6. Phase Equilibrium in Simple Systems; the Phase Rule

From now on we will be making use of the concept of the <u>free energy per mole</u> (the ***chemical potential*** μ).

6.1 The Equilibrium Condition

For a system in equilibrium, the chemical potential of each constituent must be the same everywhere in the system.
If there are several phases present, i.e., several phases in equilibrium with one another, ***the chemical potential of each substance must have the same value in every phase*** in which that substance appears.

For a system of one component,

$$\mu = \boldsymbol{G}/n$$

so that, $\mathrm{d}\boldsymbol{G} = -\boldsymbol{S}\mathrm{d}T + V\mathrm{d}p$ becomes

$$\mathrm{d}\mu = -\boldsymbol{S}_m\,\mathrm{d}T + V_m\,\mathrm{d}p$$

where the subscript "$_m$ " denotes the molar (for one mole) value.

$(\partial\mu/\partial T)_p = -\boldsymbol{S}_m$ $\qquad$ $(\partial\mu/\partial p)_T = V_m$

For the 3 phases of a single substance,

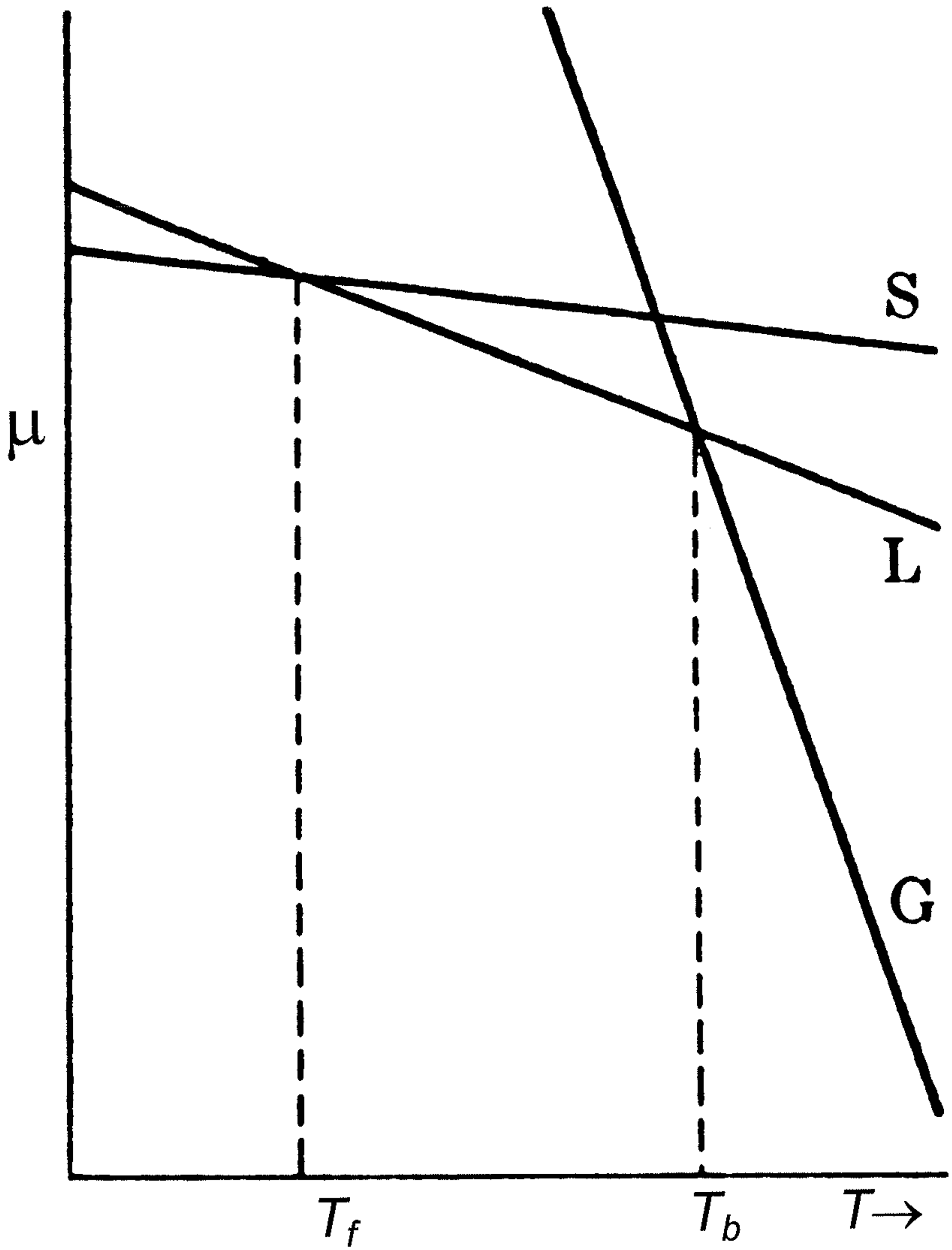
$$(\partial\mu_{solid}/\partial T)_p = -\boldsymbol{S}_{m,solid}$$

$$(\partial\mu_{liquid}/\partial T)_p = -\boldsymbol{S}_{m,liquid}$$

$$(\partial\mu_{gas}/\partial T)_p = -\boldsymbol{S}_{m,gas}$$

At any temperature,

$$\boldsymbol{S}_{m,gas} \gg \boldsymbol{S}_{m,liquid} > \boldsymbol{S}_{m,solid}$$



μ versus T at constant pressure

The thermodynamic conditions for equilibrium between phases at constant pressure are:

Solid and liquid coexist at the intersections of the curves, at which temperatures,

$$\mu_{solid} = \mu_{liquid} \quad at\ T_f$$
$$\mu_{liquid} = \mu_{gas} \quad at\ T_b$$

Below T_f the solid has the lowest chemical potential.

Between T_f and T_b the liquid has the lowest chemical potential.

Above T_b the gas has the lowest chemical potential.

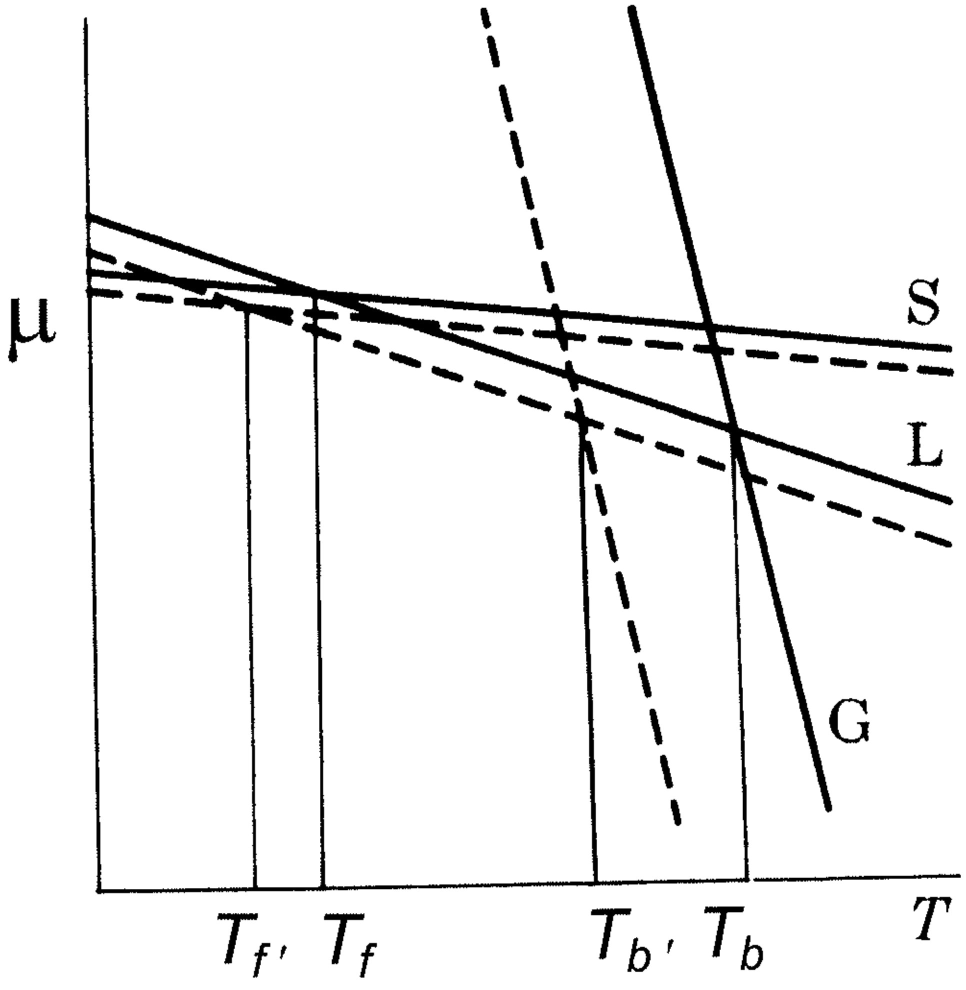
The phase with the lowest value of the chemical potential is the stable phase.

What happens when a solid is heated under constant pressure is entirely a consequence of the entropy values: Heat is absorbed in the transformation from solid to liquid and from liquid to gas. Thus, at low temperatures the system is completely solid, at T_f the liquid forms, the liquid is stable until it vaporizes at a temperature T_b .

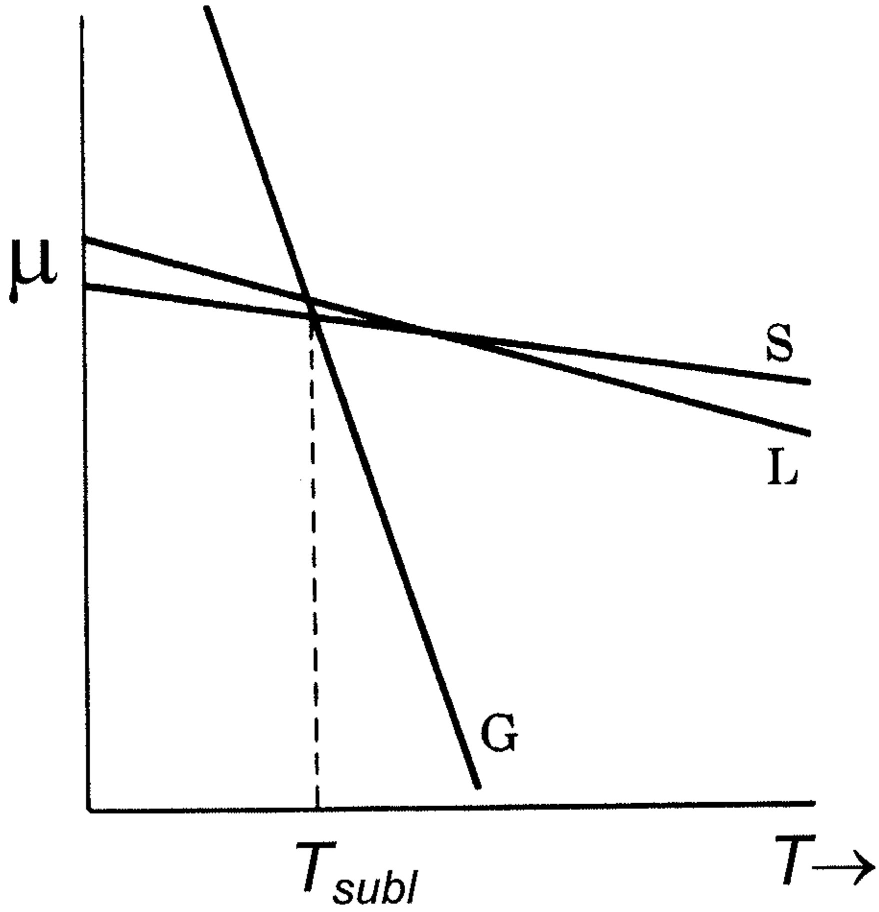
On the other hand, what happens to the phases if the pressure is changed is entirely a consequence of the V_m values:

$$V_{m,gas} \gg V_{m,liquid} > \text{or} < V_{m,solid}$$

Suppose $V_{m,liquid} > V_{m,solid}$
the effect of the pressure on melting and boiling points is shown here:



If the pressure is reduced to a sufficiently low value, the boiling point of the liquid may even fall below the melting point of the solid. Then there is no temperature at which the liquid is stable, the solid sublimes. Here is an example:



6.2 The Clapeyron Equation; solid-liquid, liquid gas, solid-gas equilibria

The condition for equilibrium between phases α and β of a pure substance is

$$\mu_\alpha(T,p) = \mu_\beta(T,p) \qquad (1)$$

If the pressure is changed to a value p+dp , the equilibrium temperature will change to T+dT, and the value of μ will change to μ+dμ. The new equilibrium condition is

$$\mu_\alpha(T,p) + d\mu_\alpha = \mu_\beta(T,p) + d\mu_\beta \quad (2)$$

(2) - (1) gives

$$d\mu_\alpha = d\mu_\beta$$

$$d\mu_\alpha = -\boldsymbol{S}_{m,\alpha}\, dT + V_{m,\alpha}\, dp$$

$$d\mu_\beta = -\boldsymbol{S}_{m,\beta}\, dT + V_{m,\beta}\, dp$$

$$-\boldsymbol{S}_{m,\alpha}\, dT + V_{m,\alpha}\, dp = -\boldsymbol{S}_{m,\beta}\, dT + V_{m,\beta}\, dp$$

$$(\boldsymbol{S}_{m,\beta} - \boldsymbol{S}_{m,\alpha})dT = (V_{m,\beta} - V_{m,\alpha})dp$$

$$\boxed{dp/dT = (\boldsymbol{S}_{m,\beta} - \boldsymbol{S}_{m,\alpha}) / (V_{m,\beta} - V_{m,\alpha})}$$

the ***Clapeyron equation***

The liquid gas equilibrium:

For all substances,

$(\boldsymbol{S}_{m,\text{gas}} - \boldsymbol{S}_{m,\text{liquid}}) = \Delta_{vap}\boldsymbol{H}/T$ is +

$(V_{m,\text{gas}} - V_{m,\text{liquid}})$ is +

Then,

$dp/dT = \Delta_{vap}\boldsymbol{H}/\{T(V_{m,\text{gas}} - V_{m,\text{liquid}})\}$ is + (a)

Points on this gas-liquid curve (Clapeyron eq.) are those sets of (p, T) values at which liquid coexists with gas.

The solid gas equilibrium:

For all substances,

$(\boldsymbol{S}_{m,\text{gas}} - \boldsymbol{S}_{m,\text{solid}}) = \Delta_{subl}\boldsymbol{H}/T$ is +

$(V_{m,\text{gas}} - V_{m,\text{solid}})$ is +

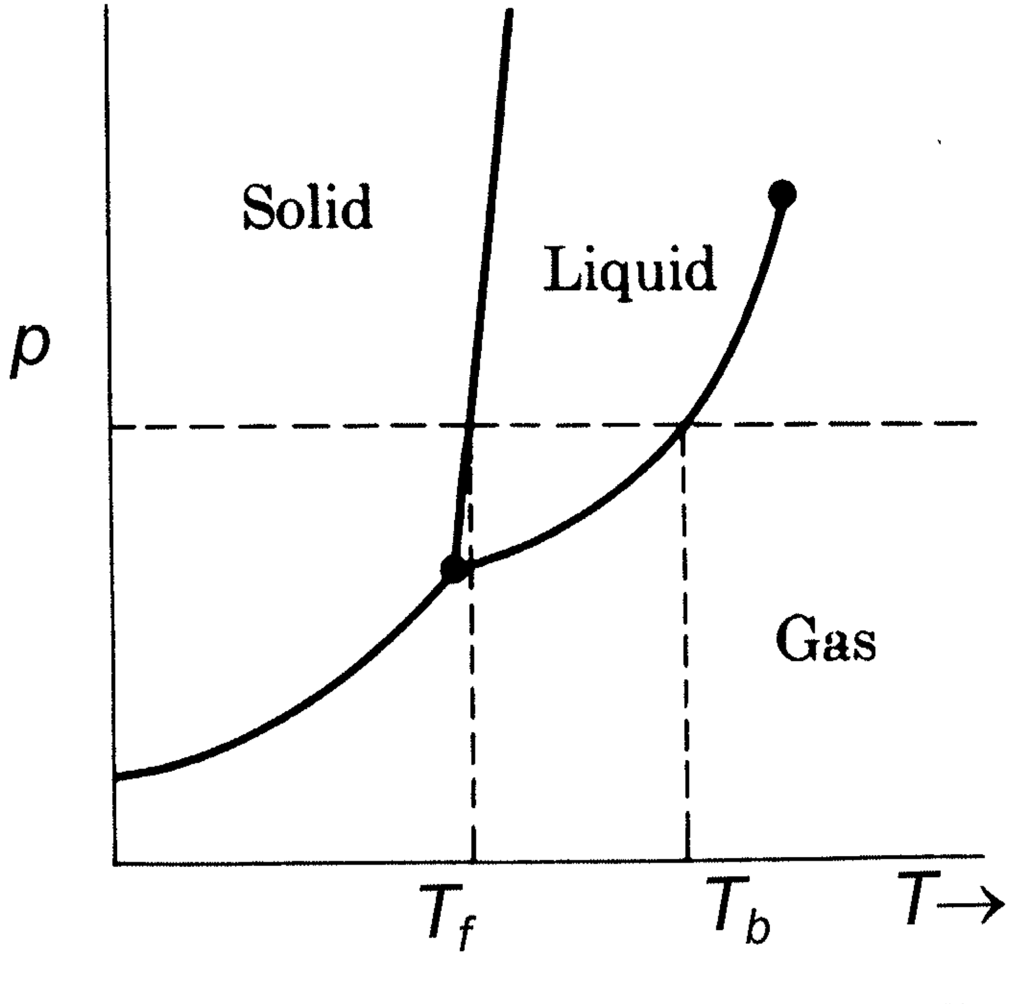
Then,

$dp/dT = \Delta_{subl}\boldsymbol{H}/\{T(V_{m,\text{gas}} - V_{m,\text{solid}})\}$ is + (b)

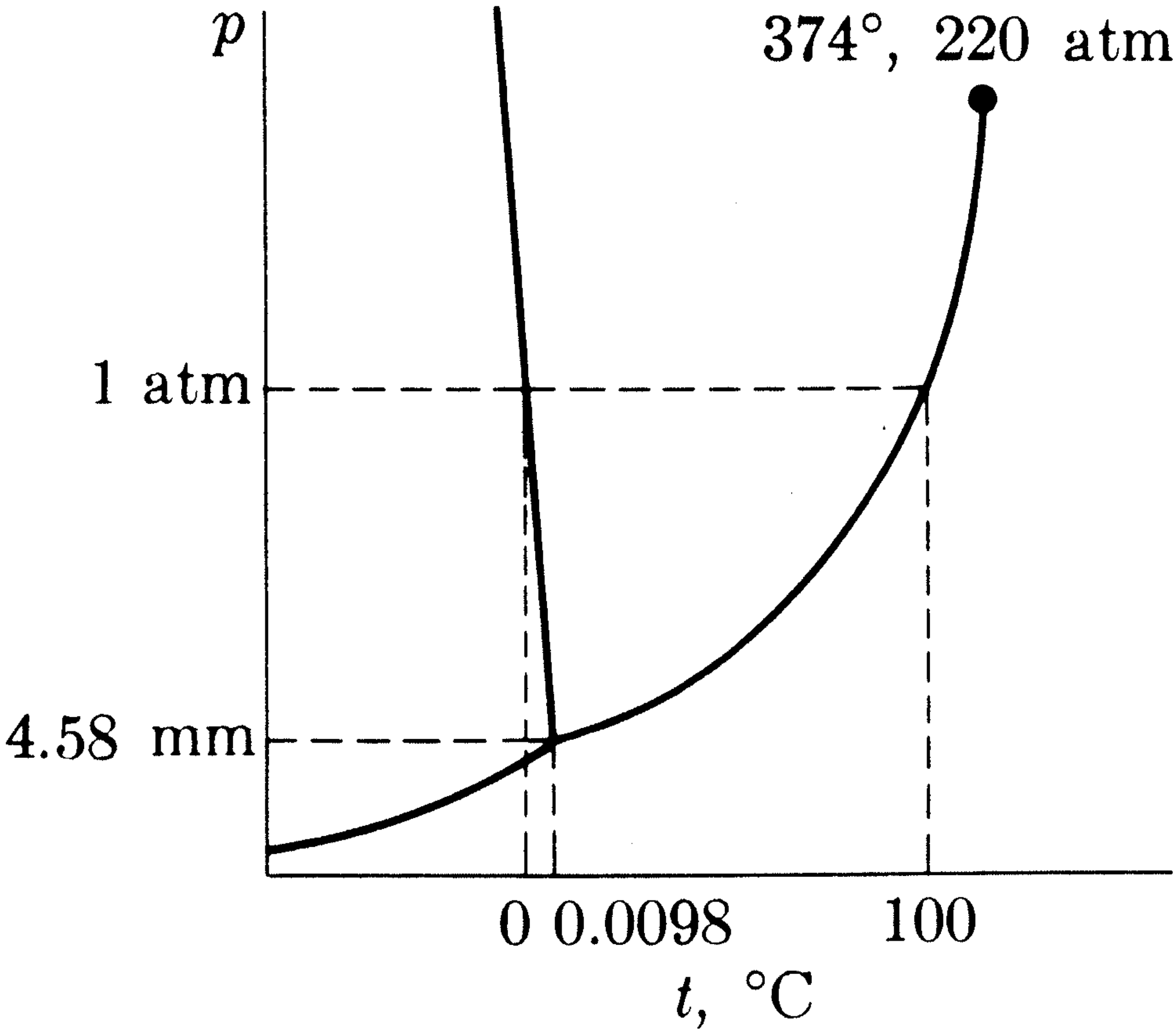
Points on this gas-solid curve (Clapeyron eq.) are those sets of (p, T) values at which solid coexists with gas.

The intersection of these 2 curves is called the ***triple point***, at which unique $(T,p)_{\text{triple}}$ value the 3 phases can coexist in equilibrium.

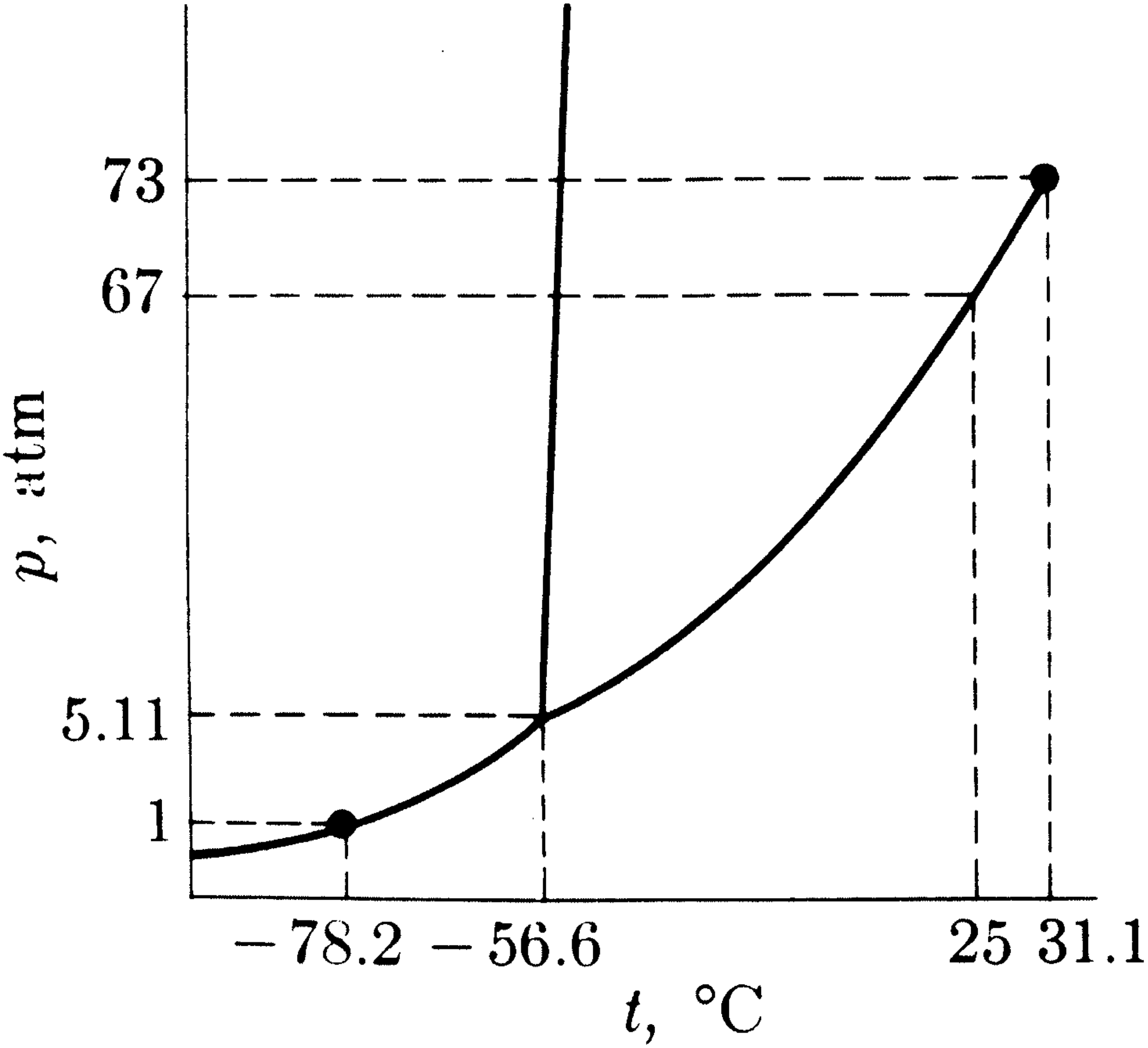
$d\mu_{\text{solid}} = d\mu_{\text{liquid}}$ and $d\mu_{\text{liquid}} = d\mu_{\text{gas}}$



An equilibrium diagram or so-called ***phase diagram***



Phase diagram for H_2O



Phase diagram for CO_2

Integrated forms of the Clapeyron Eq.

$$\mathrm{d}p/\mathrm{d}T = \Delta_{fus}\boldsymbol{H}/\{T(V_{m,\mathrm{liquid}} - V_{m,\mathrm{solid}})\} \quad \text{(c)}$$

$$\int (V_{m,\mathrm{liquid}} - V_{m,\mathrm{solid}})\mathrm{d}p = \int \Delta_{fus}\boldsymbol{H}\,\mathrm{d}T/T$$

In general, V_m may be a weak function of p and $\Delta_{fus}\boldsymbol{H}$ may be a function of T. <u>If</u> these are very nearly constant, then

$$\int \mathrm{d}p \approx \Delta_{fus}\boldsymbol{H}/(V_{m,\mathrm{liquid}} - V_{m,\mathrm{solid}}) \int \mathrm{d}T/T$$

$$\boxed{p_2 - p_1 \approx \{\Delta_{fus}\boldsymbol{H}/(V_{m,\mathrm{liquid}} - V_{m,\mathrm{solid}})\}\ln[T_{fus}(p_2)/T_{fus}(p_1)]}$$

Usually the melting point increases as p increases. Not so for water in which, <u>unusually</u>, melting point lowers under pressure, because $V_{m,\mathrm{liquid}} < V_{m,\mathrm{solid}}$.

$$\mathrm{d}p/\mathrm{d}T = \Delta_{vap}\boldsymbol{H}/\{T(V_{m,\mathrm{gas}} - V_{m,\mathrm{liquid}})\} \quad \text{(a)}$$

Since $V_{m,\mathrm{gas}} >> V_{m,\mathrm{liquid}}$ and <u>if</u> $\Delta_{vap}\boldsymbol{H}$ *is only weakly dependent on* T, and <u>if</u> ideal gas behavior, $V_{m,\mathrm{gas}} \approx RT/p$, then

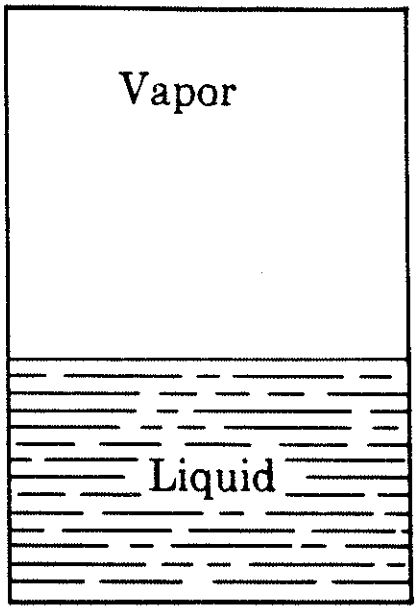
$$dp/dT = \Delta_{vap}\boldsymbol{H}p/RT^2$$

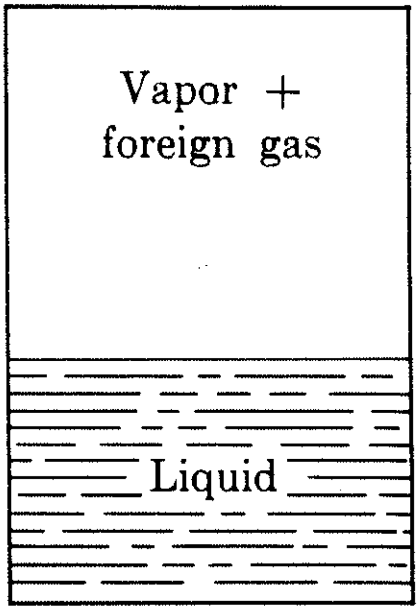
$$\int \mathrm{d}p/p \approx \Delta_{vap}\boldsymbol{H}/R \int \mathrm{d}T/T^2$$

$$\boxed{\ln (p/p_0) \approx \Delta_{vap}\boldsymbol{H}/R \left[-\frac{1}{T} + \frac{1}{T_0} \right]}$$

Effect of pressure on vapor pressure

What if the vapor and the liquid are not subjected to the same pressure? Consider a foreign gas (insoluble in the liquid) mixed with the vapor:





What is the equilibrium vapor pressure of A in the presence of foreign gas E?

The equilibrium conditions are:
in the presence of gas E:

❀ $\mu_{\mathrm{LIQ}}(T, p_{tot} = p_A + p_E) = \mu_{\mathrm{VAP}}(T, p_A)$

in the absence of gas E:

❀ $\mu^*_{\mathrm{LIQ}}(T, p^*_A) = \mu_{\mathrm{VAP}}(T, p^*_A)$

Subtract to get:

$$\mu_{\mathrm{LIQ}}(T, p_{tot}) - \mu^*_{\mathrm{LIQ}}(T, p^*_A) = \mu_{\mathrm{VAP}}(T, p_A) - \mu_{\mathrm{VAP}}(T, p^*_A)$$

This equation is the integrated form of

$$\int d\mu_{\mathrm{LIQ}} = \int d\mu_{\mathrm{VAP}}$$

Since $d\boldsymbol{G} = V dp - \boldsymbol{S} dT$, then $(\partial \mu / \partial p)_T = V_m$
so that $\int d\mu_{\mathrm{LIQ}} = \int d\mu_{\mathrm{VAP}}$ becomes

$$\int V_{m\,\mathrm{LIQ}}\, dp = \int V_{m\,\mathrm{VAP}}\, dp$$

LHS integrated from p^*_A to $p_{tot} = p_A + p_E$
RHS integrated from p^*_A to p_A
LHS $= V_{m\,\mathrm{LIQ}}(p_{tot} - p^*_A)$
If the vapor behaves ideally, then
RHS $= \int V_{m\,\mathrm{VAP}}\, dp$
$= \int RT dp/p = RT \ln(p_A / p^*_A)$

$$\boxed{V_{m\,\mathrm{LIQ}}(p_{tot} - p^*_A) = RT \ln(p_A / p^*_A)}$$

Alternate derivation:

The equilibrium condition is:

❀ $\mu_{\text{vap}}(T,p) = \mu_{\text{liquid}}(T,p_{tot})$

Therefore p will depend on p_{tot}.

differentiate this eq. with respect to p_{tot}:

$(\partial\mu_{\text{vap}}/\partial p)_T\,(\partial p/\partial p_{tot})_T = (\partial\mu_{\text{liquid}}/\partial p_{tot})_T$

Use $(\partial\mu/\partial p)_T = V_m$ in both sides,

$V_{m,\text{vap}}\,(\partial p/\partial p_{tot})_T = V_{m,\text{liquid}}$

$$\boxed{(\partial p/\partial p_{tot})_T = V_{m,\text{liquid}}/V_{m,\text{vap}}}$$

If the vapor behaves ideally, then

$V_{m,\text{vap}} \approx RT/p$ *leads to*

$$(RT/p)\mathrm{d}p = V_{m,\text{liquid}}\,\mathrm{d}p_{tot}$$

Integrate from no foreign gas (vapor pressure is p^*_A) to some foreign gas (vapor pressure is p_A):

$$\boxed{RT\ln(p_A/p^*_A) = V_{m,\text{liquid}}(p_{tot} - p^*_A)}$$

EXAMPLE:

1. At 298 K we have

	$\Delta G_f^{\ominus}{}_{T=298K}$ kcal mol^{-1}	$S^{\ominus}{}_{T=298K}$ cal K^{-1} mol^{-1}
Rhombic sulfur	0	7.62
Monoclinic sulfur	0.023	7.78

Assuming that the entropies vary only slightly with temperature, sketch the value of μ versus T for the two forms of sulfur. From the data, determine the equilibrium temperature for the transformation,

Rhombic sulfur→ Monoclinic sulfur

$\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$

$\mathrm{d}\mu = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$ [V and $\boldsymbol{S}$ are for 1 mole]

At 1 bar, let $\boldsymbol{S}$ vary only slightly with temperature, integrate between 298 K and T,

$\int \mathrm{d}\mu_m = -\int_{298}^{T} \boldsymbol{S}_m \mathrm{d}T$ for monoclinic

$\mu_m(\mathrm{T}) - \mu_m(298\ \mathrm{K}) = -\boldsymbol{S}^{\ominus}{}_m(T\text{-}298)$

$\int \mathrm{d}\mu = -\int_{298}^{T} \boldsymbol{S}_r \mathrm{d}T$ for rhombic

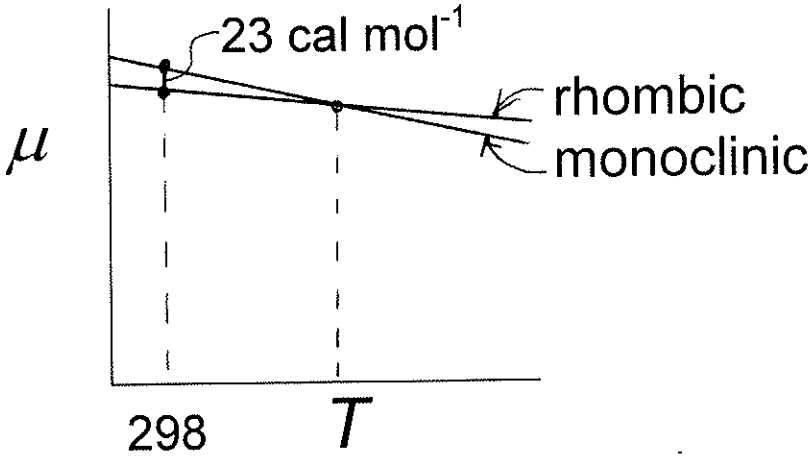
$\mu_r(\mathrm{T}) - \mu_r(298\ \mathrm{K}) = -\boldsymbol{S}^{\ominus}{}_r(T\text{-}298)$

$\boxed{\text{at equilibrium, } \mu_m(T) = \mu_r(T)}$

$\mu_m(298) - \boldsymbol{S}^{\ominus}{}_m(T\text{-}298) = \mu_r(298) - \boldsymbol{S}^{\ominus}{}_r(T\text{-}298)$

$23 \quad -7.78(T\text{-}298) = \quad 0.0 \quad -7.62(T\text{-}298)$

Solving for T, we find $T = 441.8$ K



6.3 The Phase Diagram, the Phase Rule

How many independent variables are required to describe the state of a system?

2 phases: $\mu_\alpha(T,p) = \mu_\beta(T,p)$ (1)

This constraint means that only one (T or p) need be specified to completely reproduce the system. The system has <u>one degree of freedom</u>.

3 phases: $\mu_\alpha(T,p) = \mu_\beta(T,p)$ (1)

$\mu_\gamma(T,p) = \mu_\beta(T,p)$ (2)

These 2 relations completely determine T and p. The system has <u>no degrees of freedom</u>. No other information is necessary to completely specify the state of the system.

F = 3 - P the ***Phase Rule***

for a *1-component* system

F is the number of independent variables that need to be specified to define the state of the system
P is the number of phases
C is the number of components, # of chemically independent species

[The number of intensive variables that would be needed to describe the state of the system]

−

[The number of equations that relate these variables to one another]

= [the number of independent variables that need to be specified to define the state of the system]

$$\begin{array}{ll} & PC + 2 \\ - & P + C(P-1) \\ \hline & = C - P + 2 \end{array}$$

$= C - P + 2 \quad = \quad F$ **The Phase Rule**

Kind of variable	Total number of variables
Temperature and pressure:	2
Composition variables: (in each phase the mole fraction of each component must be specified; thus, C mole fractions are required to describe one phase; PC are needed to describe P phases):	PC
Total number of variables:	$PC + 2$

Kind of equation	Total number of equations
In each phase there is a relation between the mole fractions: $x_1 + x_2 + \cdots + x_C = 1$ For P phases, there are P equations:	P
The equilibrium conditions: For each component there exists a set of equations: $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \cdots = \mu_i^{\mathrm{P}}$ There are $P - 1$ equations in the set. Since there are C components, there are $C(P - 1)$ equations:	$C(P - 1)$
Total number of equations:	$P + C(P - 1)$