanics is the derivation, from microscopic interactions, of such equations of state. Simple examples are the ideal gas law,

$$PV - Nk_B T = 0$$

where N is the number of molecules in the system and k_B is Boltzmann's constant; the van der Waals equation,

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) - Nk_B T = 0$$

where a, b are constants; the virial equation of state

$$P - \frac{Nk_B T}{V} \left[1 + \frac{NB_2(T)}{V} + \frac{N^2 B_3(T)}{V^2} + \dots \right] = 0$$

where the functions $B_2(T)$, $B_3(T)$ are called virial coefficients; and in the case of a paramagnet, the Curie law,

$$M - \frac{CH}{T} = 0$$

where C is a constant called the Curie constant. These equations of states are approximations, and we shall use them primarily to illustrate various principles. The virial equation of state is, in principle, exact, but calculation of more than a few of the virial coefficients is very difficult.

2 Law's of Thermodynamics

2.1 Zeroth Law

The zeroth law can be thought of as the statement that matter in equilibrium can be assigned values for the temperature, pressure and chemical potentials, which in principle can be measured. Formally the law can be stated as:

If system A is in equilibrium with systems B and C then B is in equilibrium with C .

The zeroth law allows us to introduce universal scales for temperature, pressure etc.

Another way of looking at the zeroth law is through an analogy with mechanics. In equilibrium the forces are balanced. This implies that the intensive variables are constant throughout the system. In particular:

$$\begin{aligned} T = \text{const.} &\rightarrow \text{Thermal equilibrium} \\ P = \text{const.} &\rightarrow \text{Mechanical equilibrium} \\ \mu = \text{const.} &\rightarrow \text{Chemical equilibrium} \end{aligned}$$

The zeroth law has a fairly straightforward statistical interpretation and this will allow us to make contact between the thermodynamic and statistical description. You will understand this better when you study Statistical mechanics.

2.2 First Law

The first law of thermodynamics restates the law of conservation of energy. However, it also partitions the change in energy of a system into two pieces, heat and work:

$$dE = dQ - dW$$

dE is the change in internal energy of the system, dQ the amount of heat added to the system, and dW the amount of work done by the system during an infinitesimal process

Aside from the partitioning of the energy into two parts, the formula distinguishes between the infinitesimals dE , and, $\delta Q, \delta W$. The difference between the two measurable quantities δQ and δW is found to be the same for any process in which the system evolves between two given states, independently of the path. This indicates that dE is an exact differential or, equivalently, that the internal energy is a state function. The same is not true of the differentials δQ and δW . hence the difference in notation.

Consider a system whose state can be specified by the values of a set of state variables x_j (e.g., the volume, the number of moles of the different constituents, the magnetization, the electric polarization, etc.) and the temperature. As mentioned earlier, thermodynamics exploits an analogy with mechanics and we write, for the work done during an infinitesimal process,

$$\delta W = - \sum_j X_j dx_j$$

where the X_j 's can be thought of as generalized forces and the x_j 's as generalized displacements.

Before going on to discuss the second law, we pause to introduce some terminology. A thermodynamic transformation or process is any change in the state variables of the system. A spontaneous process is one that takes place without any change in the external constraints on the system, and is due simply to the internal dynamics. An adiabatic process is one in which no heat is exchanged between the system and its surroundings. A process is isothermal if the temperature is held fixed, isobaric if the pressure is fixed, isochoric if the density is constant, and quasistatic if the process is infinitely slow. A reversible process is by nature quasistatic and follows a path in thermodynamic space which can be exactly reversed. If this is not possible, the process is irreversible. An example of a reversible process is the slow adiabatic expansion of a gas against a piston on which a force is exerted externally. This force is infinitesimally less than PA , where P is the pressure of the gas and A the area of the piston. An example of an irreversible process is the free adiabatic expansion of a gas into a vacuum. In this case the initial state of the gas can be recovered if one compresses it and removes excess heat. This is, however, not the same thermodynamic path.

2.3 Second Law

The second law of thermodynamics introduces the entropy S as an extensive state variable and states that for an infinitesimal reversible process at temperature T , the heat given to the system is

$$\delta Q|_{rev} = TdS$$

while for an irreversible process

$$\delta Q|_{irrev} \leq TdS$$

If we are only interested in thermodynamic equilibrium states we can use $\delta Q|_{rev} = TdS$ and treat the entropy S as the generalized displacement which is coupled to the 'force' T . The above formulation of the second law is due to Gibbs

We present next two equivalent statements of the second law of thermodynamics. The Kelvin version is:

There exists no thermodynamic process whose sole effect is to extract a quantity of heat from a system and to convert it entirely to work.

The equivalent statement of Clausius is:

No process exists in which the sole effect is that heat flows from a reservoir at a given temperature to a reservoir at a higher temperature.

A corollary of these statements is that the most efficient engine operating between two reservoirs at temperatures T_1 and T_2 is the Carnot engine. The Carnot engine is an idealized engine in which all the steps are reversible. We show the Carnot cycle for an ideal gas working substance in the next Figure

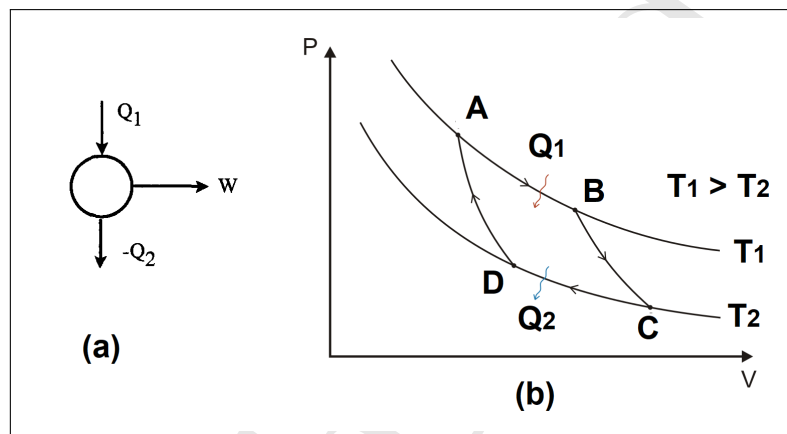


Figure 1: Carnot cycle for an ideal gas

In step AB heat Q_1 is absorbed by the gas, which expands isothermally and does work in the process. The next step, BC , is adiabatic and further work is done. In step CD heat $(-Q_2)$ is given off to the low-temperature reservoir and work is done on the gas. Step DA returns the working substance adiabatically to its original state.

The efficiency, η , of the engine is defined to be the ratio of the total work done in one cycle to the heat absorbed from the high-temperature reservoir:

$$\eta = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1}$$

In this equation we have followed the convention of the first law that heat transfer is positive if added to the working system. Suppose now that a second more efficient engine operates between the same two temperatures. We can use this engine to drive the Carnot engine backwards since it is reversible, Q_1 , Q_2 , and W will simply change sign and η will remain the same.

In the next figure .2(a) the Carnot engine is denoted by C , the other hypothetical super-engine, with efficiency $\eta_S > \eta_C$ is denoted by S . We use all the work done by engine S to drive engine C . Let the heat absorbed from the reservoirs be Q_{1C} , Q_{1S} , Q_{2S} , Q_{2C} . By assumption we have

$$\eta_S = \frac{W}{Q_{1S}} > \frac{-W}{Q_{1C}} = \eta_C$$

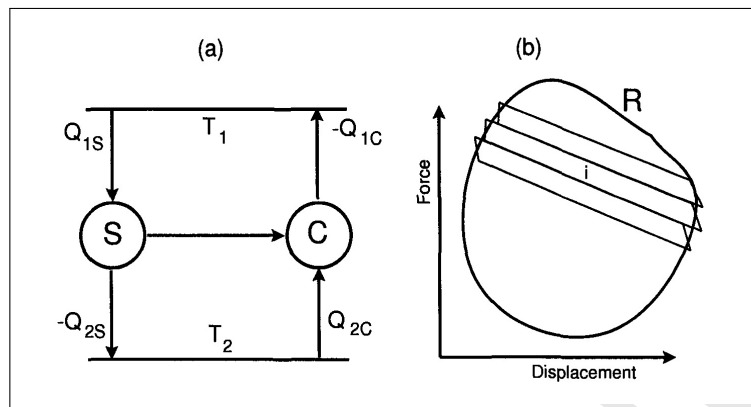


Figure 2: (a) Carnot engine (C) driven in reverse by an irreversible engine (S). (b) Arbitrary reversible process covered by infinitesimal Carnot cycles.

The inequality implies that $|Q_{1C}| > Q_{1S}$ and the net effect of the entire process is to transfer heat from the low-temperature reservoir to the high-temperature reservoir. This violates the Clausius statement of the second law. Similarly, if we take only part of the work output of engine S, and adjust it so that there is no net heat transfer to the low-temperature reservoir, a contradiction of the Kelvin statement of the second law results. We conclude that no engine operating between two reservoirs at fixed temperatures is more efficient than a Carnot engine. Equivalently, all reversible engines operating between fixed temperatures have the same efficiency and are Carnot engines.

The result that all Carnot engines operating between two temperatures have the same efficiency can be used to define a temperature scale. One possible definition is

$$\frac{T_2}{T_1} = 1 - \eta_C(T_1, T_2)$$

where $\eta_C(T_1, T_2)$ is the Carnot efficiency. Using an ideal gas as a working substance, one can easily show that this temperature scale is identical with the ideal gas (or absolute) temperature scale. Substituting for η in equation $\eta = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1}$ we have, for a Carnot cycle,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

With this equation we are in a position to define the entropy. Consider an arbitrary reversible cyclic process such as the one drawn in (b) of the previous figure. We can cover the region of the $P - V$ plane, enclosed by the reversible cycle R with a set of Carnot cycles operating between temperatures arbitrarily close to each other. For each Carnot cycle we have, $\sum_i \frac{Q_i}{T_i} = 0$

As the number of Carnot cycles goes to infinity, the integral of dQ/T over the uncompensated segments of these cycles approaches $\int_R \frac{dQ}{T} = 0$

Thus the expression dQ/T is an exact differential for reversible processes and we define the state function,

whose differential it is, to be the entropy S . For reversible processes the first law can therefore be written in the form

$$dE = TdS - dW = TdS + \sum_j X_j dx_j$$

The fact that the Carnot cycle is the most efficient cycle between two temperatures allows us to obtain an inequality for arbitrary processes. Consider a possibly irreversible cycle between two reservoirs at temperatures T_1 and T_2 .

$$\frac{Q_1 + Q_2}{Q_1} \leq \frac{Q_{1C} + Q_{2C}}{Q_{1C}} = \eta_C$$

This implies that $Q_2/Q_1 \leq -T_2/T_1$ and

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0$$

Generalizing to an arbitrary process, we obtain

$$\oint \frac{dQ}{T} \leq 0$$

where the equality holds for reversible processes. Since the entropy is a state function, $\oint dS = 0$ for any reversible closed cycle. We can imagine an arbitrary process combined with a reversible process to form a cycle and we therefore obtain for an arbitrary infinitesimal process $T\Delta S \geq \Delta Q$

Combining this with the first law we have, for arbitrary infinitesimal processes,

$$T\Delta S \geq \Delta E + \Delta W$$

where, once again, the equality holds for reversible processes.

A further consequence of the foregoing discussion is that the entropy of an isolated system cannot decrease in any spontaneous process. Imagine a spontaneous process in which the system evolves from point A to point B in the next figure in the thermodynamic space. (Note that the irreversible path cannot be represented as a curve in the $P - T$ plane. The dotted line represents a reversible path connecting the same endpoints.)

Since the system is isolated $\Delta Q = 0$ and

$$\int_A^B dS \geq \int_A^B \frac{dQ}{T} = 0 \quad \implies \quad S(B) - S(A) \geq 0$$

Since spontaneous processes tend to drive a system toward equilibrium, we conclude that the equilibrium state of an isolated system is the state of maximum entropy.

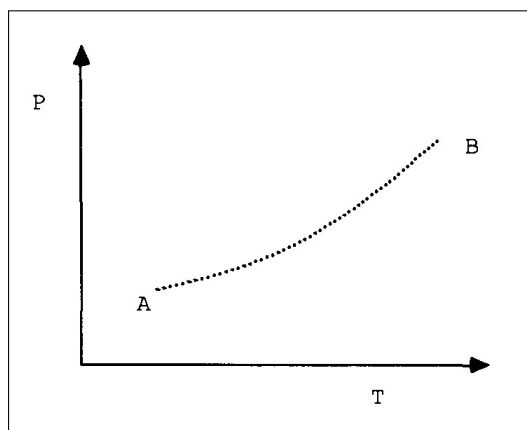


Figure 3: Thermodynamic Path

3 Thermodynamic Potentials

The term thermodynamic potential derives from an analogy with mechanical potential energy. In certain circumstances the work obtainable from a macroscopic system is related to the change in the appropriately defined thermodynamic potential. The simplest example is the internal energy $E(S, V)$ for a PVT system. The second law for reversible processes reads

$$dE = TdS - PdV = dQ - dW$$

In a reversible adiabatic transformation the decrease in internal energy is equal to the amount of work done by the expanding system. If the transformation is adiabatic but not reversible, $dQ = 0$ and the first law yields

$$\Delta E = -(\Delta W)_{irrev}$$

with the same change in E as in a reversible transformation connecting the same endpoints in the thermodynamic space. However, the change in entropy is not necessarily zero and must be calculated along a reversible path:

$$\Delta E = (\Delta Q)_{rev} - (\Delta W)_{rev}$$

Subtracting and using $(dQ)_{rev} = TdS$, we find that

$$(\Delta W)_{rev} - (\Delta W)_{irrev} = \int TdS \geq 0$$

Thus the decrease in internal energy is equal to the maximum amount of work obtainable through an adiabatic process, and this maximum is achieved if the process is reversible.

We now generalize the formulation to allow other forms of work, as well as the exchange of particles between the system under consideration and its surroundings. This more general internal energy is a function of the entropy, the extensive generalized displacements, and the number of particles of each species: $E = E(S, \{x_i\}, \{N_j\})$ with a differential (for reversible processes)

$$dE = TdS + \sum_i X_i dx_i + \sum_j \mu_j dN_j$$

Here N_j is the number of molecules of type j and the chemical potential μ_j is defined by the previous equation. We are now in a position to introduce a number of other useful thermodynamic potentials. The Helmholtz free energy A , is related to the internal energy through a Legendre transformation:

$$A = E - TS$$

The quantity A is a state function with differential

$$\begin{aligned} dA &= dE - TdS - SdT \\ &= -SdT + \sum_i X_i dx_i + \sum_j \mu_j dN_j \end{aligned}$$

As in the case of the internal energy, the change in Helmholtz free energy may be related to the amount of work obtainable from the system. In a general infinitesimal process

$$\begin{aligned} dA &= dE - d(TS) \\ &= dQ - TdS - SdT - dW \\ &= -pdV - SdT \end{aligned}$$

Thus

$$dW = (dQ - TdS) - SdT - dA$$

In a reversible transformation $dQ = TdS$. If the process is isothermal as well as reversible we have $dW = -dA$ and the Helmholtz free energy plays the role of a potential energy for reversible isothermal processes. If the process in question is isothermal but not reversible, we have $dQ - TdS \leq 0$. and

$$(dW)_{irrev} = dQ - TdS - dA \leq -dA$$

which shows that $-dA$ is the maximum amount of work that can be extracted, at constant temperature, from the system. We also see, from the previous equation, that if the temperature and generalized displacements are fixed ($T, \{x_i\}, \{N_j\}$) is the state of minimum Helmholtz free energy.

Another thermodynamic potential which is often useful is the Gibbs free energy G . For a PVT system we write $G = A + PV$

This function is again a state function with a differential

$$dG = dA + PdV + VdP = -SdT + VdP$$

In a general process

$$\begin{aligned} dG &= dE - d(TS) + d(PV) \\ &= (\bar{d}Q - TdS) - (\bar{d}W - PdV) + VdP - SdT \end{aligned}$$

We see that the relations

$$\begin{aligned} \bar{d}W - PdV &= 0 \\ \bar{d}Q - TdS &\leq 0 \end{aligned}$$

imply that the Gibbs potential can only decrease in a spontaneous process at fixed T and P .

In many applications one considers processes which take place at ambient pressure. In such a process there may be volume change (e.g. due to release of gases in a chemical reaction). The PdV work then represents work against the environment and is commonly not considered to be available work. We write

$$\bar{d}W = \int PdV + W_{other}$$

where W_{other} could represent electric energy in a fuel cell. It is then easy to show that $-\Delta G$ is the maximum amount of other work that can be extracted at fixed T . The maximum occurs when the process is reversible.

One further potential that is very useful in statistical physics is the grand potential $\Omega_G(T, V, \{\mu\})$. This potential is obtained from the internal energy through the transformation

$$\Omega_G(T, V, \{\mu\}) = E - TS - \sum_i N_i \mu_i$$

And has the differentials

$$d\Omega_G = -SdT - PdV - \sum_i N_i d\mu_i$$

The grand potential is necessary for the description of open systems (systems that can exchange particles with their surroundings).

4 Maxwell's Relations

It follows from the differential form

$$\begin{aligned} dA &= dE - TdS - SdT \\ &= -SdT + \sum_i X_i dx_i + \sum_j \mu_j dN_j \end{aligned}$$

for a single-component PVT system that

$$\begin{aligned}\left(\frac{\partial A}{\partial T}\right)_{N,V} &= -S \\ \left(\frac{\partial A}{\partial V}\right)_{T,N} &= -P \\ \left(\frac{\partial A}{\partial N}\right)_{T,V} &= \mu\end{aligned}$$

It is a well-known result from the theory of partial differentiation that higher order derivatives are independent of the order in which the differentiation is carried out; that is, if ϕ is a single-valued function of the independent variables x_1, x_2, \dots, x_n , then

$$\frac{\partial}{\partial x_i} \left(\frac{\partial \phi}{\partial x_j} \right) = \frac{\partial}{\partial x_j} \left(\frac{\partial \phi}{\partial x_i} \right)$$

By applying this result to the previous equation we immediately obtain the Maxwell's relations:

$$\begin{aligned}\left(\frac{\partial S}{\partial V}\right)_{T,N} &= \left(\frac{\partial P}{\partial T}\right)_{V,N} \\ \left(\frac{\partial S}{\partial N}\right)_{V,T} &= -\left(\frac{\partial \mu}{\partial T}\right)_{V,N} \\ \left(\frac{\partial P}{\partial N}\right)_{V,T} &= -\left(\frac{\partial \mu}{\partial V}\right)_{T,N}\end{aligned}$$

Similarly, in the case of the Gibbs potential we find from

$$dG = dA + PdV + VdP + \mu dN = -SdT + VdP + \mu dN$$

$$\begin{aligned}\left(\frac{\partial G}{\partial T}\right)_{N,P} &= -S \\ \left(\frac{\partial G}{\partial P}\right)_{T,N} &= V \\ \left(\frac{\partial G}{\partial N}\right)_{T,P} &= \mu\end{aligned}$$

from which we have the additional Maxwell relations:

$$\begin{aligned}\left(\frac{\partial S}{\partial P}\right)_{T,N} &= -\left(\frac{\partial V}{\partial T}\right)_{P,N} \\ \left(\frac{\partial V}{\partial N}\right)_{P,T} &= \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \\ \left(\frac{\partial S}{\partial N}\right)_{P,T} &= -\left(\frac{\partial \mu}{\partial T}\right)_{P,N}\end{aligned}$$

You already know the internal energy equation

$$dE = TdS - PdV + \mu dN$$

From here you can get

$$\begin{aligned}\left(\frac{\partial E}{\partial S}\right)_{N,V} &= T \\ \left(\frac{\partial E}{\partial V}\right)_{S,N} &= -P \\ \left(\frac{\partial E}{\partial N}\right)_{S,V} &= \mu\end{aligned}$$

Hence you get

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_{S,N} &= -\left(\frac{\partial P}{\partial S}\right)_{V,N} \\ \left(\frac{\partial T}{\partial N}\right)_{S,V} &= \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \\ \left(\frac{\partial P}{\partial N}\right)_{S,V} &= -\left(\frac{\partial \mu}{\partial V}\right)_{S,N}\end{aligned}$$

You can get another sets of equations from enthalpy relation

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

From here you can get

$$\begin{aligned}\left(\frac{\partial H}{\partial S}\right)_{P,N} &= T \\ \left(\frac{\partial H}{\partial P}\right)_{S,N} &= V \\ \left(\frac{\partial H}{\partial N}\right)_{S,P} &= \mu\end{aligned}$$

Hence you get

$$\begin{aligned}\left(\frac{\partial T}{\partial P}\right)_{S,N} &= \left(\frac{\partial V}{\partial S}\right)_{P,N} \\ \left(\frac{\partial T}{\partial N}\right)_{S,P} &= \left(\frac{\partial \mu}{\partial S}\right)_{P,N} \\ \left(\frac{\partial V}{\partial N}\right)_{S,P} &= \left(\frac{\partial \mu}{\partial P}\right)_{S,N}\end{aligned}$$

You already have studied the four Maxwell relations in much simpler form without considering the chemical potential.

1. $dU = TdS - PdV$; hence, $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
2. $dH = TdS + VdP$; hence, $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
3. $dA = -SdT - PdV$; hence, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
4. $dG = -SdT + VdP$; hence, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

The usefulness of these relations is demonstrated in the next section, in which we derive relations between some of the most commonly measured response functions.

5 Response function

A great deal can be learned about a macroscopic system through its response to various changes in externally controlled parameters. Important response functions for a PVT system are the specific heats at constant volume and pressure,

$$C_V = \left(\frac{dQ}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$C_P = \left(\frac{dQ}{dT} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

The isothermal and adiabatic compressibilities,

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$$

and the coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N}$$

Intuitively, we expect the specific heats and compressibilities to be positive and $C_P > C_V, K_T > K_S$. In this section we derive relations between these response functions. The intuition that the response functions are positive will be justified in the following section in which we discuss thermodynamic stability. We begin with the assumption that the entropy has been expressed in terms of T and V and that the number of particles is kept fixed. Then

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

$$T \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

$$C_P - C_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

We now use the Maxwell relations and the chain rule

$$\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial x}{\partial y} \right)_z = -1$$

We get

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

$$C_P - C_V = -T \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P^2 = \frac{TV}{K_T} \alpha^2$$

In a similar way we obtain a relation between the compressibilities K_T and K_S . Assume that the volume V has been obtained as function of S and P .

Then we get

$$dV = \left(\frac{\partial V}{\partial P} \right)_S dP + \left(\frac{\partial V}{\partial S} \right)_P dS$$

$$-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S - \frac{1}{V} \left(\frac{\partial V}{\partial S} \right)_P \left(\frac{\partial S}{\partial P} \right)_T$$

$$K_T - K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial S} \right)_P \left(\frac{\partial S}{\partial P} \right)_T$$

The Maxwell relation and $\left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial S}{\partial T} \right)_P^{-1}$ gives

$$K_T - K_S = \frac{TV}{C_P} \alpha^2$$

Now we have useful relations

$$C_P (K_T - K_S) = K_T (C_P - C_V) = TV \alpha^2$$

And

$$\frac{C_P}{C_V} = \frac{K_T}{K_S}$$

6 Conditions for Equilibrium and Stability

We consider two systems in contact with each other. It is intuitively clear that if heat can flow freely between the two systems and if the volumes of the two systems are not separately fixed, the parameters will evolve so as to equalize the pressure and temperature of the two systems. These conclusions can easily be obtained from the principle of maximum entropy. Suppose that the two systems have volumes V_1 , and V_2 , energies E_1 and E_2 , and that the number of particles in each, as well as the combined energy and total volume, are fixed. In equilibrium, the total entropy

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

must be a maximum. Thus

$$\begin{aligned} dS &= \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1} dE_1 + \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2} dE_2 + \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1} dV_1 + \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2} dV_2 \\ &= \left[\left(\frac{\partial S_1}{\partial E_1} \right)_{V_1} - \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2} \right] dE_1 + \left[\left(\frac{\partial S_1}{\partial V_1} \right)_{E_1} - \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2} \right] dV_1 = 0 \end{aligned}$$

where we have used the constraint $E_1 + E_2 = \text{const.}$ $V_1 + V_2 = \text{const.}$ We have

$$\left(\frac{\partial S_j}{\partial E_j} \right)_{V_j} = \left(\frac{\partial E_j}{\partial S_j} \right)_{V_j}^{-1} = \frac{1}{T_j} \quad \text{and} \quad \left(\frac{\partial S_j}{\partial V_j} \right)_{E_j} = \frac{P_j}{T_j}$$

So we get

$$\begin{aligned} \frac{1}{T_1} &= \frac{1}{T_2} \\ \frac{P_1}{T_1} &= \frac{P_2}{T_2} \end{aligned}$$

or $T_1 = T_2$, $P_1 = P_2$, which is the expected result. More generally, one finds that when the conjugate displacements are unconstrained, all generalized forces of two systems in equilibrium must be equal.

To this point we have required only that the equilibrium state correspond to a stationary state of the entropy. Requiring this stationary state to be a maximum will provide conditions on the second derivatives of the entropy. These conditions are local in nature. A stronger (global) condition is that the entropy be a concave function of the generalized displacements

Some of the most useful stability criteria are obtained from the Gibbs potential rather than from the entropy and we proceed to consider a small (but macroscopic) system in contact with a much larger reservoir.

This reservoir is assumed to be so large that fluctuations in the small system do not change the temperature or pressure of the reservoir, which we denote by T_0 and P_0 . The Gibbs potential is a minimum in equilibrium, and for the small system we have

$$G_1(P_0, T_0) = E_1 - T_0 S_1 + P_0 V_1$$

Suppose now that there is a fluctuation in the entropy and volume of this system. To second order in the fluctuating quantities,

$$\begin{aligned} \delta G_1 &= \delta S_1 \left(\frac{\partial E_1}{\partial S_1} - T_0 \right) + \delta V_1 \left(\frac{\partial E_1}{\partial V_1} + P_0 \right) \\ &+ \frac{1}{2} \left[(\delta S_1)^2 \left(\frac{\partial^2 E_1}{\partial S_1^2} \right) + 2\delta S_1 \delta V_1 \left(\frac{\partial^2 E_1}{\partial S_1 \partial V_1} \right) + (\delta V_1)^2 \left(\frac{\partial^2 E_1}{\partial V_1^2} \right) \right] \end{aligned}$$

which must be greater than zero if the state specified by P_0, T_0 is the state of minimum Gibbs potential. Since $\partial E_1 / \partial S_1 = T_0$ and $\partial E_1 / \partial V_1 = -P_0$ we obtain the condition

$$(\delta S)^2 \left(\frac{\partial^2 E}{\partial S^2} \right) + 2\delta S \delta V \left(\frac{\partial^2 E}{\partial S \partial V} \right) + (\delta V)^2 \left(\frac{\partial^2 E}{\partial V^2} \right) > 0$$

where we have dropped the subscripts. The fluctuations in the entropy and volume are independent of each other, and we can guarantee that the above expression is positive if we require that $E(S, V)$ satisfies the conditions

$$\begin{aligned} \frac{\partial^2 E}{\partial S^2} &> 0 \\ \frac{\partial^2 E}{\partial V^2} &> 0 \\ \frac{\partial^2 E}{\partial S^2} \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V} \right)^2 &> 0 \end{aligned}$$

The first inequality reduces to

$$\left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V} > 0 \quad \text{or} \quad C_V > 0$$

while the second implies

$$-\left(\frac{\partial P}{\partial V} \right)_S = \frac{1}{V K_S} > 0 \quad \text{or} \quad K_S > 0$$

and the final inequality yields

$$\frac{T}{V K_S C_V} > \left(\frac{\partial T}{\partial V} \right)_S^2$$

These inequalities are special cases of Le Chatelier's principle, which states that if a system is in equilibrium, any spontaneous changes in its parameters will bring about processes that tend to restore the system to equilibrium. In our situation such spontaneous processes raise the Gibbs potential. Other stability criteria can be obtained by using one of the other thermodynamic potentials

7 Thermodynamics of Phase Transitions

A typical phase diagram for a one-component PVT system looks like next figure

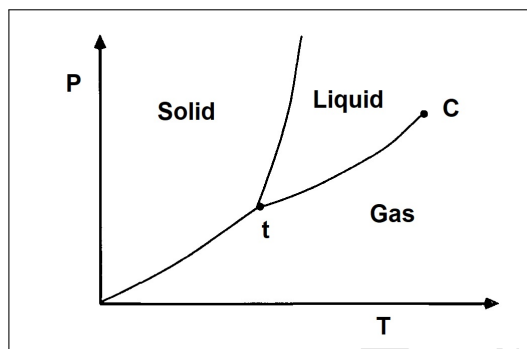


Figure 4: Phase diagram of a simple one-component PVT system.

The solid lines separate the $P-T$ plane into regions in which different phases are the stable thermodynamic states. As the system passes through one of these lines, called coexistence curves, a phase transition occurs, generally accompanied by the absorption or liberation of latent heat. In the figure there are two special points, the triple point P_t, T_t , and the critical point, P_c, T_c . At the critical point the properties of the fluid and vapor phase become identical and much of our study of phase transitions in later chapters will focus on the region of the phase diagram around this point. We note that the properties of the system vary smoothly along any curve which does not cross a coexistence curve. Thus, it is possible to pass continuously from the vapor to the liquid phase by taking the system to high enough temperature, increasing the pressure, and then lowering the temperature again. It is not possible to avoid the liquid-solid coexistence curve this curve extends to $P \rightarrow \infty, T \rightarrow \infty$

We consider a single-component PVT system on either side of the liquid- gas or liquid-solid coexistence curve. The coexisting phases may be thought of as two equilibrium systems in contact with each other. We therefore have

$$T_1 = T_2$$

$$P_1 = P_2$$

$$\mu_1 = \mu_2$$

where the subscripts 1 and 2 refer to the two phases. From the relation $G(P, T, N) = \mu N$ we get

$$g_1(T, P) = g_2(T, P)$$

where g_1 , and g_2 are the Gibbs potential per particle in phases 1 and 2, respectively. The above relation must hold along the entire coexistence curve and hence

$$dg_1 = -s_1 dT + v_1 dP = dg_2 = -s_2 dT + v_2 dP$$

for differentials (dT, dP) along the coexistence curve. Thus

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{L_{12}}{T(v_1 - v_2)}$$

where L_{12} is the latent heat per particle needed to transform the system from phase 2 to phase 1. The above is known as the Clausius-Clapeyron equation. As a simple example, consider a transition from liquid to vapor with $v_1 \gg v_2$ and with $v_1 = k_B T/P$. Then

$$\frac{dP}{dT} \approx \frac{PL_{12}}{k_B T^2}$$

As a final topic we now briefly discuss the Gibbs phase rule. This rule allows one to limit the topology of a phase diagram on the basis of some very general considerations. Consider first a single-component PVT system with a

phase diagram as shown in Previous Figure For two-phase coexistence the chemical potential $\mu(P, T)$ must be the same in the two phases, yielding a curve in the $P - T$ plane. Similarly, three-phase coexistence implies that

$$\mu_1(P, T) = \mu_2(P, T) = \mu_3(P, T)$$

which, in general, will have a solution only at an isolated point, the triple point. Four-phase coexistence is ruled out unless there are hidden fields separate from the temperature and pressure.

One can also see that the critical point P_c, T_c will be an isolated point for a PVT system. At the critical point the liquid and vapor densities, or specific volumes, are equal. This condition yields a second equation,

$$v_1(P_c, T_c) = \left.\frac{\partial g_1}{\partial P}\right|_{P_c, T_c} = v_2(P_c, T_c) = \left.\frac{\partial g_2}{\partial P}\right|_{P_c, T_c}$$

which together with $\mu_1(P_c, T_c) = \mu_2(P_c, T_c)$ determines a unique point in the $P - T$ plane.

In a multicomponent system the situation is more complicated. We take as thermodynamic variables P, T , and $c_{ij}, i = 1, 2, \dots, r$, where c_{ij} is the mole fraction of constituent i in phase j of an r -component system. Suppose that there are s coexisting phases. Since

$$\sum_{i=1}^r c_{ij} = 1$$

there are $s(r - 1) + 2$ remaining independent variables. Equating the chemical potentials for the r components gives $r(s - 1)$ equations for these variables. If a solution is to exist, we must have at least as many variables as equations, that is,

$$s(r - 1) + 2 \geq r(s - 1)$$

or

$$s \leq r + 2$$

Therefore, at most, $r + 2$ phases can coexist in a mixture of r constituents.

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