Chapter 8
Phase Diagram, Relative Stability of Solid, Liquid, and Gas

Three states of matter: solid, liquid, gas (plasma)
At low T: Solid is most stable.
At high T: liquid or gas is most stable.
Ex: Most stable phase of H_2O under 1 atm:
T<0℃→Solid(Ice), @RT→Liquid (Water), T>100℃→Gas (Vapor)

☞ This chapter develops criterion for most stable state of a matter
   at given T and P.

8.1 What determines the relative stability of solid, liquid, and gas?

Phase ≡ A form of matter that is uniform w.r.t. chemical composition
on microscopic and macroscopic scales.

Ex. Water in a beaker = single phase (liquid)
   Water + ice mixture (two phases = liquid + solid)
☞ In this section the condition under which a pure substance
   spontaneously forms a solid, liquid, or gas is discussed.

What determines which state is most stable at given T and P?
☞ The Gibbs free energy, G(T, P, n) be minimized (Chapter 6).

In a pure substance:
$$\mu = (\frac{dG}{dn})_{T,P} = (\frac{d(nG_m)}{dn})_{T,P} = G_m \qquad \text{(a)}$$

Differentiation of (a) gives
$$d\mu = dG_m \qquad \text{(b)}$$
$$dG = -SdT + VdP \qquad \text{(6.19)}$$

This Eq descries the change of G with T and P.

Then, from (b) for molar quantity:

$$dG_m = d\mu = -S_m dT + V_m dP \quad (8.1)$$

S_m = Molar entropy, V_m = Molar volume (Extensive)

The variation of μ with T and P can be determined from (8).

$$\left(\frac{d\mu}{dT}\right)_P = -S_m < 0 \quad \text{and} \quad \left(\frac{d\mu}{dP}\right)_T = V_m > 0 \quad (8.2)$$

Since $S_m>0$, $V_m>0 \rightarrow$ μ decreases with T and increases with P.

Effect of temperature

Since, $S \propto \ln T$ (dS=dq/T=CpdT/T, ΔS=CplnT), $\left[\left(\frac{d\mu}{dT}\right)_P\right]$ becomes steeper as T increases → Approximately straight line over a limited range of T.

Also,

$S_m{}^{solid} < S_m{}^{liquid} < S_m{}^{gas}$ (c) $\quad (= -\left(\frac{d\mu}{dT}\right)_P)$

(2) + (c) →Figure 8.1
Functional relationship between μ and T in gas, liquid and solid.
The stable state of the system at any given T is that phase which has lowest μ (Gm)[eq (a)].

Assume the initial state = ● in Figure 8.1.

Then the most stable state = solid since solid has the lowest μ (liquid and gas have much higher μ) at the given T.
As T increases one approaches
$$\mu(\text{solid}) = \mu(\text{liquid}) \text{ @ } T_m \text{ (Melting temperature)}$$
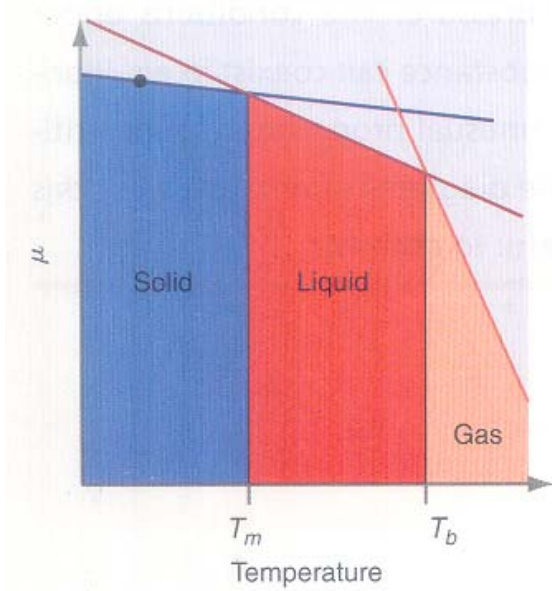

FIGURE 8.1

The chemical potential of a substance in the solid (blue curve), liquid (red curve), and gaseous (orange curve) states is plotted as a function of the temperature for a given value of pressure. The substance melts at the temperature T_m, corresponding to the intersection of the solid and liquid curves. It boils at the temperature T_b, corresponding to the intersection of the liquid and gas curves. The temperature ranges in which the different phases are the most stable are indicated by shaded areas. The three curves shown are actually slightly concave downwards, but have been approximated as straight lines.

@ T_m, solid and liquid coexist in thermodynamic equilibrium.
@ $T = T_m + dT$, solid will melt completely (Liquid phase).

Similarity,
@ $T = T_b$ (Boiling temperature) liquid and gas coexist in equilibrium.
Then @ $T > T_b$, system is completely in gaseous phase.

If the temperature is changed too quickly, equilibrium state may not be reached.
►Superheated liquid (metastable) is a liquid above T_b (Supercooled liquid is a liquid below T_m). It is dangerous because it could bring large volume expansion upon vaporization
►Boiling stone is added to avoid the formation of superheated liquid.
►Glass is made by cooling a viscous liquid fast enough to avoid crystallization.

Effect of pressure

$$\left(\frac{d\mu}{dP}\right)_T = V_m \qquad (8.2)$$

Since Vm(gas) >> Vm(liquid)>Vm(solid) for most substance.
(Compare μ of solid line (low P=P$_1$) and dashed line(high P=P$_2$))
→ Increase of μ is greater along solid < liquid < gas (Figure 8.2)

Note boiling point elevation(T$_b$→T$_b$') and freezing point elevation(T$_m$→ T$_m$') for Vm(solid)<Vm(liquid) (Figure 8.2 left) or, boiling point elevation(T$_b$→T$_b$') and freezing point depression for Vm(solid) > Vm(liquid) (Figure 8.2 right) with increasing P.
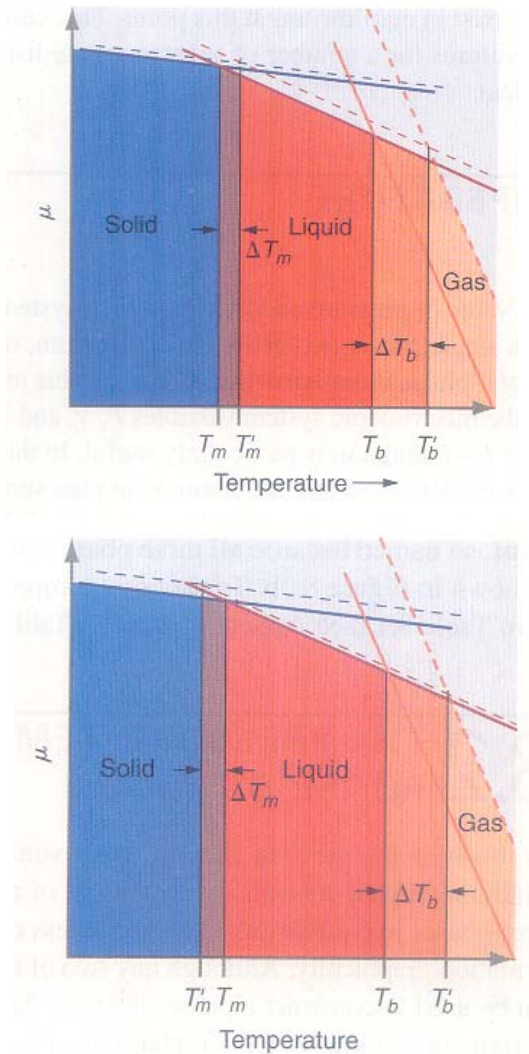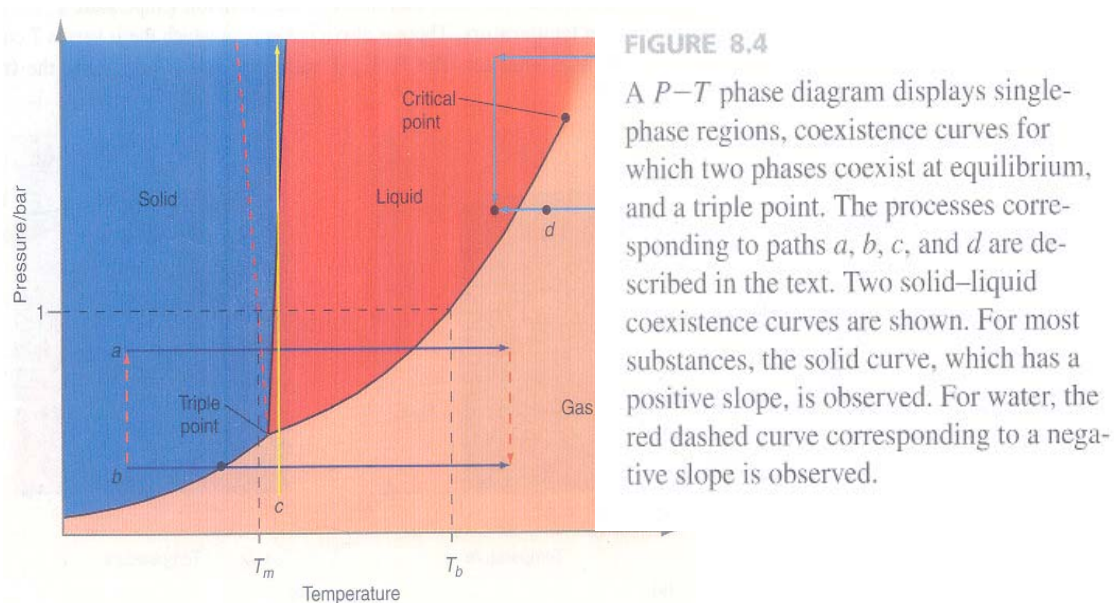

FIGURE 8.2

The solid curves show μ as a function of temperature for all three phases at $P = P_1$. The dashed curves show the same information for $P = P_2$, where $P_2 > P_1$. The unprimed temperatures refer to $P = P_1$ and the primed temperatures refer to $P = P_2$. The left diagram applies if $V_m^{liquid} > V_m^{solid}$. The right diagram applies if $V_m^{liquid} < V_m^{solid}$. The shifts in the solid and liquid curves are greatly exaggerated. The colored areas correspond to the temperature range in which the phases are most stable. The shaded area between T_m and T'_m is either solid or liquid, depending on P. The shaded area between T_b and T'_b is either liquid or gas, depending on P.

8.2 The P-T Phase Diagram

Displays stability reason for a pure substance as a function of T and P (Figure 8.4).

Figure 8.4

FIGURE 8.4

A $P-T$ phase diagram displays single-phase regions, coexistence curves for which two phases coexist at equilibrium, and a triple point. The processes corresponding to paths a, b, c, and d are described in the text. Two solid–liquid coexistence curves are shown. For most substances, the solid curve, which has a positive slope, is observed. For water, the red dashed curve corresponding to a negative slope is observed.

►Most (P, T) points correspond to a single phase.

►At triple point, three phases coexist. For water it's 273.16K, 611Pa.

►All (P,T) points where two phases coexist at equilibrium fall on a curve. (coexistence curve).

►Solid-gas, liquid-gas curve slopes are always positive. Solid-liquid curve is positive when (solid density>liquid density), and negative when (solid density<liquid density).

►T_b (b.p) is defined as the temperature where vapor pressure = external pressure.

►Standard b.p is the temperature at which the vapor pressure is 1 bar (normal bp is at 1 atm).

►See Table 8.2 for normal b.p and freezing point for substances.
  Note $\triangle H_{fusison}$ << $\triangle H_{vaporization}$

Table 8.2

TABLE 8.2 MELTING AND BOILING TEMPERATURES AND ENTHALPIES OF TRANSITION AT 1 ATM PRESSURE

Substance	Name	T_m (K)	ΔH_{fusion} (kJ mol^{-1}) at T_m	T_b (K)	$\Delta H_{vaporization}$ (kJ mol^{-1}) at T_b
Ar	Argon	83.8	1.12	87.3	6.43
Cl_2	Chlorine	171.6	6.41	239.18	20.41
Fe	Iron	1811	13.81	3023	349.5
H_2	Hydrogen	13.81	0.12	20.4	0.90
H_2O	Water	273.15	6.010	373.15	40.65
He	Helium	0.95	0.021	4.22	0.083
I_2	Iodine	386.8	14.73	457.5	41.57
N_2	Nitrogen	63.5	0.71	77.5	5.57
Na	Sodium	370.87	2.60	1156	98.0
NO	Nitric oxide	109.5	2.3	121.41	13.83
O_2	Oxygen	54.36	0.44	90.7	6.82
SO_2	Sulfur dioxide	197.6	7.40	263.1	24.94
Si	Silicon	1687	50.21	2628	359
W	Tungsten	3695	52.31	5933	422.6
Xe	Xenon	161.4	1.81	165.11	12.62
CCl_4	Carbon tetrachloride	250	3.28	349.8	29.82
CH_4	Methane	90.68	0.94	111.65	8.19
CH_3OH	Methanol	175.47	3.18	337.7	35.21
CO	Carbon monoxide	68	0.83	81.6	6.04
C_2H_4	Ethene	103.95	3.35	169.38	13.53
C_2H_6	Ethane	90.3	2.86	184.5	14.69
C_2H_5OH	Ethanol	159.0	5.02	351.44	38.56
C_3H_8	Propane	85.46	3.53	231.08	19.04
C_5H_5N	Pyridine	231.65	8.28	388.38	35.09
C_6H_6	Benzene	278.68	9.95	353.24	30.72
C_6H_5OH	Phenol	314.0	11.3	455.02	45.69
$C_6H_5CH_3$	Toluene	178.16	6.85	383.78	33.18
$C_{10}H_8$	Naphthalene	353.3	17.87	491.14	43.18

Sources: Data from Lide, D. R., Ed., *Handbook of Chemistry and Physics*, 83rd ed. CRC Press, Boca Raton, FL, 2002; Lide, D. R., Ed., *CRC Handbook of Thermophysical and Thermochemical Data*. CRC Press, Boca Raton, FL, 1994; and Blachnik, R., Ed., *D'Ans Lax Taschenbuch für Chemiker und Physiker*, 4th ed. Springer, Berlin, 1998.

►Note P refers to vapor pressure along gas-solid, gas-liquid curves, and in all regions refers to external pressure.

►The solid-liquid coexistence curve traces out T_m=f(P). Tm increases with P if the slope is +, and decreases if the slope is -.

►The liquid-vapor coexistence curve traces out T_b=f(P). Slope is much smaller than solid-liquid coexistence curve→Tb(bp) strongly depends on pressure. (Ex. Pressure cooker: 1 bar increase → ca 20℃ increase in bp).

►Critical point

Extending the liquid-gas coexistence curve indefinitely gives T=Tc and P=Pc. Above the critical point, there is no distinction between liquid and gas, and these substances are called supercritical fluids (Discussed in 8.9).

Now Consider 4 processes a, b, c, and d to demonstrate the usefulness of P-T diagram

Path a

An isobaric (=constant pressure process)

Within the solid phase

$$q_p = \triangle H = C_p^{\,solid} \triangle T$$

So, $\triangle T = q_p/C_p^{\,solid}$

→Temperature increases linearly with q_p

@ $T=T_m$

Heat taken up per mole of the system = $\triangle H_{fusion}$

(No temperature rise until the complete melting of the system)

Now in liquid

$$\triangle T = q_p/C_p^{\,liquidl}$$

@ $T=T_b$

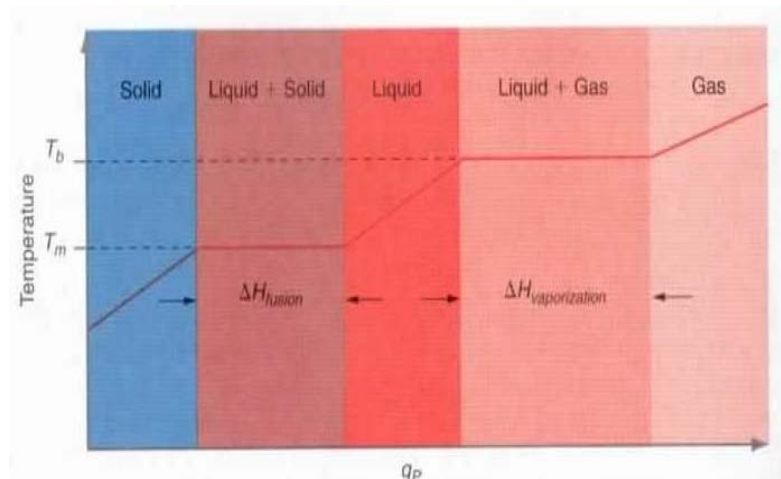Heat taken up per mole of the system = $\triangle H_{vaporization}$

Finally the system enters single gas phase region.

(See temperature profile in Figure 8.5)

$$\triangle T = q_p/C_p^{\,gas}$$

FIGURE 8.5

The temperature versus heat curve is shown for the process corresponding to path a in Figure 8.4. The temperature rises linearly with q_P in single-phase regions, and remains constant along the two-phase curves as the relative amounts of the two phases in equilibrium change (not to scale).

Path b

The point is below the triple point → Solid is directly converted into gaseous phase (Sublimation). (See the temperature profile in Figure 8.6)

Path b can be reached by an alternative 3 step route (Enthalpy change is the same since H=state function).
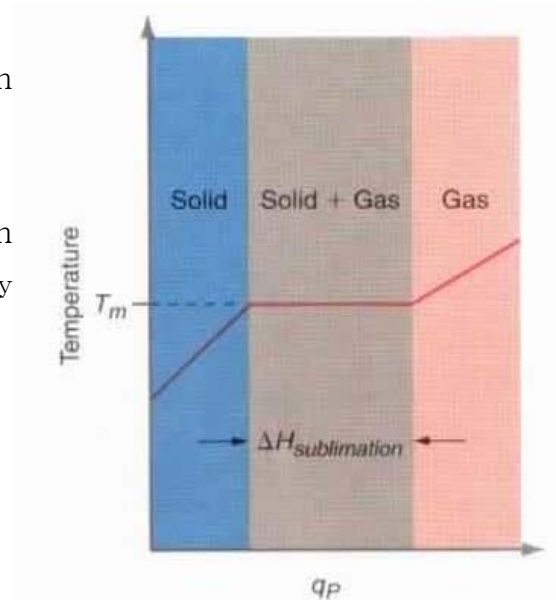
Near the triple point

For infinitesimally small dP

Path a, P_{tp} + dP (Above triple point)

Path b, P_{tp} − dP (Below tirple point)

As dP → 0, then △H → 0 for the two steps, Then

$$\triangle H = \triangle H_{sublimation} = \triangle H_{fusion} + \triangle H_{vaporation}$$

(8.4)

Path c

Isothermal compression.

$$Gas \xrightarrow{compressed} Liquid \xrightarrow{compressed} Solid$$

Condensation and crystallization give off heat to the surrounding.

Path d

FIGURE 8.6

The temperature versus heat curve is shown for the process corresponding to path b in Figure 8.4. The temperature rises linearly with q_P in single-phase regions, and remains constant along the two-phase curves as the relative amounts of the two phases in equilibrium change (not to scale).

Constant pressure heating or cooling.

Same overall process can be carried out in four steps.

8.3 The Phase Rule

The coexistence of two phases (α, β) of a substance requires that the chemical potentials in the two phases are equal:

$$\mu_{\alpha,i}(T,P) = \mu_{\beta,i}(T,P) \quad (8.5) \quad \text{(for multicomponent system)}$$

Only one of the two state variables (T or P) is independent and the other is determined by Eq (8.5).

Or, mathematically # of variable = 2 (T, P)

$\qquad\qquad$ # of equation = 1 (Eq 8.5)

So, degree of freedom = 2 - 1 = 1

So, two phase coexistence curve is given by P(T), or T(P)

If three phases α, β, γ coexist in equilibrium

$$\mu_{\alpha}(T,P) = \mu_{\beta}(T,P) = \mu_{\gamma}(T,P)$$

Then # of variable = 2

$\qquad$ # of equation = 2

So, degree of freedom = 2 - 2 = 0

⇒ Triple point is automatically determined (invariant).

Degree of freedom (Thermodynamic)

$\qquad$ F = c - p + 2

$\qquad\qquad$ c = # of component

$\qquad\qquad$ p = # of phase

►For single component system:

$\qquad$ F = 1 - p + 2 = 3 - p $\qquad$ (8.7)

 For coexistence curve:

$\qquad$ F = 3 - 2 = 1

For triple point

     F = 3 - 3 = 0

8.4 P-V, and P-V-T Phase Diagrams

Superposition of P-T phase diagram (Figure 8.4 etc) and P-V phase diagram (Figure 8.11) ⇒ P-V-T phase diagram. (Figure 8.12)

See Figure 8.11 for P-V diagram.

Process a = Solid → Gas at constant pressure (Above triple point).
Passes two coexistence regions.

Process b = Solid → Gas at constant pressure (Below triple point).
Passes only one coexistence region (solid-gas)
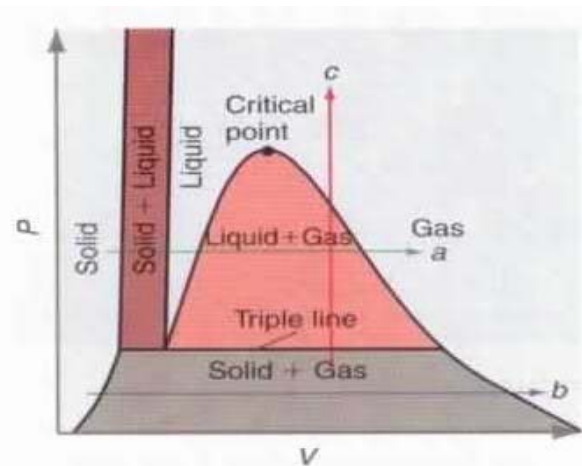This process is used for freeze drying (Sublimation of ice to vapor).

FIGURE 8.11
A P–V phase diagram displays single- and two-phase coexistence regions, a critical point, and a triple line. The two-phase coexistence areas are colored.

Process c = Constant volume path from (solid+gas) phase equilibrium to supercritical fluid.
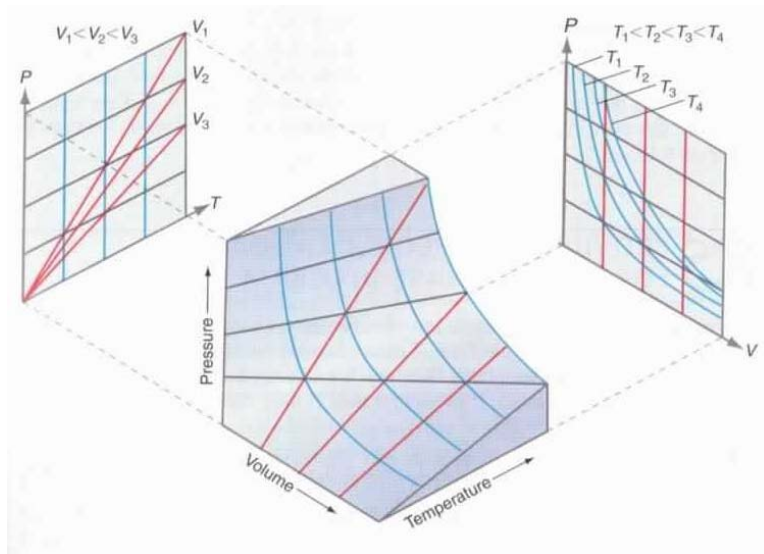
See Figure 8.12 for P-V-T

FIGURE 8.12

A *P–V–T* diagram for an ideal gas. Constant pressure, constant volume, and constant temperature paths are shown as black, red, and blue curves, respectively.

$$PV = nRT$$

8.5 Theoretical Basis for P-T Phase Diagram

If two phases, α and β, are in equilibrium at a P and T, their chemical potentials must be equal:

$$\mu_\alpha\ (T,\ P) = \mu_\beta\ (T,\ P) \qquad (8.8)$$

If the macroscopic variables are changed by a small amount as, P → P + dP, T→ T + dT such that the system pressure and temperature still lie on the coexistence curve, then

$$\mu_\alpha(T,P) + d\mu_\alpha = \mu_\beta(T,P) + d\mu_\beta \qquad (8.9)$$

In order for the two phases to remain in equilibrium,

$$d\mu_\alpha = d\mu_\beta \qquad (8.10)$$

Because dμ (=dG$_m$) can be expressed in terms of dT and dP,

$$d\mu_\alpha = -S_{m\alpha}dT + V_{m\alpha}dP \text{ and } d\mu_\beta = -S_{m\beta}dT + V_{m\beta}dP \qquad (8.11)$$

Then by (8.10)

$$-S_{m\alpha}dT + V_{m\alpha}dP = -S_{m\beta}dT + V_{m\beta}dP \qquad \text{or}$$

$$(S_{m\beta} - S_{m\alpha})dT = (V_{m\beta} - V_{m\alpha})dP \qquad (8.12)$$

Rearranging gives the **Clapeyron equation**:

$$\frac{dP}{dT} = \frac{\triangle S_m}{\triangle V_m} \qquad (8.13)$$

where $\triangle S_m = S_{m\beta} - S_{m\alpha}$ and
$\triangle V_m = V_{m\beta} - V_{m\alpha}$

The importance of the Clapeyron equation is that it allows one to calculate the slope of the coexistence curves in a P–T phase diagram if $\triangle S_m$ and $\triangle V_m$ for the transition are known.

Also at Tm (solid–liquid equilibrium),
$\Delta G_m^{fusion} = \Delta H_m^{fusion} - T \Delta S_m^{fusion} = 0$ (14)

So, $\Delta S_m^{fusion} = \Delta H_m^{fusion}/T$

<u>Solid–liquid coexistence analysis</u>

Take $\triangle S_m^{fusion} = 22$ Jmole^{-1}K^{-1} (Calculated average in Table 8.2)
$\triangle V_m^{fusion} = +4.0 \times 10^{-6}$ m^{3}mole^{-1} (Note H$_2$0 has "–" value)

Then,

$$\left(\frac{dP}{dT}\right)_{fusion} = \frac{\triangle S_m^{fusion}}{\triangle V_m^{fusion}} \simeq \frac{22\,Jmole^{-1}K^{-1}}{\pm 4.0 \times 10^{-6}m^3mole^{-1}}$$
$$= \pm 5.5 \times 10^6 PaK^{-1} = \pm 55\ bar\ K^{-1} \qquad (8.15)$$
$$(1\text{bar} = 10^5\text{Pa})$$

⇒ See the very steep solid–liquid coexistence curve in Figure 8.4.
⇒ Small pressure effect on melting. Increase of P by 55 bar ⇒
Increase of T$_m$ by 1 degree.

Liquid-gas coexistence curve analysis

We know:
$\triangle H_m^{vaporization} > 0$ (Endothermic) and
$\triangle V_m^{vaporization} = V_m^{gas} - V_m^{liquid} > 0$
$\Rightarrow (dP/dT)_{vaporization} > 0$ $(\Delta S_m^{fusion} = \Delta H_m^{fusion}/T)$

$\triangle S_m^{vaporization} = 95$ Jmol^{-1}K^{-1} (Average in Table 8.2).
$V_m^{IG} \simeq 20$ L mol^{-1}.
$V_m^{gas} \gg V_m^{liquid} \to \triangle V_m^{vaporization} \approx 20 \times 10^{-3}$ m^{3}mol^{-1}.
Then, the slope of the liquid-gas coexistence curve is given by

$$(\frac{dP}{dT})_{vaporation} = \frac{\triangle S_m^{vaporization}}{\triangle V_m^{vaporization}} \simeq \frac{95\,Jmole^{-1}K^{-1}}{2.0\times10^{-2}m^3mole^{-1}}$$
$$\simeq 4.8\times10^3 Pa^1 K^{-1} = 4.8\times10^{-2} Pa\,K^{-1}$$
(8.16)

Three order of magnitude smaller slope than liquid-solid curve.
→Inversion gives much greater value, viz $(dT/dP)_{vaporization} \approx 21$Kbar^{-1}
$\Rightarrow$ Great pressure effect on boiling.

8.6 Using the Clausius-Clapeyron Equation to Calculate Vapor Pressure as a Function of T

Clapeyron eq is valid for both solid-liquid and liquid-vapor equilibrium.

For solid-liquid coexistence curve

$$\int_{P_i}^{P_f} dP = \int_{T_i}^{T_f} \frac{\triangle S_m^{fusion}}{\triangle V_m^{fusion}} dT = \int_{T_i}^{T_f} \frac{\triangle H_m^{fusion}}{\triangle V_m^{fusion}} \frac{dT}{T} \approx \frac{\triangle H_m^{fusion}}{\triangle V_m^{fusion}} \int_{T_i}^{T_f} \frac{dT}{T}$$
(17)

ΔH_m^{fusion} and ΔV_m^{fusion} are assumed constant for small change of T.

Assume $(T_f - T_i)/T_i$ is small, then

$$P_f - P_i = \frac{\triangle H_m^{fusion}}{\triangle V_m^{fusion}} ln \frac{T_f}{T_i} = \frac{\triangle H_m^{fusion}}{\triangle V_m^{fusion}} ln \frac{T_i + \triangle T}{T_i} = \frac{\triangle H_m^{fusion}}{\triangle V_m^{fusion}} ln(1 + \frac{\triangle T}{T_i}) \approx \frac{\triangle H_m^{fusion}}{\triangle V_m^{fusion}} \frac{\triangle T}{T_i} \qquad (18)$$

Note vapor pressure of solid varies linearly with T.
Note $ln(1 + x) \doteqdot x$ for small x by Taylor series expansion as follow.

$$f(x) = f(a) + \frac{f'(a)}{1!}(x - a) + \frac{f''(a)}{1!}(x - a)^2 +$$

<u>For liquid-vapor coexistence curve</u>

(Use dH=TdS+ VdP (dP=0), ΔV=V^{Gas})

$$\frac{dP}{dT} = \frac{\triangle S_m^{vaporization}}{\triangle V_m^{vaporization}} \approx \frac{\triangle H_m^{vaporization}}{TV_m^{gas}} = \frac{P \triangle H_m^{vaporization}}{RT^2}$$

$$\frac{dP}{P} = \frac{\triangle H_m^{vaporization}}{R} \frac{dT}{T^2} \qquad (19)$$

Assuming the ΔH_m^{fusion} is constant over the temperature range, variation of vapor pressure with temperature is obtained by

$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\triangle H_m^{vaporization}}{R} \times \int_{T_i}^{T_f} \frac{dT}{T^2}$$

$$ln \frac{P_f}{P_i} = - \frac{\triangle H_m^{vaporization}}{R} \times \left(\frac{1}{T_f} - \frac{1}{T_i} \right) \qquad (20)$$

Note the vapor pressure of liquid rises exponentially with temperature. Same procedure can be followed for solid-gas coexistence curve to give (20) with $\triangle H^{sublimation}$ substituted for $\triangle H^{vaporization}$.

By using Eq (20):
$\triangle H^{vaporization}$ can be calculated by measuring the vapor pressure as a function of temperature (EX 8.2).

EXAMPLE PROBLEM 8.2

The normal boiling temperature of benzene is 353.24 K, and the vapor pressure of liquid benzene is 1.19×10^4 Pa at 20.0°C. The enthalpy of fusion is 9.95 kJ mol^{-1}, and the vapor pressure of solid benzene is 137 Pa at -44.3°C. Calculate the following:

a. $\Delta H_m^{vaporization}$

b. $\Delta S_m^{vaporization}$

c. Triple point temperature and pressure

Solution

a. We can calculate $\Delta H_m^{vaporization}$ using the Clausius-Clapeyron equation because we know the vapor pressure at two different temperatures:

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{vaporization}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\Delta H_m^{vaporization} = -\frac{R \ln \dfrac{P_f}{P_i}}{\left(\dfrac{1}{T_f} - \dfrac{1}{T_i} \right)} = -\frac{8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} \times \ln \dfrac{101{,}325\ \mathrm{Pa}}{1.19 \times 10^4\ \mathrm{Pa}}}{\left(\dfrac{1}{353.24\ \mathrm{K}} - \dfrac{1}{273.15\ \mathrm{K} + 20.0\ \mathrm{K}} \right)}$$

$$= 30.7\ \mathrm{kJ\,mol^{-1}}$$

b. $\Delta S_m^{vaporization} = \dfrac{\Delta H_m^{vaporization}}{T_b} = \dfrac{30.7 \times 10^3\,\mathrm{J\,mol^{-1}}}{353.24\ \mathrm{K}} = 86.9\ \mathrm{J\,mol^{-1}\,K^{-1}}$

c. At the triple point, the vapor pressures of the solid and liquid are equal:

$$\ln \frac{P_{tp}^{liquid}}{P°} = \ln \frac{P_i^{liquid}}{P°} - \frac{\Delta H_m^{vaporization}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{T_i^{liquid}} \right)$$

$$\ln \frac{P_{tp}^{solid}}{P°} = \ln \frac{P_i^{solid}}{P°} - \frac{\Delta H_m^{sublimation}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{T_i^{solid}} \right)$$

$$\ln \frac{P_i^{liquid}}{P°} - \ln \frac{P_i^{solid}}{P°} - \frac{\Delta H_m^{sublimation}}{RT_i^{solid}} + \frac{\Delta H_m^{vaporization}}{RT_i^{liquid}}$$

$$= \frac{\left(\Delta H_m^{vaporization} - \Delta H_m^{sublimation} \right)}{RT_{tp}}$$