

## 7. THERMODYNAMIC POTENTIALS, NATURAL VARIABLES & MAXWELL RELATIONS.

### Some More Thermodynamic Potentials.

The Gibbs Function, sometimes known as the Gibbs Free Energy or Gibbs Potential has already been introduced in its magnetic form when dealing with the thermodynamics of paramagnetism. There we defined the magnetic Gibbs function

$$G^{Mag} = U - TS - B_0 \mathcal{M}$$

Recall here that the third term on the RHS is the equivalent of  $PV$  for a gas system (ie. related to the work done) and they were used to obtain the Maxwell relation derived earlier

$$\left( \frac{\partial S}{\partial B_0} \right)_T = \left( \frac{\partial \mathcal{M}}{\partial T} \right)_{B_0}$$

$G^{Mag}$  is an example of what are known as Thermodynamic Potentials. Further examples of thermodynamic potentials that we have already come across are the internal energy,  $U$ , the sum of the individual energies of all of the constituent atoms of the system given in differential form by the thermodynamic identity;

$$dU = TdS - PdV$$

and the enthalpy,  $H$ , a potential function found useful in isobaric situations ie. where the pressure is constant, given by

$$H = U + PV.$$

The Gibbs function or Gibbs free energy for a fluid is

$$G = U - TS + PV$$

Note the plus sign for the  $PV$  term in this definition of  $G$  compared with  $B_0\mathcal{M}$ . This is because minus  $PdV$  is the work done by a fluid system whereas plus  $B_0d\mathcal{M}$  is the work done by the paramagnetic system. The Gibbs function is a very useful example of a thermodynamic potential that we may choose to define in order to simplify the analysis of a certain group of problems. A further potential that we choose to define that can be of great use in certain problems is the Helmholtz potential or Helmholtz free energy,  $F$ , defined as

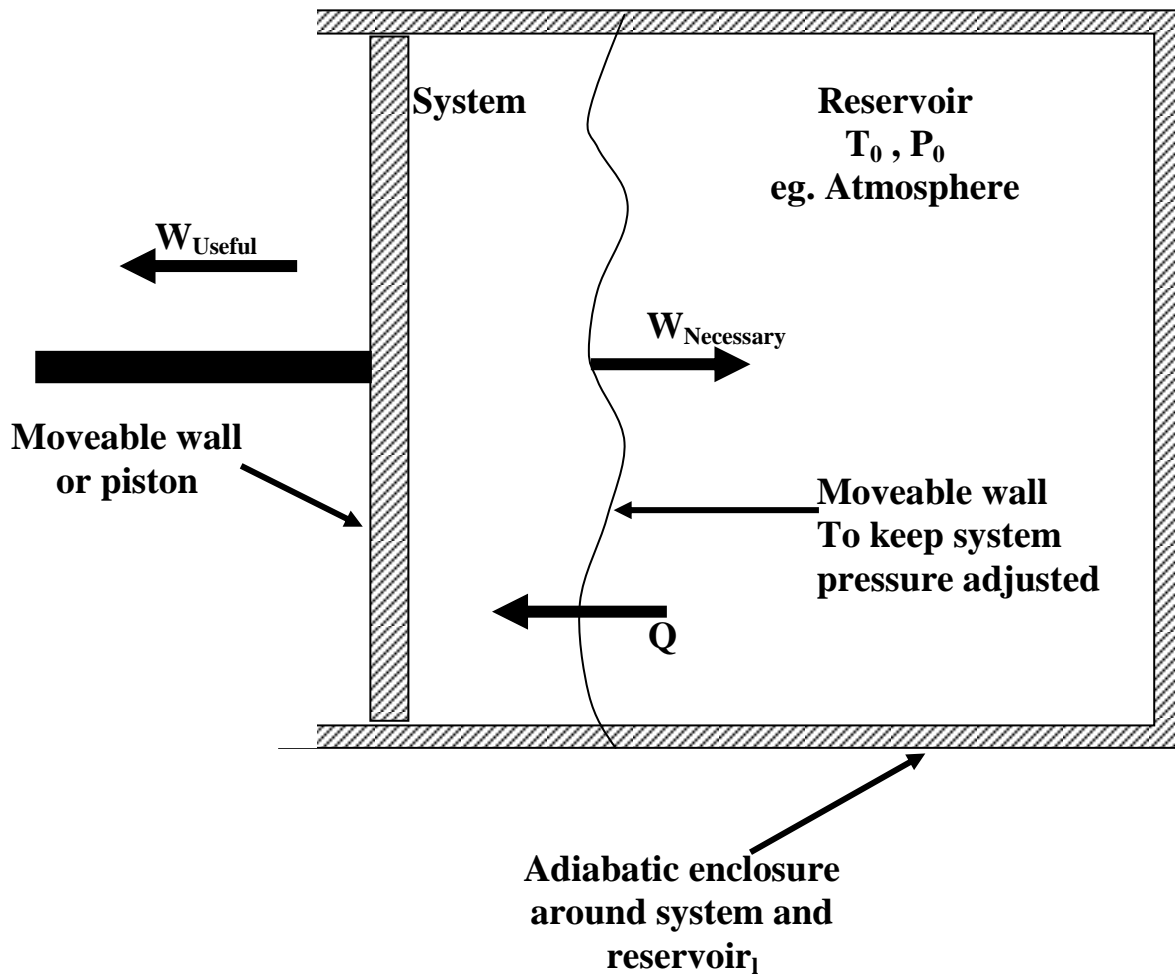
$$F = U - TS$$

Just like  $U$ ,  $H$  and  $S$  the new functions  $G$  and  $F$  are both **functions of state**. We can see this through their definitions which all involve functions of state only viz  $U$ ,  $T$ ,  $S$ ,  $P$  and  $V$  which have unique values for a particular equilibrium state.  $H$ ,  $G$  and  $F$  must also, therefore have unique values for any given equilibrium state. This in turn means that the change in  $G$  or  $F$ ,  $\Delta G$  and  $\Delta F$  respectively, are independent of path taken from initial to final state or equivalently that  **$dG$  and  $dF$  are both perfect differentials**. Their use becomes apparent when we are interested in systems that are not isolated but that are in contact with a reservoir such that observations/experiments are carried under conditions of;

1. **Constant temperature and pressure (Gibbs function) or**
2. **Constant temperature and volume (Helmholtz function )**

eg. systems open to the atmosphere in contrast to the isolated systems we have been interested in up until now.

It would be useful to find a way to characterize the equilibrium state of such open systems in the same way that we could for isolated systems, ie. We want to find a condition analogous to the maximum entropy condition that we may use for an isolated system that will be equally useful for these open systems.



We will consider the above system in local equilibrium (eg. we may allow chemical reactions to be taking place). The system can absorb heat and can **DO WORK ON** the surroundings and on the reservoir.

- (i) **Work on the reservoir** is  $W_{\text{Necessary}}$  in order that the laws of thermodynamics are maintained
- (ii) **Work on the surroundings** is  $W_{\text{Useful}}$

We can apply the first law to the system to obtain

$$\Delta U = \Delta Q + \Delta W = Q - W_{\text{Total}}$$

$$\Delta U = Q - W_{\text{Necessary}} - W_{\text{Useful}}$$

**Note the use of the sign convention for work done by the system.**

The system plus reservoir are thermally isolated by the adiabatic wall implying that for spontaneous changes  $\Delta S + \Delta S_0 \geq 0$

Where  $\Delta S$  is the entropy change of the system and  $\Delta S_0$  the entropy change of the surroundings

$$\Delta S_0 = \frac{-Q}{T_0}$$

$$\Delta S - \frac{Q}{T_0} \geq 0$$

$$T_0 \Delta S \geq Q = \Delta U + W_{Total} = \Delta U + W_{Useful} + W_{Necessary}$$

$$W_{Necessary} = P_0 dV$$

This allows us to write

$$-\Delta U + T_0 \Delta S - P_0 \Delta V \geq W_{Useful}$$

Or

$$-\Delta U + T_0 \Delta S \geq W_{Total}$$

The  $\Delta$  denotes changes in the **system variables**.

As  $T_0$  is held constant (the system is in thermal contact with a heat reservoir) we can write

$$-\Delta(U - TS) \geq W_{Total}$$

And because  $P_0$  is also held constant

$$-\Delta(U - TS + PV) \geq W_{Useful}$$

Now we see the point of  $F$  and  $G$  as we can write in succinct form

$$-\Delta F \geq W_{Total}$$

$$-\Delta G \geq W_{Useful}$$

This is the case of  $T = T_0$  and  $P = P_0$  throughout the change but we can let these differ between the initial and final states if required by the problem.

We can now restrict the problem a bit by giving the entire system rigid walls (constant volume) so that  $W_{Total}$  is zero.

$$W_{Total} = W_{Necessary} + W_{Useful} = 0$$

Or

$$W_{Necessary} = -W_{Useful}$$

This then tells us that

$$-\Delta F \geq 0 \quad \text{or in other words} \quad \Delta F \leq 0$$

**True equilibrium corresponds to a minimum in  $F = U - TS$** , which can be obtained by **lowering  $U$**  or by **increasing  $S$** . This of course corresponds to what we know already from classical physics and from the second law respectively.

**We are now able to make two important statements as follows;**

(i) **The equilibrium condition for a system held at constant volume and temperature  $T$  by a heat reservoir is that the Helmholtz free energy should be a minimum**

If only the outer wall around system plus reservoir is rigid then we can say that

$$W_{Useful} = 0$$

And this in turn allows us to make a statement about the Gibbs free energy

$$-\Delta G \geq 0 \quad \text{or in other words} \quad \Delta G \leq 0$$

(ii) **The equilibrium condition for a system held at constant pressure and temperature is**

**the Gibbs free energy should be a minimum**

**These two statements are forms of the second law, valid for non-isolated systems, which take account of entropy changes both in the system and in the surroundings.**

We now look at the natural variables on which  $F$  and  $G$  depend by looking first at their definitions and the incrementals that result from these definitions as has been done for other functions of state previously

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

As always we can find simplification in the above by invoking the 1<sup>st</sup> law in the form of the thermodynamic identity

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

And we have found the natural variables of  $F$  as the above implies that

$$F = F(V, T)$$

And as we have done previously we use the natural variables of  $F$  to write the incremental  $dF$  as

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

and by comparison with the earlier equation obtained via the thermodynamic identity

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

*We have found expressions for the thermodynamic parameters,  $P$  and  $S$  in terms of partial differentials of the Helmholtz free energy wrt one of its natural variables!*

It further follows that as  $dF$  is a perfect differential we may make use of the fact

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

Implying from our expressions for  $P$  and  $S$  that

$$\left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T \quad \text{which is a new **Maxwell Relation**}$$

We can carry out the same series of operations to investigate  $G$  and find a further Maxwell Relation

$$G = U - TS + PV$$

$$dG = dU - TdS - SdT + PdV + VdP$$

From the first law  $dU - TdS = -PdV$

and we simplify dG

$$dG = -SdT + VdP$$

We can see that the natural variables of  $G$  are  $T$  and  $P$  allowing us to write

$$G = G(T,P)$$

As previously we use the natural variables of  $G$  to write the incremental dG as

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

And by comparing again the coefficients of the increments of the natural variables in the two equations we find

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

*We have again found expressions for the thermodynamic parameters,  $S$  and  $V$  in terms of partial differentials of the Gibbs function wrt one of its natural variables!*

And again by making use of the fact that dG is a perfect differential we may write,

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T} \qquad \Rightarrow \qquad \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right)$$

This allows us to write down another **Maxwell Relation**

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



We have now explored four potentials, found their natural variables, and to go with them identified four Maxwell relations which we bring together here.:

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

$$H = U + PV \quad H(S, P) \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

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

$$G = U - TS + PV \quad G(T, P) \quad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

### General Observations Concerning Maxwell Relations, the Thermodynamic Potentials and Equations of State

Once we have defined any particular thermodynamic potential,  $\Phi$  say, then the incremental form for  $\Phi$  may be written completely generally as

$$d\Phi = \sum_i x_i dy_i$$

**Where  $x_i$  and  $y_i$  are known as conjugate pairs and the  $y_i$  are the natural variables of  $\Phi$ .**

In the same way that in mechanics the force acting multiplied by the incremental displacement in a mechanical system gives the incremental change in energy,  $U = Fdx$ , conjugate variables consist of a generalized force and a generalized displacement for example in a  $P$ - $V$ - $T$  system they would be pressure  $P$  as a generalized force and  $dV$  the generalized displacement and  $dW = -PdV$  then  $P$  and  $V$  are a pair of conjugate variables, similarly  $dQ = TdS$  and  $T$  and  $S$  are the generalized force and displacement and form a conjugate pair of variables

We see this for example in the case of the Gibbs function

$$dG = -SdT + VdP$$

with  $(S, T)$  and  $(V, P)$  being conjugate pairs and  $(T, P)$  the natural variables.

We have also seen that we can obtain thermodynamic parameters in terms of partial differentials of the potential wrt its natural variables;

$$x_j = \left( \frac{\partial \Phi}{\partial y_i} \right)_{y_{i \neq j}}$$

In the case of the Gibbs function we obtained  $S$  and  $V$ . These equations are equations of state since they specify values of functions of state in terms of the variation of the potential wrt its natural variable.

Finally where  $x_i$  and  $y_i$  are conjugate variables and  $y_i$  is a natural variable of the potential we obtained from cross differentials of the state equations

$$\left( \frac{\partial}{\partial x_j} \left( \frac{\partial \Phi}{\partial y_k} \right)_{y_{i \neq k}} \right)_{x_{i \neq j}} = \left( \frac{\partial}{\partial y_k} \left( \frac{\partial \Phi}{\partial x_j} \right)_{x_{i \neq j}} \right)_{y_{i \neq k}}$$

And from these we obtained the Maxwell relations.

## Applications of Maxwell Relations.

### (i) For fluids

To begin with we examine the specific heat of a fluid at constant volume, a quantity which involves the internal energy (recall that for  $C_p$  it was more natural to swap  $U$  for  $H$ )

$$U = U(T, V)$$

where the natural variables have been switched to  $T$  and  $V$  from  $S$  and  $V$ .

We have an expression for  $C_V$ , the specific heat at constant volume;  $C_V = \left( \frac{\partial U}{\partial T} \right)_V$

Which may be rephrased as  $dV = 0$  for  $C_V$  and therefore  $dU = TdS$ .

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

Importantly  $C_V$  can of course be measured;

Using the thermodynamic identity;

$$\left( \frac{\partial U}{\partial V} \right)_T = \frac{TdS - PdV}{dV} \quad \Rightarrow \quad \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P$$

We can rewrite this using one of the Maxwell relations;  $\left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T$  as;

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

### Example Ideal Gas

$$PV = nRT \quad \Rightarrow \quad \left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}$$

therefore

$$\left( \frac{\partial U}{\partial V} \right)_T = \frac{nRT}{V} - P = \frac{PV}{V} - P = 0$$

Ie.  $\Delta U$  on an isotherm is zero as was discovered some time back.

### Example: Magnet

$$U = U(\mathcal{M}, T)$$

$$\left( \frac{\partial U}{\partial T} \right)_{\mathcal{M}} = C_{\mathcal{M}} = \frac{dU}{dT} \Big|_{\mathcal{M}=\text{const}} = T \frac{dS}{dT} \Big|_{\mathcal{M}=\text{const}} + B_0 \frac{d\mathcal{M}}{dT} \Big|_{\mathcal{M}=\text{const}}$$

But

$$B_0 \frac{d\mathcal{M}}{dT} \Big|_{\mathcal{M}=\text{const}} = 0$$

And therefore

$$T \left. \frac{dS}{dT} \right|_{\mathcal{M}=\text{const}} = C_M$$

$$\left. \frac{dU}{d\mathcal{M}} \right|_{T=\text{const}} = T \left. \frac{dS}{d\mathcal{M}} \right|_{T=\text{const}} + B_0$$

$$\left( \frac{\partial U}{\partial \mathcal{M}} \right)_T = T \left( \frac{\partial S}{\partial \mathcal{M}} \right)_T + B_0$$

To go further we need a further Maxwell relation;

$$F = U - TS$$

$$dF = dU - TdS - SdT = TdS + B_0d\mathcal{M} - TdS - SdT$$

$$dF = -SdT + B_0d\mathcal{M}$$

$$-\left( \frac{\partial S}{\partial \mathcal{M}} \right)_T = \left( \frac{\partial B_0}{\partial T} \right)_{\mathcal{M}}$$

Using this in our earlier expression

$$\left( \frac{\partial U}{\partial \mathcal{M}} \right)_T = -T \left( \frac{\partial B_0}{\partial T} \right)_{\mathcal{M}} + B_0$$

And we have from previous work the Curie law  $B_0 = \frac{\mu_0 T}{CV} \mathcal{M}$

For a paramagnet

$$\left(\frac{\partial U}{\partial M}\right)_T = -\frac{T\mu_0\mathcal{M}}{CV} + B_0 = 0$$

Therefore we may conclude that

$$U^{Mag} = U(T)$$

**Example: Specific Heat Capacity at constant pressure.**

To find  $C_P$  we use  $S = S(V,T)$

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

Making a change  $dT$  at constant pressure

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

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

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

And therefore using the same Maxwell relation  $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$  and our previous

result for  $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$

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

We can use a cyclical relation and the reciprocal relation twice to obtain;

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

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

The volume expansion coefficient is given by

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

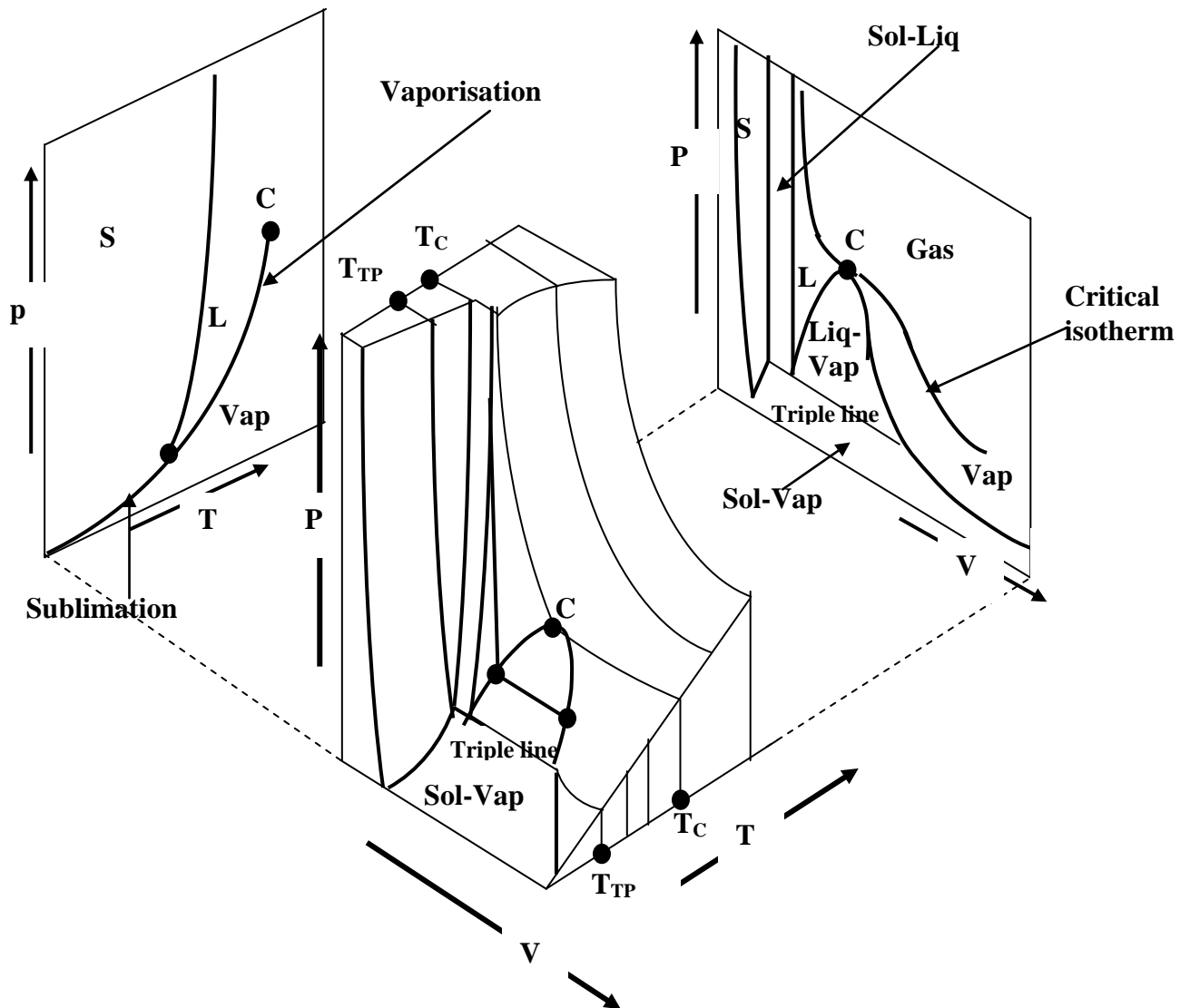
And the isothermal bulk modulus is given by

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

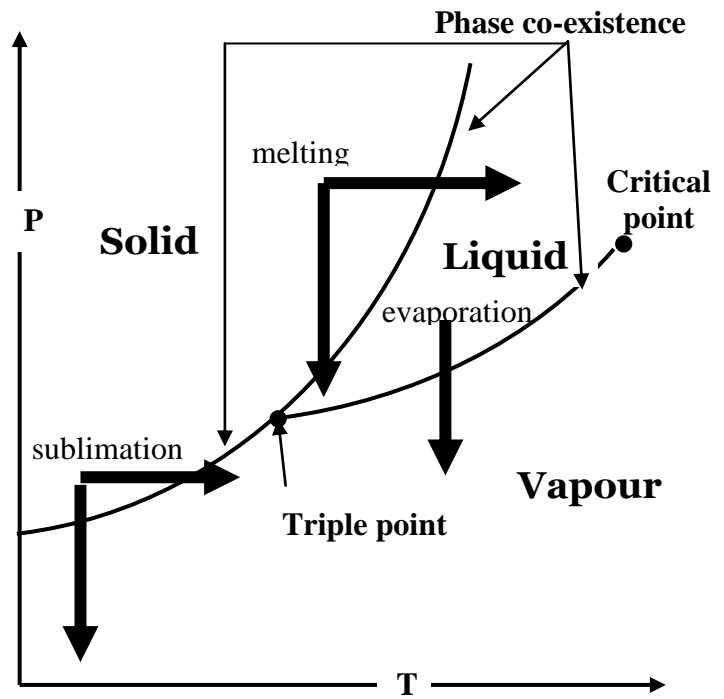
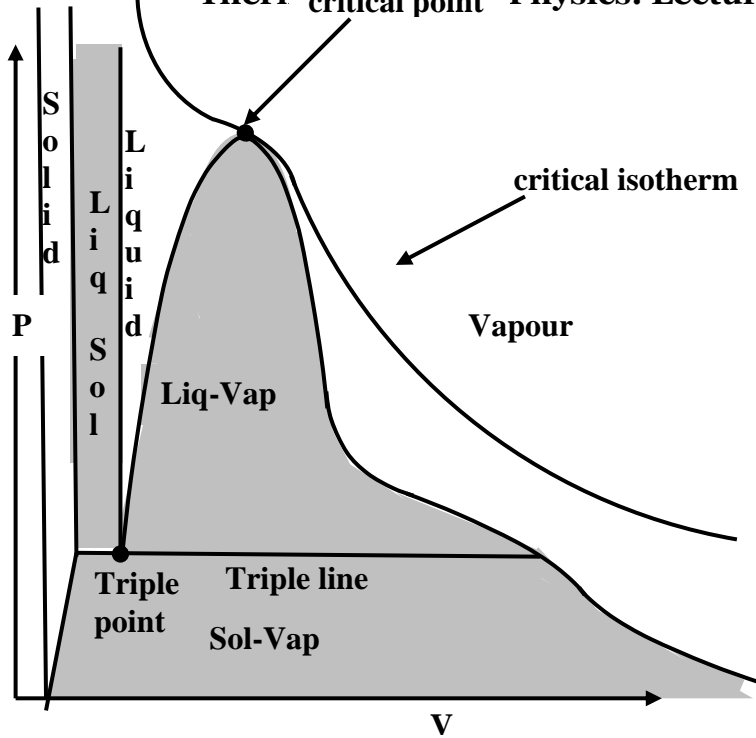
So we can finally obtain for the specific heat at constant volume the expression;

$$C_P = C_V + T \left(\frac{\kappa}{V}\right) (V\beta)^2 = C_V + TV\kappa\beta^2$$

## 8. PHASES AND PHASE CHANGE



Even for the simple  $P$ - $V$ - $T$  system of a fluid/gas we have so far in our use of  $P$ - $V$  or  $P$ - $T$  diagrams ignored the existence of different phases (eg. Solid, Liquid, Gas ). The full representation of this system's behavior including all phases can be represented on a very complex  $P$ - $V$ - $T$  phase diagram as shown above but we recall that only two of the three variables are independent and we can represent the above phase diagram on  $P$ - $V$  diagram at constant  $P$  or on a  $P$ - $T$  diagram at constant  $V$  and these would represent slices through the 3D phase diagram shown above at the chosen value of  $P$  or  $V$ . Examples are shown in the above diagram but we can represent the information in 2D  $P$ - $V$  or  $P$ - $T$  diagrams by projections on the  $PV$  or  $PT$  axes. Such diagrams are shown below.

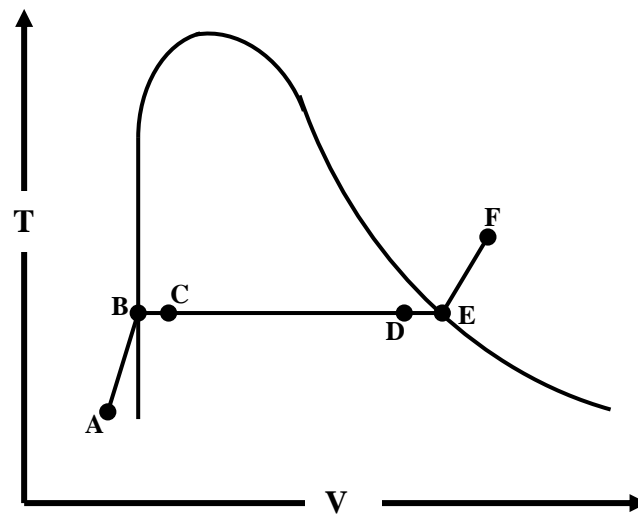
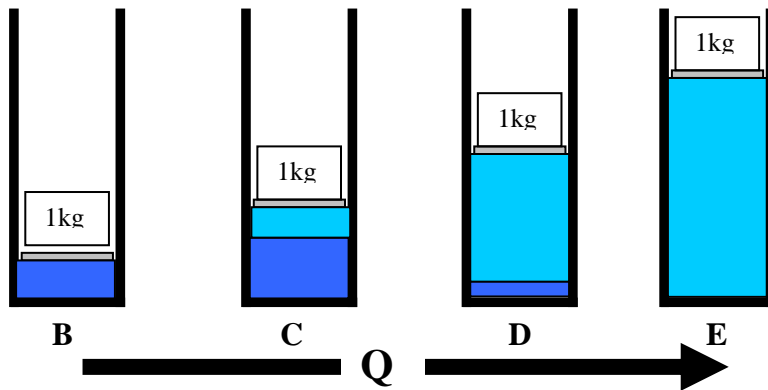


The  $P$ - $V$  and  $P$ - $T$  diagrams shown above are for fixed values of  $T$  and  $V$  respectively and show coexistence curves, lines of  $P$  and  $V$  which are boundaries between one phase and another. These boundaries are lines of co-existence and where the lines of co-existence meet is the triple point. The shaded area on the  $P$ - $V$  diagram is a region of co-existence. Some of the features of the  $P$ - $V$  diagram are that at higher volume the vapour phase appears. The solid phase exists at low volume where increase in pressure is not altering the volume reflecting the relative incompressibility of the solid phase. On the  $P$ - $T$  diagram a few phase changes are indicated. At low temperature and pressure the solid may pass directly into the vapour phase without passing through the liquid phase by increasing temperature or lowering pressure. This is known as sublimation.

There is a **critical temperature** above which compression produces no transition from a gas to a liquid or condensation. The **gas and the vapor become indistinguishable at the critical point** with the same density. Above the critical temperature we refer to a gas and below the critical temperature we refer to vapour. The liquid/vapour and solid/vapour co-existence regions are separated by the triple line on the  $P$ - $V$  diagram. Along that line as the volume is reduced (at constant pressure) the ratio of vapour:liquid:solid varies and in general the amount of each phase may vary from 0 to 100%.



We may now consider a simple process crossing the phase boundaries as represented in the diagram and on a T-V diagram shown below.



The process begins with a cylinder containing a fixed mass of liquid water. The pressure transmitted by a frictionless piston is maintained constant. Heating now begins and the water heats up to a state B on the liquid/vapour coexistence boundary where vaporisation just begins. The heating continues taking the system isothermally to C where there is a small amount of vapour and a large quantity of the water is present as liquid. Adding more heat will continue the isothermal process through the liquid/vapour co-existence region and as we proceed from left to right to state D. The ratio of vapour to liquid in terms of mass will continue to grow with the majority of the water as vapour at D. Continuing with the heating the isothermal process is still followed until the phase boundary at E where the water is now almost completely in vapour form. Any further heating will raise the temperature of the vapour to state F. All along the line BE the quantity of vapour varies continuously from 0% to 100%.

Along this line while the total volume varies the pressure and temperature remain the same for all states and we need something else to define a state at an arbitrary point on BE, the two phase region. This property is something called “**quality**” and is defined as the mass fraction in the vapour state, ie.

$$x = \frac{m_{vap}}{m_{vap} + m_{liq}}$$

The quality is related to the specific volume  $v$  as

$$v = (1 - x)v_{liq} + xv_{vap}$$

Or rewritten

$$x = \frac{v - v_{liq}}{v_{vap} - v_{liq}}$$

We can check that this is true by expressing the intensive properties  $v$  and  $x$  in terms of their extensive counterparts,  $V$  and  $M$

$$v = \frac{M_{liq}}{M_{liq} + M_{vap}} \frac{V_{liq}}{M_{liq}} + \frac{M_{vap}}{M_{liq} + M_{vap}} \frac{V_{vap}}{M_{vap}}$$

$$v = \frac{V_{liq}}{M_{liq} + M_{vap}} + \frac{V_{vap}}{M_{liq} + M_{vap}} = \frac{V_{liq} + V_{vap}}{M_{liq} + M_{vap}}$$

$$v = \frac{V_{tot}}{M_{tot}}$$

To express the quality,  $x$ , we may use any mass specific quantity ( $u$ ,  $h$ ,  $s$ ...).

Referring to the diagram, if volume is on a linear scale then at point D for example

$$x = \frac{BD}{BE}$$

## The role of the Gibbs function in describing phase changes.

Importantly, in the different phases the functions of state ( $U, S, F, G$ ) will have different values and vary in mathematically different ways and this we now consider in order to obtain some understanding of the process of phase change.

Consider that the substance has a total mass  $M$  and it co-exists in two phases eg. vapour phase and liquid phase. We may then straightforwardly begin our analysis by asserting

$$M = M^{\mathcal{V}} + M^{\mathcal{L}} = \text{constant}$$

As noted we need to account for different Gibbs functions for each phase,  $G^{\mathcal{V}}$  and  $G^{\mathcal{L}}$ . We let  $g^{\mathcal{V}}$  and  $g^{\mathcal{L}}$  be the Gibbs functions per unit mass or specific Gibbs function for each phase.

$$G = M^{\mathcal{V}} g^{\mathcal{V}} + M^{\mathcal{L}} g^{\mathcal{L}}$$

As we have already seen in our discussion of the Gibbs function, the condition for equilibrium at fixed  $P$  and  $T$  is that the Gibbs function must be minimized ie.  $dG = 0$  for any change including a change from vapour to liquid (condensation) or vice versa (evaporation). This is then the requirement that

$$dG = d(M^{\mathcal{V}} g^{\mathcal{V}} + M^{\mathcal{L}} g^{\mathcal{L}})$$

$$dG = g^{\mathcal{V}}(T, P) dM^{\mathcal{V}} + g^{\mathcal{L}}(T, P) dM^{\mathcal{L}}$$

We have conservation of mass

$$dM = dM^{\mathcal{V}} + dM^{\mathcal{L}} = 0 \quad \Rightarrow \quad dM^{\mathcal{V}} = -dM^{\mathcal{L}}$$

Giving

$$dG = (g^{\mathcal{V}} - g^{\mathcal{L}})dM^{\mathcal{V}} = 0 \quad \text{for any } dM^{\mathcal{V}}$$

We then have the equilibrium condition for the co-existence of the phases that

$$g^{\mathcal{V}}(T, P) = g^{\mathcal{L}}(T, P)$$

along the liquid/vapour co-existence line in the  $P$ - $V$  diagram and similarly

$$g^{\mathcal{L}}(T, P) = g^{\mathcal{S}}(T, P)$$

and

$$g^{\mathcal{V}}(T, P) = g^{\mathcal{S}}(T, P)$$

Along their respective co-existence curves, the melting and sublimation curves respectively.

The  $g(T, P)$  are three different functions and the above condition is only true along the co-existence lines and furthermore at the triple point;

$$g^{\mathcal{V}}(T, P) = g^{\mathcal{L}}(T, P) = g^{\mathcal{S}}(T, P)$$

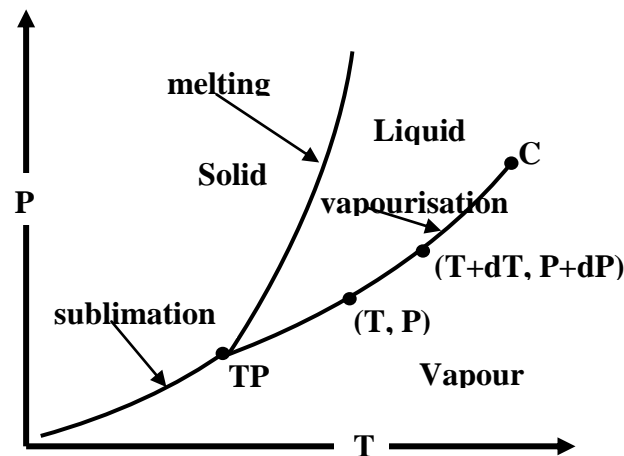
At a unique value of  $T$  and  $P$  where the triple point is a uniquely defined reference state. This leads to the **Gibbs phase rule** for a simple substance eg  $PVT$  fluid that only three phases may coincide.

### First Order Phase Changes.

Examples of first order phase changes are the liquid-vapour transition, the liquid-solid transition. Each of these transitions involves;

- (i) A change of density or specific volume.
- (ii) A Latent heat

We may focus upon the vapour liquid transition using the  $P$ - $T$  diagram as shown below



The line joining the triple point to the critical point is a co-existence curve and all along this curve we have the condition  $g^{\mathcal{L}}(T, P) = g^{\mathcal{V}^o}(T, P)$  so at nearby points on that curve

$$g^{\mathcal{L}}(T + dT, P + dP) = g^{\mathcal{V}^o}(T + dT, P + dP)$$

We will find how  $dT$  and  $dP$  are related ie. we find the slope of the co-existence curve as follows;

Using Taylor's theorem to rewrite the above

$$g^{\mathcal{L}}(T, P) + \left(\frac{\partial g^{\mathcal{L}}}{\partial T}\right)_P dT + \left(\frac{\partial g^{\mathcal{L}}}{\partial P}\right)_T dP + \dots = g^{\mathcal{V}^o}(T, P) + \left(\frac{\partial g^{\mathcal{V}^o}}{\partial T}\right)_P dT + \left(\frac{\partial g^{\mathcal{V}^o}}{\partial P}\right)_T dP + \dots$$

Re-arrange so that  $dT$  and  $dP$  appear on different sides of the equation

$$dT \left\{ \left(\frac{\partial g^{\mathcal{L}}}{\partial T}\right)_P - \left(\frac{\partial g^{\mathcal{V}^o}}{\partial T}\right)_P \right\} = dP \left\{ -\left(\frac{\partial g^{\mathcal{L}}}{\partial P}\right)_T + \left(\frac{\partial g^{\mathcal{V}^o}}{\partial P}\right)_T \right\}$$

We can now use previously discovered thermodynamic relations,

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad s = -\left(\frac{\partial g}{\partial T}\right)_P$$

And

$$V = \left( \frac{\partial G}{\partial P} \right)_T \qquad v = \left( \frac{\partial g}{\partial P} \right)_T$$

To re-write

$$dT(s^{\mathcal{V}} - s^{\mathcal{L}}) = dP(v^{\mathcal{V}} - v^{\mathcal{L}})$$

And

$$\frac{dP}{dT} = \frac{s^{\mathcal{V}} - s^{\mathcal{L}}}{v^{\mathcal{V}} - v^{\mathcal{L}}}$$

We can consider taking a fixed quantity of matter from the vapour state to the liquid state in a phase transition at the phase boundary. Such a transition will involve an increase in order with the accompanying decrease in entropy.

Latent heats are normally given as positive quantities and in this case (vapour – liquid) we need  $\Delta s$  to be negative as order has increased and therefore

$$\Delta Q_R = T\Delta S = -\text{Latent Heat} - \mathcal{L}_{\mathcal{V} \rightarrow \mathcal{L}}$$

$$\Delta Q_R = T\Delta s = -\mathcal{L}_{\mathcal{V} \rightarrow \mathcal{L}}$$

Where  $\mathcal{L}_{\mathcal{V} \rightarrow \mathcal{L}}$  is the latent heat of condensation (vapour to liquid) per unit mass and we need the minus sign to ensure that the change in entropy is negative.

But we have just found an expression involving the entropy change in such a phase transition and

$$s^{\mathcal{L}} - s^{\mathcal{V}} = -\frac{\mathcal{L}_{\mathcal{V} \rightarrow \mathcal{L}}}{T}$$

$$\frac{dP}{dT} = \frac{\ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}}}{T(v^{\mathcal{V}^{\circ}} - v^{\mathcal{L}})}$$

This is the **Clausius Clapeyron Equation** for the phase boundary

While the **Clausius Clapeyron equation holds for any phase boundary** we may explore the vapour/liquid boundary or vaporization curve and obtain a simplified expression for this boundary where normally  $v^{\mathcal{V}^{\circ}} \gg v^{\mathcal{L}}$  and it is a good approximation to treat the vapour as an ideal gas. Consider 1 mole and let  $\ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}}$  and  $v^{\mathcal{V}^{\circ}}$  be the latent heat and volume per mole.

$$v^{\mathcal{V}^{\circ}} = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}}}{RT^2 / P} = \frac{\ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}} P}{RT^2}$$

We can take  $\ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}}$  as a constant over a small temperature/pressure range

$$\frac{dP}{P} = \ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}} \frac{dT}{RT^2}$$

Integrating

$$\ln P = -\ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}} \frac{1}{RT} + \text{const}$$

which we may rewrite as

$$\ln \frac{P}{P_0} = -\ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}} \frac{1}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

Where  $\text{const} = \ln P_0 + \frac{\ell_{\mathcal{V}^{\circ} \rightarrow \mathcal{L}}}{T_0}$

Where  $P_0$  and  $T_0$  are any known pressure, temperature pair along the liquid-vapor curve.

Finally we obtain an alternative expression for the Clausius Clapeyron equation **at the liquid/vapour boundary**

$$P = P_0 \exp\left(-\frac{\ell_{\mathcal{V}^o \rightarrow \mathcal{L}}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$$

This relates pressure and temperature along the liquid/vapour boundary ie. it gives the relation of the boiling point of the substance as pressure is varied where for example, in the case of water, when  $P = P_0$  is 1 atmosphere we have  $T = T_0 = 373.15$  K. If we use these values of  $T_0$  and  $P_0$  in the equation we can find the boiling point,  $T$  at any given pressure  $P$ .

We note here that the same approximations may be made at the solid/vapour boundary or sublimation curve with an identical relation between pressure and temperature along this boundary  $\ln P = -\ell_{\mathcal{S} \rightarrow \mathcal{V}^o} \frac{1}{RT} + const$ . If we note that at

the triple point sublimation and vaporisation curves meet then we can equate the two curves to find the triple point pressure or temperature if the latent heats are known eg. At the triple point we require;

$$\ln P_{TP} = -\ell_{\mathcal{V}^o \rightarrow \mathcal{L}} \frac{1}{RT_{TP}} + C_1 = -\ell_{\mathcal{V}^o \rightarrow \mathcal{S}} \frac{1}{RT_{TP}} + C_2$$

The Clausius Clapeyron equation relates to any phase change and we could have asked about the liquid-solid transition again involving an increase in order and therefore a decrease in entropy whence the same arguments give the Clausius Clapeyron equation at that boundary as

$$\frac{dP}{dT} = \frac{\ell_{\mathcal{L} \rightarrow \mathcal{S}}}{T(v^{\mathcal{L}} - v^{\mathcal{S}})}$$

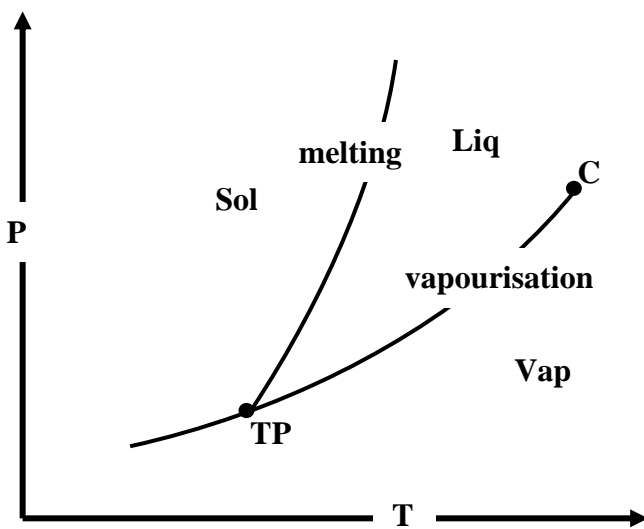
We cannot here use the approximations as the specific volumes are not very different and we cannot treat the liquid as an ideal gas.



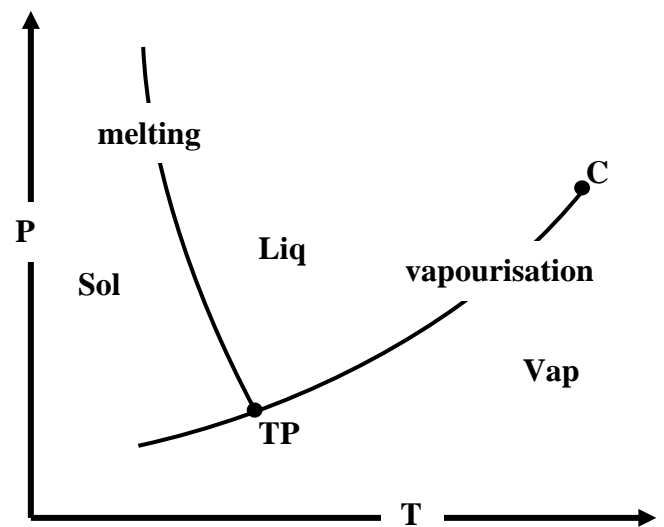
Most materials contract upon freezing and  $v^{\mathcal{F}} < v^{\mathcal{L}}$  which involves a positive slope

$\frac{dP}{dT}$  on the  $PT$  diagram for the melting curve. We know, however, that water behaves in an odd fashion where it expands on freezing and  $v^{\mathcal{F}} = 1.09 \text{ cm}^3 \text{ g}^{-1} < v^{\mathcal{L}} = 1.00 \text{ cm}^3 \text{ g}^{-1}$ . The latent heat of melting is  $333 \text{ J g}^{-1}$ . With this data we may calculate the slope of the melting curve

$$\frac{dP}{dT} = \frac{333 \text{ J g}^{-1}}{273.15(1.00 - 1.09) \text{ cm}^3 \text{ g}^{-1}} = -13.54 \text{ J cm}^{-3} \text{ K}^{-1} = -13.54 \times 10^6 \text{ Pa K}^{-1}$$



P-T diagram for typical substance



P-T diagram for water

### Higher order phase changes.

We need to ask now why these phase changes are called first order phase changes?

We have been using the condition  $g^{\mathcal{V}^o}(T, P) = g^{\mathcal{L}}(T, P)$  in the previous discussion but we also have

$$s^{\mathcal{V}^o} = - \left( \frac{\partial g^{\mathcal{V}^o}}{\partial T} \right)_P \neq s^{\mathcal{L}} = - \left( \frac{\partial g^{\mathcal{L}}}{\partial T} \right)_P$$

$$v^{\mathcal{V}^o} = \left( \frac{\partial g^{\mathcal{V}^o}}{\partial P} \right)_T \neq v^{\mathcal{L}} = \left( \frac{\partial g^{\mathcal{L}}}{\partial P} \right)_T$$

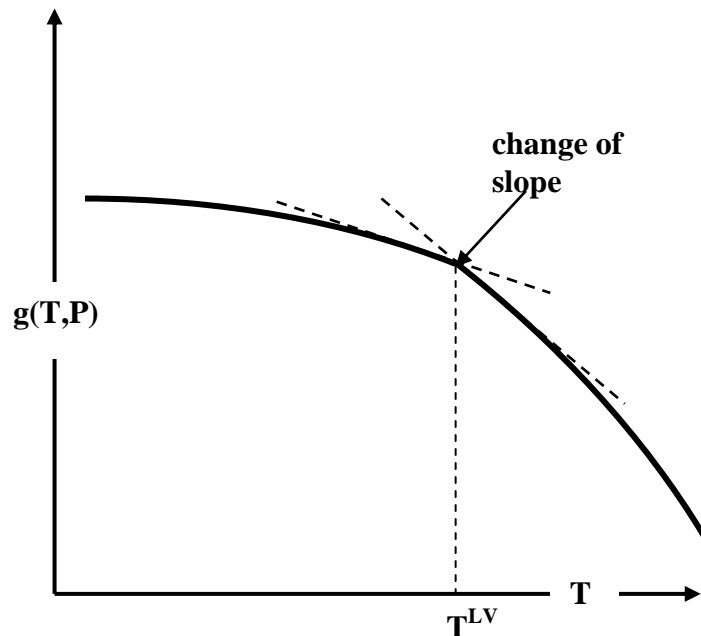
In other words **g is continuous at the transition but its first derivative is not continuous** but has a finite jump in value at the transition ( $s^{\mathcal{V}^o} - s^{\mathcal{L}} \neq 0$  and  $v^{\mathcal{V}^o} - v^{\mathcal{L}} \neq 0$ ).

We also have

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\left(\frac{\partial s}{\partial T}\right)_P = -\frac{c_P}{T} < 0$$

and

$$\left(\frac{\partial^2 g}{\partial P^2}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_T < 0$$



The above sketch shows how we would expect  $g$  to behave as temperature is increased to above the boiling point.

Other types of phase change exist where the first derivatives are continuous but the second derivatives are discontinuous and this would show up in discontinuities in measurable quantities such as

**$c_P$  (specific heats),**

**$\beta$  (thermal expansion coefficients),**

**$K$  (compressibility).**

Which involve the second derivatives as seen below.

Such transitions are called second order transitions eg. Ferromagnetic transitions, superfluid transition in  $^4\text{He}$  and specific heat anomalies are the signature of such transitions.

The second derivative of  $g$  can be related to experimental quantities as follows;

$$c_P = T \left( \frac{\partial s}{\partial T} \right)_P = -T \left( \frac{\partial^2 g}{\partial T^2} \right)_P$$

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P = \frac{1}{v} \frac{\partial^2 g}{\partial T \partial P}$$

$$K = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T = -\frac{1}{v} \left( \frac{\partial^2 g}{\partial P^2} \right)_T$$

All of these quantities will act as indicators of second order phase transitions when showing a discontinuity at the phase transition temperature, They also show some very interesting and singular behaviour. If the transition temperature is at  $T_C$  then it is found that;

$$c_P = (T - T_C)^{-\alpha} \qquad T \approx T_C$$

$$K = (T - T_C)^{-\gamma} \qquad T \approx T_C$$

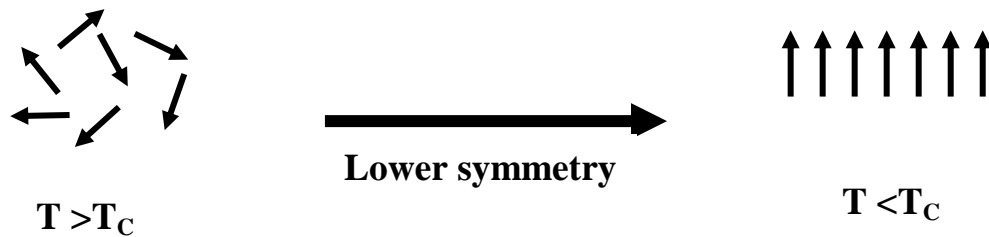
Other examples may be found, for example in a ferromagnet the magnetic moment behaves as

$$\mathcal{M} = (T_C - T)^\beta \qquad \text{and the susceptibility is} \qquad \chi_M = (T - T_C)^{-\gamma}$$

The quantities,  $\alpha$ ,  $\beta$ ,  $\gamma$  are known as **CRITICAL EXPONENTS**.

At a second order phase transition the symmetry of the system changes. The discovery of note is that the exponents  $\alpha$ ,  $\beta$ ,  $\gamma$  are independent of material and dependent on the dimensionality and nature of the symmetry change!

**eg. Ferromagnetic phase transition.**



This ubiquitous property of critical exponents is known as **UNIVERSALITY**.

The research methods that have been developed in this area of condensed matter physics has since been taken over by elementary particle physicists and has aided advances in that very different field of study!

## 9. THE THIRD LAW OF THERMODYNAMICS

We have already seen how we may define a new state function called entropy and that entropy changes are measured by

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ_R}{T}$$

And with  $\Delta Q_R = T\Delta S$  we have a further definition of heat capacity;

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial S}{\partial \ln T} \right)_V \quad C_P = T \left( \frac{\partial S}{\partial T} \right)_P = \left( \frac{\partial S}{\partial \ln T} \right)_P$$

We may integrate either of these to find  $S$  as a function of  $T$

$$S(T) = \int \frac{C_V}{T} dT$$

We could try to find  $S$  by making the integral into a definite integral

$$S(T) - S(T_0) = \int_{T_0}^T \frac{C_V}{T} dT \quad \Rightarrow \quad S(T) = S(T_0) + \int_{T_0}^T \frac{C_V}{T} dT$$

In other words we obtain  $S(T)$  to some arbitrary constant  $S(T_0)$  and we could make the reference temperature  $T_0$  absolute zero.

We may now look briefly at the third law of thermodynamics which attempts (among other things) to give information about the entropy at absolute zero,  $S(0)$ .

This is again, a law that doesn't have a satisfying expression in mathematical terms and it is embodied in several statements. We can list these first and then try to examine what they are telling us.

**(i) Macroscopic Statement.**

*It is impossible to reduce the temperature of a macroscopic system to absolute zero in a finite number of steps or processes.*

**(ii) Nernst Statement or Nernst heat theorem (1906)**

*The entropy difference between two distinct equilibrium states of a substance tends to zero at absolute zero.*

*(The entropy of all equilibrium states tends to the same value at absolute zero!)*

The distinct equilibrium states correspond to states whose difference is defined by some difference in an external parameter. For the examples we have examined so far this could be an ideal gas and the pressure or a paramagnetic salt and the applied external field ( $P$ ,  $B_0$  etc.). Nernst was the first to make some statement on the third law and he arrived at his statement by studying chemical reactions and electrolytic cells. He was measuring the change in enthalpy,  $\Delta H$  which determines the heat of reaction (exothermic, endothermic etc) and the change in Gibbs function,  $\Delta G$ , which determines in which direction a reaction will go.

Recalling that  $G = H - TS$  we have at constant  $T$

$$\Delta G = \Delta H - T\Delta S$$

As  $T \rightarrow 0$  then we should expect  $\Delta G \rightarrow \Delta H$ . His experiments confirmed this but also showed that  $G$  and  $H$  approached each other asymptotically. This implied that  $\Delta S \rightarrow 0$  as  $T \rightarrow 0$  and Nernst's statement can also be written;

*Near absolute zero all reactions in a system in internal equilibrium take place with no change in entropy.*

**(iii) Planck Statement (1911)**

*The entropy of all perfect crystals is the same at absolute zero and may be taken as zero.*

By perfect crystal a perfect repeating lattice of atoms is envisaged. The Planck statement is nowadays extended to all systems in equilibrium as follows;

*The entropy of all systems in internal equilibrium is the same at absolute zero and may be taken to be zero.*

By internal equilibrium we refer back to a previous discussion on the thermodynamic potentials where we find that for a given circumstance the appropriate potential is at a minimum eg.  $P$  and  $T$  being constant would require that  $G$  is at a minimum. An objection may be raised to this designation of zero for the entropy of all systems at absolute zero as it implies that the ground state is non-degenerate and  $\Omega = 1$  if we are to treat the statistical Boltzmann interpretation ( $S = k_B \ln \Omega$ ) as a correct interpretation of the physical origin of entropy. For instance if a perfect crystal is composed of  $N$  atoms of nuclear spin  $I$  then in the absence of a magnetic field to lift the degeneracy the ground state has a degeneracy of  $(2I + 1)$  and the entropy according to Boltzmann should be

$$S = Nk_B \ln(2I + 1)$$

right down to absolute zero.

We may get around this contradiction by noting that the individual components of the system are able to exchange energy with one another through spin-interaction of their dipole magnetic fields and this creates a magnetic spin wave whose ground state is non-degenerate at much lower temperatures where  $k_B T \ll E_{\text{int}}$ . ie. As absolute zero is approached there is a collective state, the spin wave, into which all spins are incorporated, this state being non-degenerate (the specification of one spin effectively specifies all the others that have a phase relation to it).

**(iv) Simon Statement.**

*The entropy component from each aspect of a system which is in internal thermodynamic equilibrium tends separately, to zero at absolute zero.*

By “aspect” Simon was referring to one of the subsystems of the components of the main system eg. the electron spin component to the entropy, the lattice component, the nuclear spin component.....Recalling that entropy is additive (it is an extensive property of a system) we require this to be the case for the total entropy to go to zero.

$$S_{\text{Tot}} = S_1 + S_2 + \dots S_i$$

Where the subscript I refers to a particular aspect.

All of the above statements are equivalent ways of expressing the third law.

We may also gain insight into the meaning of the third law by considering the Boltzmann's statistical description of entropy;

$$S = k_B \ln \Omega$$

Where  $\Omega$  is the number of distinct microscopic arrangements, of the entities, that give rise to the particular equilibrium macrostate whose entropy we are interested in. For all physical systems, as  $T \rightarrow 0$  the system falls into its ground state, **a unique lowest energy state**. As this happens  $\Omega \rightarrow 1$  and this means that  $S \rightarrow 0$ .

The third law has important consequences that may be experimentally observed because it requires that  $\Delta S$  tends to zero at absolute zero (Nernst statement). Any physical quantity whose value depends on the change in entropy will therefore be affected by the third law at very low temperatures and we now look at a few such quantities;

a) **Specific Heat Capacity tends to zero as  $T \rightarrow 0$ .**

Using our definitions of heat capacity;

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

Clearly  $\Delta \ln T \rightarrow -\infty$  as  $T \rightarrow 0$  so it is essential that  $C_V \rightarrow 0$  in order that  $\Delta S \rightarrow 0$ . An identical argument applies to  $C_P$

For most **solids** it is found that at **low temperature**

$$C_P = aT + bT^3$$



Where the first term is due to an electron contribution (heat absorption serving to raise the average energy of the electron distribution) and the second to a lattice contribution (heat absorption contributing to the atomic vibrations of the solid).

**b) Thermal expansion goes to zero at low temperatures.**

Taking the definition of thermal expansion

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

This can be re-written in terms of entropy using a Maxwell relation

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

giving

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

The Nernst formulation tells us that entropy change  $\Delta S \rightarrow 0$  as  $T \rightarrow 0$  therefore implying that  $\beta \rightarrow 0$  as  $T \rightarrow 0$ .

**c) Curies Law breaks down at low temperature.**

We saw earlier for paramagnets the Curie law which states

$$\chi = \frac{C}{T}$$

The third law carries the implication that  $\left(\frac{\partial S}{\partial B_0}\right)_T \rightarrow 0$  at low temperatures. To show that the two are incompatible assume that Curies law holds right down to absolute zero

$$\frac{\mu_0}{V} \mathcal{M} = \chi(T) B_0$$

$$\mathcal{M} = \frac{V\chi(T)}{\mu_0} B_0$$

Using a Maxwell relation we can obtain a link between  $\mathcal{M}$  and  $\left(\frac{\partial S}{\partial B_0}\right)_T$

$$\left(\frac{\partial \mathcal{M}}{\partial T}\right)_{B_0} = \left(\frac{\partial S}{\partial B_0}\right)_T$$

Putting these together we have

$$\left(\frac{\partial \mathcal{M}}{\partial T}\right)_{B_0} = \left(\frac{\partial S}{\partial B_0}\right)_T = \frac{VB_0}{\mu_0} \left(\frac{\partial \chi}{\partial T}\right)_{B_0} = \frac{VB_0 C}{\mu_0} \frac{\partial}{\partial T} \frac{1}{T} = -\frac{VB_0 C}{\mu_0} \frac{1}{T^2}$$

$$\left(\frac{\partial S}{\partial B_0}\right)_T = -\frac{VB_0 C}{\mu_0} \frac{1}{T^2}$$

As  $T \rightarrow 0$  the  $\Delta S$  associated with  $\Delta B_0$  must vanish by the Nernst statement which the above equation does not thereby implying that the use of the Curie law as  $T \rightarrow 0$  is mistaken and rather we should have

$$\left(\frac{\partial \chi}{\partial T}\right)_{B_0} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$

Therefore we have deduced from the third law that the Curie law,  $\chi = \frac{C}{T}$ , cannot hold down to  $T = 0$

**d) Ideal gases are a fiction at  $T = 0$** 

We have used the ideal monatomic gas over and over to act as the paradigm system allowing us to obtain tractable and very useful results. However we have already destroyed one of those results at absolute zero namely the finding that  $C_P - C_V = R$  for 1 mole of gas. We have seen that both heat capacities go to zero negating this result. Further problems arise for the ideal gas when we consider the entropy of an ideal gas

$$S = C_V \ln T + R \ln V + \text{const}$$

As  $T \rightarrow 0$ , using this equation, we find  $S = -\infty$  clearly in contradiction to the third law.

**e) First order phase changes**

In deriving the Clausius Clapeyron equation for the coexistence line of two phases we found

$$\frac{dP}{dT} = \frac{s^V - s^L}{v^V - v^L} = \frac{\Delta s}{\Delta v}$$

As  $T \rightarrow 0$ , according to the Nernst statement,  $\Delta s \rightarrow 0$ . This implies that as  $T \rightarrow 0$ ,

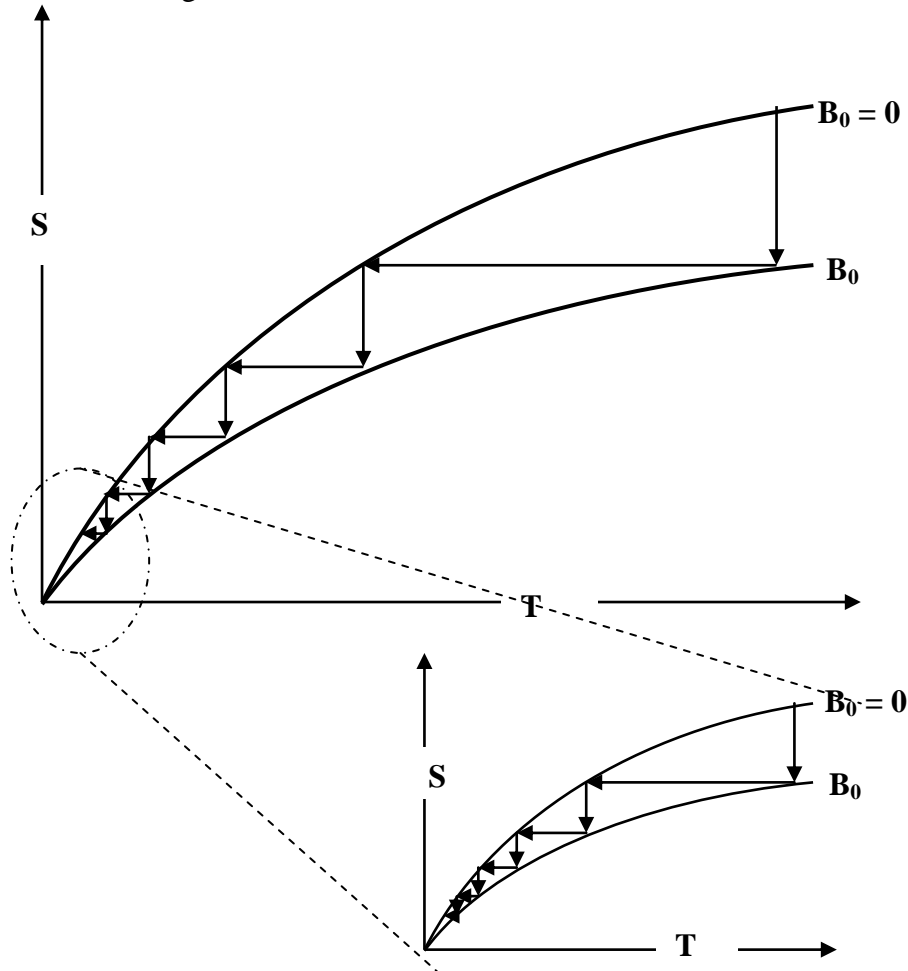
$\frac{dP}{dT} \rightarrow 0$  ie. for a coexistence curve that extends to  $T = 0$  the slope must vanish at  $T =$

0.

The final implication of the third law is that

**f) It is impossible to reach absolute zero.**

A physical argument can be given for the statement that absolute zero cannot be reached in a finite number of steps. We do this by considering the paramagnetic cooling shown in the diagrams below.



The entropy vs temperature curves with and without an applied external field is shown with the applied field curve having the lower entropy (or higher order due to electron spin alignment). The lower diagram demonstrates that even as in the upper diagram we approach  $T = 0$  after five steps, by blowing up the near origin region in the lower curve we see that the number of steps required is not reduced and that we may continue this argument ad infinitum. All that is being relied upon here is the form of  $S$  vs  $T$  with both going through the origin at  $S = T = 0$ . This is not in fact necessary to this argument as long as the Nernst statement  $\Delta S \rightarrow 0$  as  $T \rightarrow 0$  is satisfied.

There exist lengthy formal proofs of the equivalence of the Nernst and finite steps (macroscopic) forms of the statement but the above consideration is sufficient to see that they are equivalent requirements.

We can conclude by looking at the Carnot engine to see if it has anything to say about the third law. We recall the efficiency of the Carnot engine

$$\eta_C = 1 - \frac{T_2}{T_1}$$

If the temperature of the lower reservoir is absolute zero the efficiency of the Carnot engine is 1 or 100%. In other words we would get perfect conversion of heat into work contrary to the Kelvin-Planck statement of the second law. We could ask then

### **Is the Third Law yet another statement of the Second Law or is it a separate law in its own right?**

The third law is saved because it is not sensible to consider the low temperature reservoir to be at 0 K as the Carnot cycle requires that you perform an isothermal process at this temperature. However, once a system is at absolute zero it's thermodynamic state cannot be changed without warming it!

**The conclusion must be that the Third Law continues to exist  
as a law of thermodynamics in it's own right.**