PHYSICAL TRANSFORMATIONS OF PURE SUBSTANCES
Chapter 4 Outline

HW: Questions are below. Solutions are in separate file on the course web site.

Sect.	Title and Comments	Required?
1.	The Stabilities of Phases	YES
2.	Phase Boundaries We will NOT cover the phase rule (Sect. 4.2.b)	YES
3.	Three Typical Phase Diagrams You are responsible for basic phase diagrams (e.g. Fig. 4.8), but not the more complex diagrams (such as Figs. 4.7, 4.9 and 4.10); i.e. only for phase diagrams with 3 phases (solid, liquid and vapor)	MOST
4.	The Dependence of Stability on the Conditions	YES
5.	The Location of Phase Boundaries	YES
6.	The Ehrenfest Classification of Phase Transitions	NO

Chapter 4 Homework Questions

Where necessary below, you may use the following relation between Molar Volume (V_m), Molar Mass (M), and density (ρ): $V_m = \dfrac{M}{\rho}$

4.1 For this question, assume that the molar entropy of iron is constant at 53 J/mol-K.

Calculate the change in Chemical Potential of iron (in J/mol) when the temperature is increased from 100 °C to 200 °C

4.2 The molar entropy of water is temperature dependent and over the liquid range, follows the equation: $S_m^o = a + bT$ J/mol-K, a = 1.5 J/mol-K, b = 0.23 J/mol-K^3 (T is temperature in Kelvins).

Calculate the change in Chemical Potential of water (in J/mol) when the temperature is increased from 25 °C to 90 °C

4.3 The density of liquid benzene (C_6H_6, M=78) is 0.88 g/cm^3 at 25 °C.

Calculae the change in Chemical Potential of benzene (in J/mol) when the pressure is increased from 1. bar to 1,000 bar at 25 °C.

4.4 Calculate the change in Chemical Potential of CH_4(g) (in J/mol) when the pressure is increased from 1. bar to 20. bar at 25 °C.

4.5 When Benzene (C_6H_6, M=78) liquid freezes to the solid at 6.0 °C and 1 bar, the density changes from 0.88 g/cm^3 to 0.95 g/cm^3. The Enthalpy of Fusion of Benzene is 9.80 kJ/mol. Calculate the pressure (in bar) required to raise the freezing point to 15.0 °C.

4.6 Calculate the melting point of ice under a pressure of 1000 bar. Assume that the density of ice under these conditions is approximately 0.92 g/cm^3 and that of liquid water is 1.00 g/cm^3. The normal melting point (under 100 kPa pressure) is 0 °C and the Enthalpy of Fusion is 6.01 kJ/mol.

4.7 The molar volume of a certain **solid** is 161.0 cm^3/mol at 1.0 atm and 350.75 K, its normal melting point. The molar volume of the **liquid** is 163.3 cm^3/mol. At a pressure of 100.0 atm, the melting point changes to 351.26 K.

Calculate the Enthalpy and Entropy of Fusion of the solid.

4.8 The vapor pressure of dichloromethane at 24 °C is 53.3 kPa, and it's Enthalpy of Vaporization is 28.7 kJ/mol. Estimate the temperature (in °C) at which its vapor pressure is 70;0 kPa.

4.9 Napthalene ($C_{10}H_8$, M=128) melts at 80.2 °C. If the vapour pressure of the liquid is 1.3 kPa at 85.8 °C and 5.3 kPa at 119.3 °C, calculate the following:
   (a) The Enthalpy of Vaporization
   (b) The normal boiling point
   (c) The Entropy of Vaporization at the normal boiling point.

4.10 The normal boiling point of liquid mercury, Hg(l), is 357 °C. The vapor pressure of liquid mercury at 250 °C is 75 torr. [1 bar = 750 torr]

Calculate the Enthalpy of Vaporization of mercury, in kJ/mol.

Chapter 4

Physical Transformations of Pure Substances

Phase Diagrams and Phase Boundaries
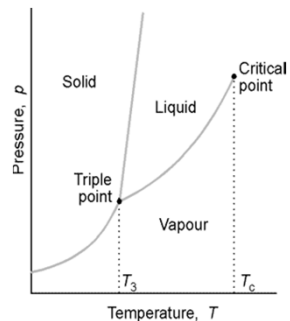
Phase Diagram

The phase diagram of a substance shows the regions of pressure and temperature at which the various phases are stable.

A typical phase diagram is shown to the right.

Phase Boundaries

These are the lines (combination of p and T) on which two phases are in equilibrium

The Critical Point

The critical temperature (T_c) is the highest temperature at which a substance can be liquified.

The vapor pressure at T_c is called the critical pressure (p_c).

The Triple Point

The triple point temperature and pressure, T_3 and p_3, is the one point in a phase diagram at which all three phases (solid, liquid and vapor) are in equilibrium.
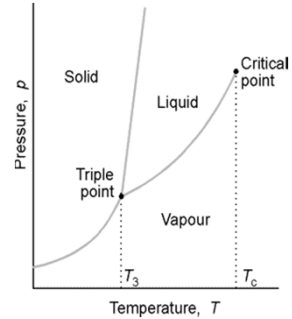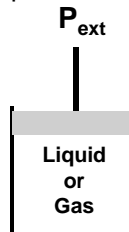

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The Boiling Point
The boiling point is the temperature at which liquid and vapor are in equilibrium.

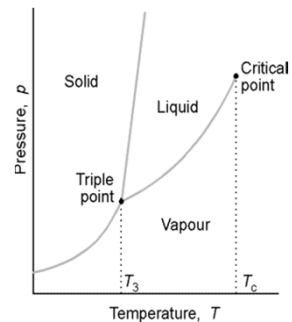The boiling point depends upon the applied (external) pressure.

P_{ext} > Vap. Press.   Liquid

P_{ext} = Vap. Press.   Liquid + Gas (boiling point)

P_{ext} < Vap. Press.   Gas

The curve, representing the combinations of p and T at which liquid and vapor are in equilibrium is often called the vaporization curve.
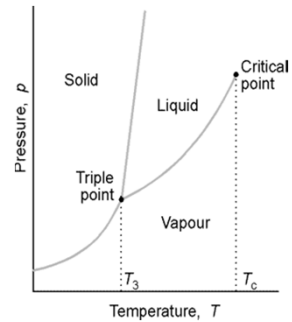
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The Melting Point

The melting (or freezing) point is the temperature at which solid and liquid are in equilibrium.

The melting point depends upon the applied (external) pressure, but to a much smaller extent than the boiling point.
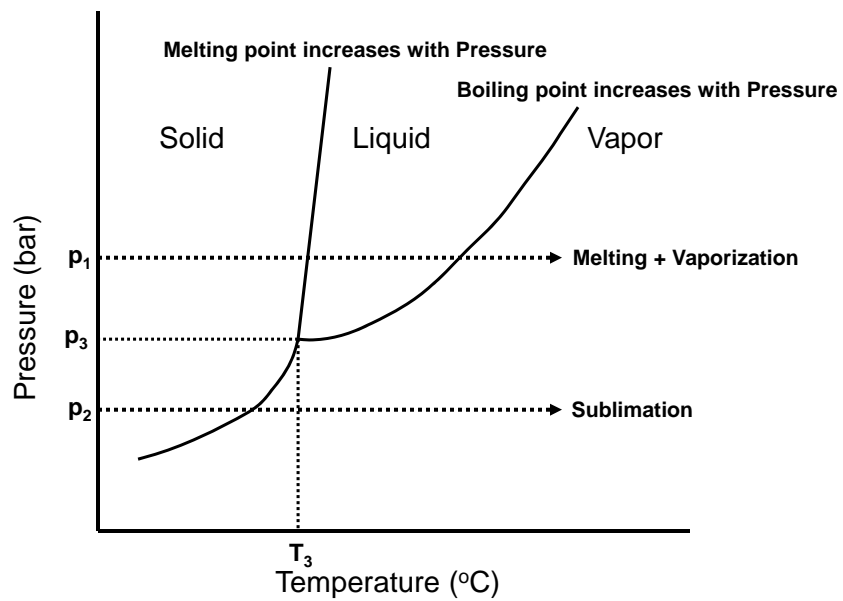
The Sublimation Curve

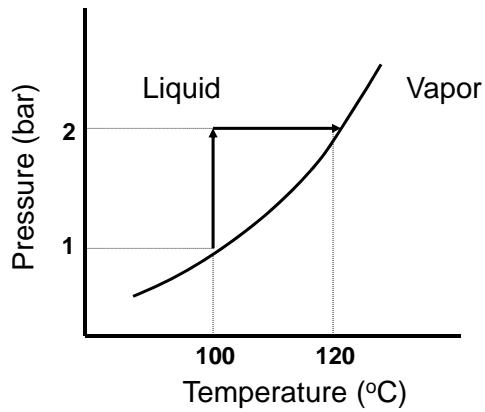This represents the combination of temperatures and pressures at which solid and vapor are in equilibrium

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A Typical Phase Diagram

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Pressure dependence of the Boiling Point

Liquid $\leftrightarrow$ Vapor

d(liq) >> d(vap)

V(liq) << V(vap)

Increased pressure shifts equilibrium in direction of lower volume.

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Pressure dependence of the Melting Point in "normal" substances
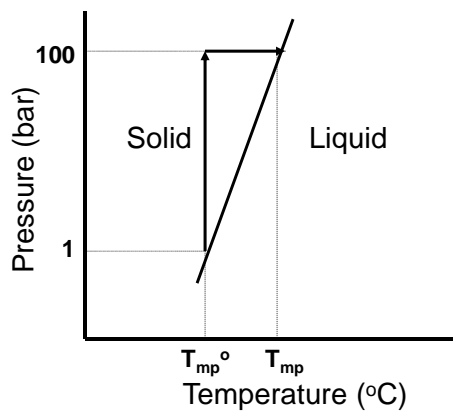
Solid $\leftrightarrow$ Liquid

d(sol) > d(liq)

V(sol) < V(liq)

Increased pressure shifts equilibrium in direction of lower volume.

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Question:

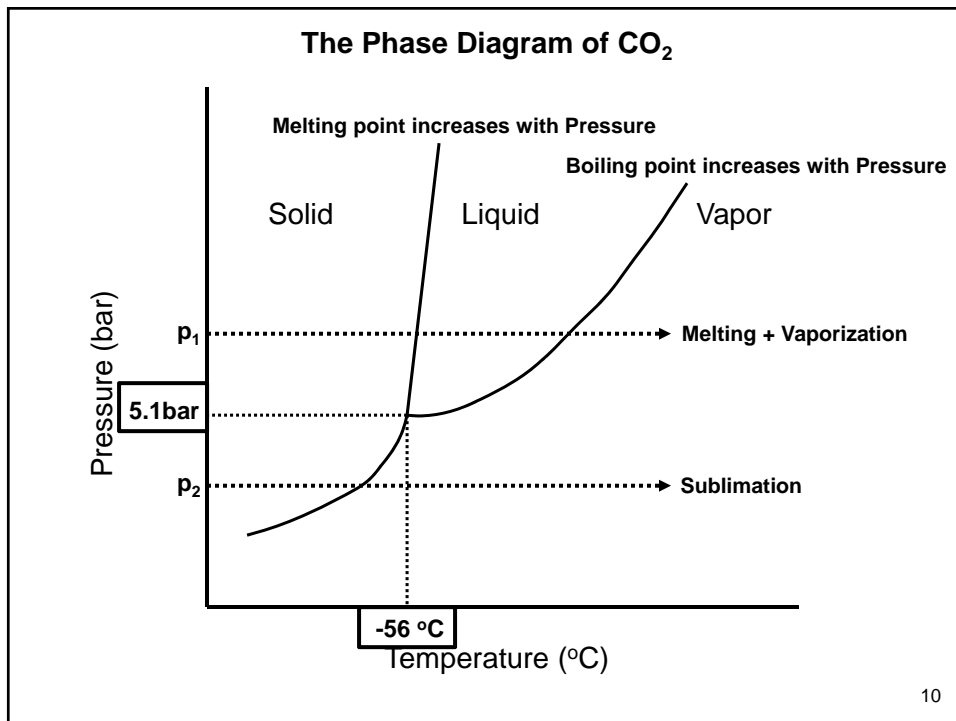Water melts and then boils (i.e. it has a liquid phase)
Benzene melts and then boils
Iron melts and then boils
Iodomethane melts and then boils
etc., etc., etc.

Why does CO_2 sublime directly from solid to vapor ???

Answer:

Because the triple point pressure of CO_2 is 5.1 bar (~5 atm.),
which is higher than the pressure of the atmosphere on Earth.

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The Phase Diagram of CO_2

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Phase Diagram of H$_2$O

Melting point decreases with Pressure

Solid   Liquid   Vapor

Pressure (bar)

P$_1$ ···→ **Melting + Vaporization**

4.6 torr

P$_2$ ···→ **Sublimation**

0.01
Temperature (^{o}C)

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Pressure dependence of the Melting Point in Water

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Pressure (bar)

Solid   Liquid

1

-1   0
Temperature (^{o}C)

Solid (ice) ↔ Liquid

d(ice) < d(liq)

V(ice) > V(liq)

Increased pressure shifts equilibrium in direction of lower volume.

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Some More Complex Phase Diagrams (FYI)

Water

This is a phase diagram of water over an extended range of pressure and temperature.

It shows the regions of stability of the various different crystal structures of ice.

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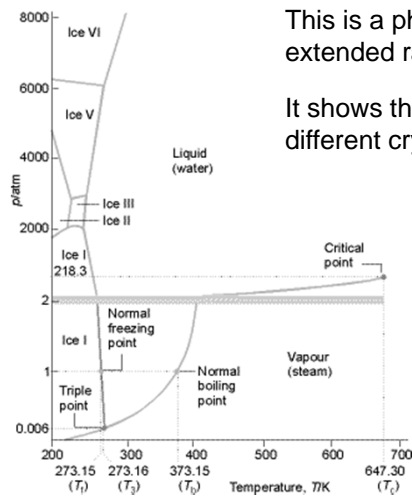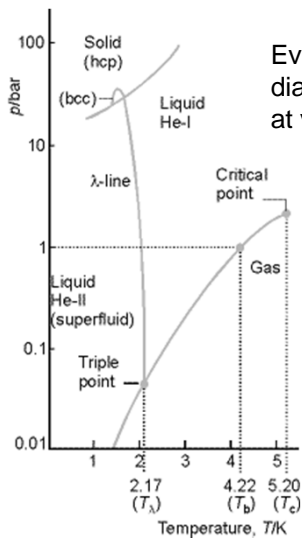## Helium

Even Helium has a fairly sophisticated phase diagram. However, all of the "action" occurs at very low temperature; $T_c \approx 5$ K

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Phase Stability and Phase Transitions

Chemical Potential

As discussed in Chapter 3, the chemical potential of a substance is defined by:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j \neq n_i}$$

However, in a pure (one component) system, the chemical potential is simply the Molar Gibbs Energy: $\boxed{\mu = G_m}$

Phase Equilibrium

Consider two phases, α and β (e.g. solid and liquid). The two phases will be in equilibrium when: $\mu_\alpha = \mu_\beta$

When the pressure and temperature are varied, they will stay in equilibrium when: $d\mu_\alpha = d\mu_\beta$

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The Temperature Dependence of Phase Stability

From Chapter 3, the temperature and pressure dependence of the Gibbs Energy is given by:

$$d\mu = dG_m = -S_m dT + V_m dp = \left(\frac{\partial \mu}{\partial T}\right)_p dT + \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

Therefore, the change in chemical potential (Molar Gibbs Energy) with rising temperature is:

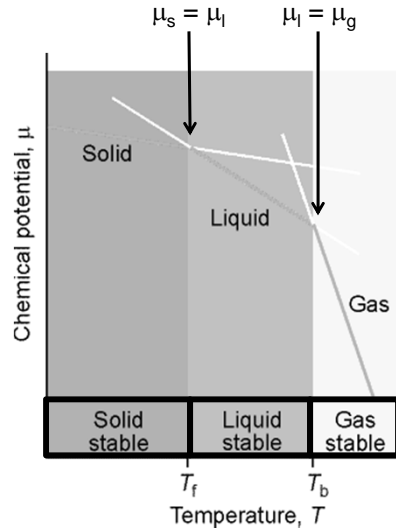$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

Notes

The entropies of all substances in all phases is positive, $S_m > 0$. Therefore μ always **decreases** with rising temperature.

Relative entropies of different phases are: $S_m(gas) \gg S_m(liq) > S_m(sol)$ Therefore, the decrease in μ with increasing temperature is greatest for the gas phase, and smallest for the solid.

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Two phases (α and β) are in equilibrium when $\mu_\alpha = \mu_\beta$

The phase with the lowest chemical potential at a given temperature is the most stable phase.

$\mu_s = \mu_l$ $\mu_l = \mu_g$

Remember:

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

Therefore:

$$\left|\left(\frac{\partial \mu}{\partial T}\right)_p^{gas}\right| > \left|\left(\frac{\partial \mu}{\partial T}\right)_p^{liq}\right| > \left|\left(\frac{\partial \mu}{\partial T}\right)_p^{sol}\right|$$

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The Effect of Pressure on the Melting Point

$$d\mu = dG_m = -S_m dT + V_m dp = \left(\frac{\partial \mu}{\partial T}\right)_p dT + \left(\frac{\partial \mu}{\partial p}\right)_T dp \longrightarrow \left(\frac{\partial \mu}{\partial p}\right)_T = +V_m$$

The chemical potential of all phases increase with rising pressure.

In most materials, $V_m(liq) > V_m(sol)$ Therefore, $\mu(liq)$ rises more rapidly than $\mu(sol)$ with increasing pressure.

This results in a higher melting point at higher pressure.
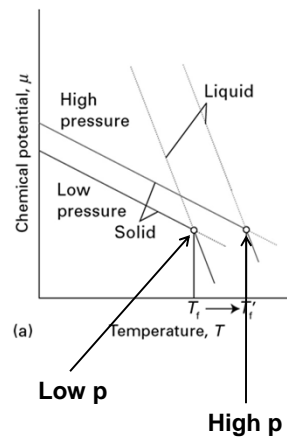

(a)

Low p

High p

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The Effect of Pressure on the Melting Point

$$d\mu = dG_m = -S_m dT + V_m dp = \left(\frac{\partial \mu}{\partial T}\right)_p dT + \left(\frac{\partial \mu}{\partial p}\right)_T dp \longrightarrow \left(\frac{\partial \mu}{\partial p}\right)_T = +V_m$$

The chemical potential of all phases increase with rising pressure.

In a few materials, most notably water, V_m(sol) > V_m(liq) Therefore, μ(sol) rises more rapidly than μ(liq) with increasing pressure.

This results in a lower melting point at higher pressure.

High p

High pressure

Liquid

Solid

Low pressure

$T_f' \leftarrow T_f$

(b) Temperature, T

Chemical potential, μ

Low p
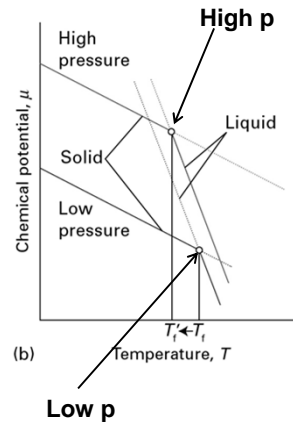
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**The Dependence of Chemical Potential (μ)
on Pressure and Temperature**

From Chapter 3, the dependence of G on T and P is given by

$$dG = -SdT + Vdp$$

If we're dealing with one mole of a substance, this equation becomes

$$dG_m = d\mu = \left(\frac{\partial \mu}{\partial T}\right)_p dT + \left(\frac{\partial \mu}{\partial p}\right)_T dP = -S_m dT + V_m dp$$

Therefore, we see that: $\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$ and $\left(\frac{\partial \mu}{\partial P}\right)_T = +V_m$

If the temperature is changed, $\Delta \mu = \int_{T_1}^{T_2} -S_m dT$

If the pressure is changed, $\Delta \mu = \int_{P_1}^{p_2} +V_m dp$

Examples of how to calculate $\Delta \mu$ are given in HW #4.1 – #4.4

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Quantitative Treatment of Phase Equilibria: The Location of Phases Boundaries

Two phases, $\alpha \rightleftharpoons \beta$ will be in equilibrium when their chemical potentials are equal:
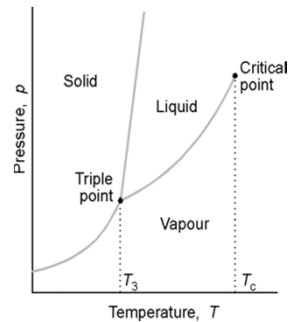
$$\mu_\beta(p,T) = \mu_\alpha(p,T)$$

For the two phases to remain in equilibrium as the pressure/temperature are changed, their variations must be equal:

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

Remembering that: $d\mu = -S_m dT + V_m dp$

the criterion for two phases to remain in equilibrium is:

$$-S_{\beta,m}dT + V_{\beta,m}dp = -S_{\alpha,m}dT + V_{\alpha,m}dp$$

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Thus, the criterion for two phases to remain in equilibrium is:

$$-S_{\beta,m}dT + V_{\beta,m}dp = -S_{\alpha,m}dT + V_{\alpha,m}dp$$

$$\left(V_{\beta,m} - V_{\alpha,m}\right)dp = \left(S_{\beta,m} - S_{\alpha,m}\right)dT$$

The Clapeyron Equation

$$\frac{dp}{dT} = \frac{S_{\beta,m} - S_{\alpha,m}}{V_{\beta,m} - V_{\alpha,m}} = \frac{\Delta_{trs}S_m}{\Delta_{trs}V_m}$$

Because the two phases are in equilibrium, we can use the relation, $\Delta_{trs}S = \Delta_{trs}H/T$, to obtain an alternative, equivalent form of the Clapeyron Equation:

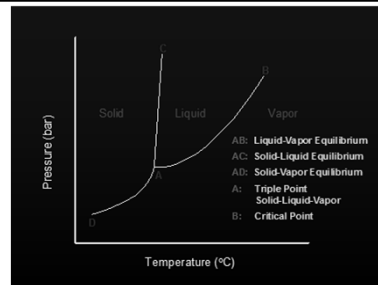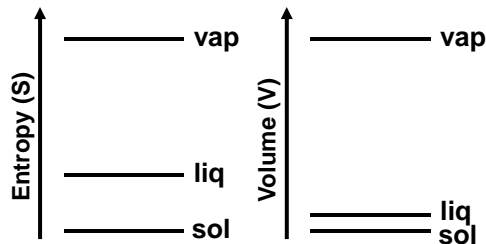$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} = \frac{\Delta_{trs}H}{T\Delta_{trs}V}$$

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Slopes of the Phase Boundaries

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} = \frac{\Delta_{trs}H}{T\Delta_{trs}V}$$

The Clapeyron Equation can be used both qualitatively and quantitatively.

In the next several slides, we will show how it can be used in a qualitative fashion to explain the relative slopes of various equilibrium curves in a phase diagram.

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Why is Slope(AD) > Slope(AB) ?

AD: Solid-Vapor

$\Delta V(s\text{-}v) = V_{vap} - V_{sol} = V_{vap}$

$\Delta S(s\text{-}v) = S_{vap} - S_{sol}$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_{vap} - S_{sol}}{V_{vap}}$$

AB: Liquid-Vapor

$\Delta V(l\text{-}v) = V_{vap} - V_{liq} = V_{vap}$

$\Delta S(l\text{-}v) = S_{vap} - S_{liq}$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_{vap} - S_{liq}}{V_{vap}}$$

Because $S_{vap} - S_{sol} > S_{vap} - S_{liq}$ or $\Delta_{sub}S > \Delta_{vap}S$

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Why is Slope(AC) >> Slope(AB) [and Slope(AD)] ?

AC: Solid-Liquid

AB: Liquid-Vapor

$\Delta V(s\text{-}l) = V_{liq}\text{-}V_{sol}$

$\Delta V(l\text{-}v) = V_{vap}\text{-}V_{liq} = V_{vap}$

$\Delta S(s\text{-}l) = S_{liq}\text{-}S_{sol}$

$\Delta S(l\text{-}v) = S_{vap}\text{-}S_{liq}$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_{liq} - S_{sol}}{V_{liq} - V_{sol}}$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_{vap} - S_{liq}}{V_{vap}}$$

Because $V_{liq}\text{-}V_{sol} << V_{vap}\text{-}V_{liq}$ or $\Delta_{fus}V << \Delta_{vap}V$

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Why is Slope(AC) < 0 in H_2O ?

AC: Solid-Liquid

H_2O

$\Delta V(s\text{-}l) = V_{liq}\text{-}V_{sol}$

$d_{liq} > d_{sol}$

$\Delta S(s\text{-}l) = S_{liq}\text{-}S_{sol}$

$V_{liq} < V_{sol}$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_{liq} - S_{sol}}{V_{liq} - V_{sol}}$$

$V_{liq}\text{-}V_{sol} < 0$

Because $V_{liq} < V_{sol}$

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Quantitative Application of the Clapeyron Equation

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} = \frac{\Delta_{trs}H}{T\Delta_{trs}V}$$

The Solid-Liquid Transition: Melting (aka Fusion)

$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V} = \frac{\Delta_{fus}H}{T\left(V_{liq} - V_{sol}\right)}$$

Over small ranges of temperature, T, $\Delta_{fus}H$ and $\Delta_{fus}V$ are approximately constant. Therefore, one can write:

$$\frac{\Delta p}{\Delta T} = \frac{p_2 - p_1}{T_2 - T_1} \approx \frac{\Delta_{fus}H}{T\left(V_{liq} - V_{sol}\right)} \quad \text{or} \quad \Delta p \approx \frac{\Delta_{fus}H}{T\left(V_{liq} - V_{sol}\right)}\Delta T$$

Note: The Clapeyron Equation cannot be used for quantitative calculations on vaporization or sublimation because it cannot be assumed that ΔV is independent of temperature, pressure for these transitions.

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Side Note: A more rigorous (but unnecessary) equation (FYI Only)

$$\frac{\Delta p}{\Delta T} = \frac{p_2 - p_1}{T_2 - T_1} \approx \frac{\Delta_{fus}H}{T\left(V_{liq} - V_{sol}\right)} \quad \text{or} \quad \Delta p \approx \frac{\Delta_{fus}H}{T\left(V_{liq} - V_{sol}\right)}\Delta T$$

It's straightforward to show that if one doesn't make the approximation that T = Constant, then the result is:

$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V} = \frac{\Delta_{fus}H}{T\left(V_{liq} - V_{sol}\right)} \longrightarrow \Delta p = \frac{\Delta_{fus}H}{\Delta_{fus}V}\int_{T_1}^{T_2}\frac{dT}{T} = \frac{\Delta_{fus}H}{\left(V_{liq} - V_{sol}\right)}\ln\left(T_2/T_1\right)$$

However, it can also be shown that if $\Delta T = T_2 - T_1 << T_1$, then the more rigorous solution reduces to the one we're using.

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{T_1 + \Delta T}{T_1}\right) = \ln\left(1 + \frac{\Delta T}{T_1}\right) = \ln\left(1 + x\right) \approx x = \frac{\Delta T}{T_1}$$

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$$\frac{\Delta p}{\Delta T} = \frac{p_2 - p_1}{T_2 - T_1} \approx \frac{\Delta_{fus}H}{T\left(V_{liq} - V_{sol}\right)}$$

Example: The melting point of benzene at 1 bar is 6.0 °C.
What is the melting point of benzene under
an applied pressure of 200 bar?

T_{mp} (200 bar) = 9.7 °C

$\Delta_{fus}H$ = 9.8 kJ/mol
M = 78 g/mol
d(sol) = 0.95 g/cm³
d(liq) = 0.88 g/cm³
1 L-bar = 100 J

Note: Similar problems on solid-liquid transitions are
given in HW #4.5 - #4.7

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Vaporization and Sublimation

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} = \frac{\Delta_{trs}H}{T\Delta_{trs}V}$$

These two phase transitions involve the gas phase and, therefore,
one **cannot** assume that $\Delta_{trs}V = V_{gas} - V_{liq}$ (or V_{sol}) = Constant.

However, it **is** valid to assume that (a) $\Delta_{trs}V \approx V_{gas}$
and (b) $V_{gas} = RT/p$ (for 1 mole)

Using $\Delta_{trs}V = RT/p$, one has:

$$\frac{dp}{dT} = \frac{\Delta_{trs}H}{T\Delta_{trs}V} = \frac{\Delta_{trs}H}{T\left(RT/p\right)} = \frac{p\Delta_{trs}H}{RT^2}$$

Separate Variables: $\dfrac{dp}{p} = \dfrac{\Delta_{trs}H}{RT^2}\,dT$

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Separate Variables:
$$\frac{dp}{p} = \frac{\Delta_{trs}H}{RT^2} dT$$

Now, integrate, assuming that $\Delta_{trs}H$ is independent of T:

$$\int_{P_1}^{P_2} \frac{dp}{p} = \frac{\Delta_{trs}H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\left[\ln p \right]_{P_1}^{P_2} = \frac{\Delta_{trs}H}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2}$$

The Clausius-Clapeyron Equation

$$\ln \left(\frac{p_2}{p_1} \right) = -\frac{\Delta_{trs}H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

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The Clausius-Clapeyron Equation

$$\ln \left(\frac{p_2}{p_1} \right) = -\frac{\Delta_{trs}H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

For vaporization, $\Delta_{trs}H = \Delta_{vap}H$
For sublimation, $\Delta_{trs}H = \Delta_{sub}H$

Applications

If one is given the enthalpy of vaporization (or sublimation) +
the vapor pressure at one temperature, then one can calculate either

(a) The vapor pressure at a second temperature or
(b) The temperature at which the vapor pressure reaches a certain value.

If one knows the vapor pressure at two temperatures, then the
enthalpy of vaporization (or sublimation) can be calculated.

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The Clausius-Clapeyron Equation

$$\ln\left(p_2 \middle/ p_1\right) = -\frac{\Delta_{trs}H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Example: The "normal boiling point"** of benzene is 80 °C, and the Enthalpy of Vaporization is 30.8 kJ/mol.

Calculate the temperature at which the vapor pressure of benzene is 150 torr.

1 bar = 750 torr

T = 33 °C

R = 8.31 J/mol-K

Note: Similar problems on liquid (or solid) to gase transitions are given in HW #4.8 - #4.10

**You should know that the "normal" boiling point is the temperature at which the vapor pressure of a substance is 1 bar.

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