

FUGACITY

It is simply a measure of molar Gibbs energy of a real gas .

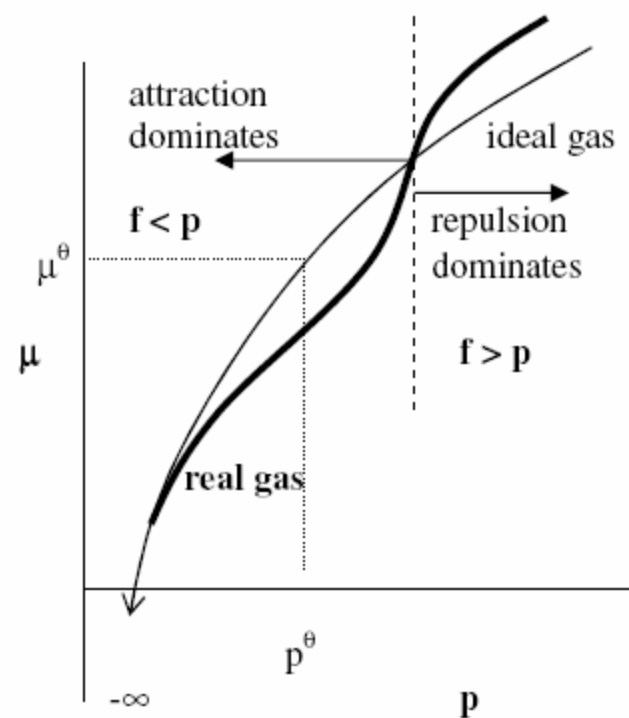
Modifying the simple equation for the chemical potential of an ideal gas by introducing the concept of a **fugacity (f)**. The fugacity is an “ effective pressure” which forces the equation below to be true for real gases:

$$\mu(p, T) = \mu^\theta(T) + RT \ln\left(\frac{f}{p^\theta}\right)$$

where $p^\theta = 1 \text{ atm}$

A plot of the chemical potential for an ideal and real gas is shown as a function of the pressure at constant temperature.

The fugacity has the units of pressure. As the pressure approaches zero, the real gas approach the ideal gas behavior and f approaches the pressure.



If fugacity is an “effective pressure” i.e, the pressure that gives the right value for the chemical potential of a real gas. So, the only way we can get a value for it and hence for μ is from the gas pressure. Thus we must find the relation between the effective pressure f and the measured pressure p .

$$\text{let } \mathbf{f = \phi p}$$

ϕ is defined as the **fugacity coefficient**. ϕ is the “fudge factor” that modifies the actual measured pressure to give the true chemical potential of the real gas.

By introducing ϕ we have just put off finding f directly. Thus, now we have to find ϕ .

Substituting for ϕ in the above equation gives:

$$\mu(p, T) = \mu^\theta(T) + RT \ln \left(\frac{p}{p^\theta} \right) + RT \ln \phi = \mu(\text{ideal gas}) + RT \ln \phi$$

$$\mathbf{\mu(p, T) - \mu(\text{ideal gas}) = RT \ln \phi}$$

This equation shows that the difference in chemical potential between the real and ideal gas lies in the term **$RT \ln \phi$** .

This is the term due to molecular interaction effects.

The equation relating f or ϕ to the measured pressure p

Note that as $p \rightarrow 0$, the real gas \rightarrow ideal gas, so that $f \rightarrow p$ and $\phi \rightarrow 1$

The chemical potential for an ideal gas and a real gas at two pressures p and p' is

$$\int_{p'}^p V_{\text{ideal,m}} dp = \int d\mu_{\text{ideal}} = \mu_{\text{ideal}}(p, T) - \mu_{\text{ideal}}(p', T) = RT \ln \left(\frac{p}{p'} \right)$$
$$\int_{p'}^p V_m dp = \int d\mu = \mu(p, T) - \mu(p', T) = RT \ln \left(\frac{f}{f'} \right)$$

Subtracting the first equation from the second gives

$$\int_{p'}^p (V_m - V_{\text{ideal,m}}) dp = RT \ln \left(\frac{f}{f'} \right) - RT \ln \left(\frac{p}{p'} \right)$$

$$\text{or} \quad \ln \left(\frac{f/p}{f'/p'} \right) = \frac{1}{RT} \int_{p'}^p (V_m - V_{\text{ideal,m}}) dp$$

Let $p' \rightarrow 0$, then in the initial state the real gas \rightarrow **the ideal gas. Thus $f' \rightarrow p'$**

$$\ln \left(\frac{f}{p} \right) = \frac{1}{RT} \int_0^p (V_m - V_{\text{ideal,m}}) dp$$

Since for an ideal gas $V_{\text{ideal,m}} = \frac{RT}{p}$ and for a real gas $V_m = \left(\frac{RT}{p}\right)Z$

where Z is the compressibility factor

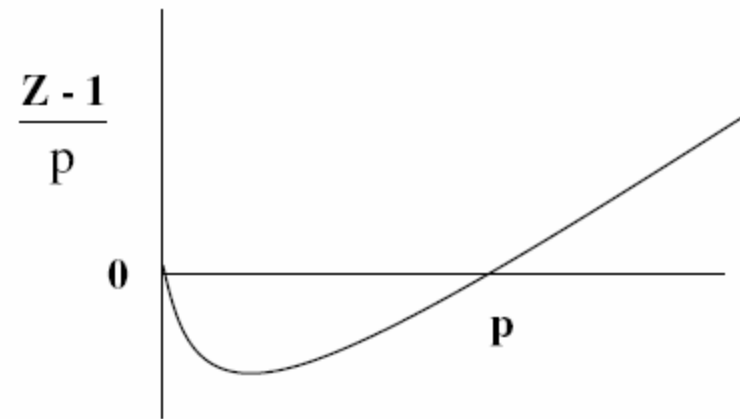
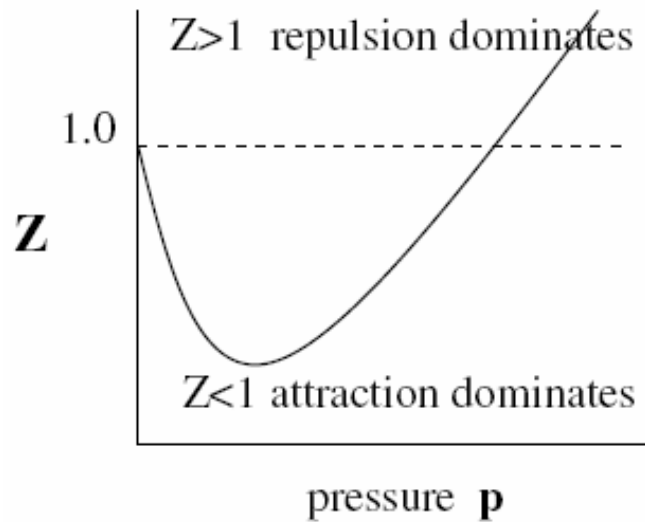
$$\ln\left(\frac{f}{p}\right) = \frac{1}{RT} \int_0^p \left[\left(\frac{RT}{p}\right)Z - \left(\frac{RT}{p}\right) \right] dp = \int_0^p \left[\frac{Z(p, T) - 1}{p} \right] dp = \ln \phi$$

$$f = p \exp \left\{ \int_0^p \left[\frac{Z(p, T) - 1}{p} \right] dp \right\}$$

The fugacity coefficient $\phi = f/p$ is given by

$$\phi = \exp \left\{ \int_0^p \left[\frac{Z(p, T) - 1}{p} \right] dp \right\}$$

Thus the fugacity of a gas is readily calculated at same pressure p if Z is known as a function of pressure up to that particular pressure.



At low to intermediate pressures $Z < 1$, attraction dominates and the area under the curve of the RHS plot, $\int \frac{Z-1}{p} dp$ is negative.

Thus $f = p \exp(\text{negative power})$. and $f < p$, $\phi < 1$.

At high pressures $Z > 1$, repulsion dominates and $\int \frac{Z-1}{p} dp > 0$ and $f > p$, $\phi > 1$

The Fugacity of van der Waals

From the compressibility factor Z of a Van der waals:

$$Z \left(= \frac{pV_m}{RT} \right) \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad Z = 1 + \left[b - \left(\frac{a}{RT} \right) \right] \left(\frac{p}{RT} \right)$$

From the fugacity equation

$$\ln \frac{f}{p} = \int_0^p \left(\frac{Z - 1}{p} \right) dp$$

$$\ln \frac{f}{p} = \int_0^p \left(b - \left(\frac{a}{RT} \right) \right) \frac{1}{RT} dp = \left(b - \left(\frac{a}{RT} \right) \right) \frac{p}{RT}$$

$$f = p \exp \left[\left(b - \left(\frac{a}{RT} \right) \right) \frac{p}{RT} \right]$$

Example: Given that the van der Waals constants of nitrogen are:

$a = 1.408 \text{ L}^2 \text{ atm mol}^{-2}$ and $b = 0.03913 \text{ L mol}^{-1}$.

Calculate the fugacity of nitrogen gas at 50 bar and 298 K.

$$\ln \frac{f}{p} = \left(b - \left(\frac{a}{RT} \right) \right) \frac{p}{RT}$$

$$\ln f = \ln p + \left(b - \left(\frac{a}{RT} \right) \right) \frac{p}{RT}$$

$$\ln f = \ln 50 + \left(0.03913 \text{ L.mol}^{-1} - \left(\frac{1.408 \text{ L}^2 \text{ .bar.mol}^{-2}}{(0.08314 \text{ L.bar.K}^{-1} \text{ .mol}^{-1})(298 \text{ K})} \right) \right) \frac{50 \text{ bar}}{(0.08314 \text{ L.bar.K}^{-1} \text{ .mol}^{-1})(298 \text{ K})}$$

fugacity (f) = 48.2 bar

Fundamental equations for open system

An open system is the one that can exchange matter with its surroundings.

Consider a two component system at temperature T and pressure p which is composed of n_1 moles of substance 1 and n_2 moles of substance 2.

The Gibbs function can be written as $\mathbf{G=G(T,p, n_1, n_2)}$. It is a function of four independent variables.

The total differential is
$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2} dp + \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} dn_2$$

For a system of constant composition ie a closed system:

$$dG = -S dT + V dp \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2} = -S \quad \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2} = V$$

Also from the earlier definition of the chemical potential : $\left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} = \mu_1 \quad \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} = \mu_2$

Gibbs function for a two component open system can be written as

$$dG = -S dT + V dp + \mu_1 dn_1 + \mu_2 dn_2 = -S dT + V dp + \sum \mu_i dn_i$$

This is the most general expression for the driving force of a system. It is very useful in examining what happens in a system at constant temperature and pressure when the amounts of n_1 and n_2 are changed. This occurs frequently in chemical and biochemical processes for example in the transfer of a solute to a solution. The starting equation in this case where $dT = 0 = dp$ is

$$dG = \mu_1 dn_1 + \mu_2 dn_2 = dw_{e,\max}$$

This equation is also interesting because we know that the reversible free energy change at constant temperature and pressure is the maximum non pV work. **This equation shows that non pV work is the result of composition changes in the system.**

This is exactly what happens in an electrochemical cell. As the electrochemical reaction occurs there are compositional changes and these lead to electrical current.

Finally, if a process is at equilibrium then $dG = 0$ and

$$\mu_1 dn_1 + \mu_2 dn_2 = 0 \quad \text{or} \quad \mu_1 dn_1 = -\mu_2 dn_2$$

This equation known as the Gibbs-Duhem equation is the starting point for many developments where equilibrium compositional changes occur under constant temperature and pressure.

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Phase Equilibrium

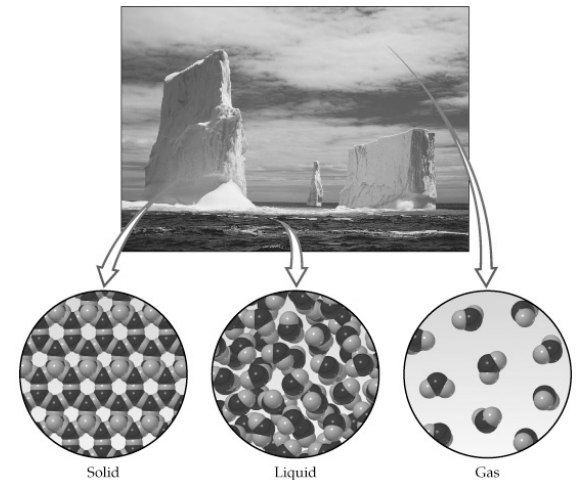
A **Phase (P)**: It is a part of a system, uniform through out in chemical composition and physical properties, that is separated a uniform component part of the system that is separated from the other homogeneous parts (e.g. solid, liquid, or gas) by boundary surface.

A phase may of course contain several chemical constituents, which may or may not be shared with other phases.

The number of phases is represented in the relation by **P**.

For example: If you have some ice floating in water, you have a solid phase present and a liquid phase. If there is air above the mixture, then that is another phase.

The **Degrees of Freedom [F]** is the number of independent intensive variables (i.e. those that are independent of the quantity of material present) that need to be specified in value to fully determine the state of the system. Typical such variables might be temperature, pressure, or concentration.



Phase Rule (F)

The number of degree of freedom for description of the intensive state of the system.

For a system involve pV work only: $F = C - P + 2$

Where C is the number of components of the system

For example: A system with one component

$$F = 1 - P + 2 = 3 - P$$

Case 1: one phase is present (a balloon full of carbon dioxide).

$$F = 3 - 1 = 2$$

There is two degrees of freedom: temperature and pressure are necessary to define the system and each one of them can be varied independently.

Case 2: two phases are present (liquid and vapor for instance):

$$F = 3 - 2 = 1$$

Either temperature or pressure (one variable) is necessary to define the system.

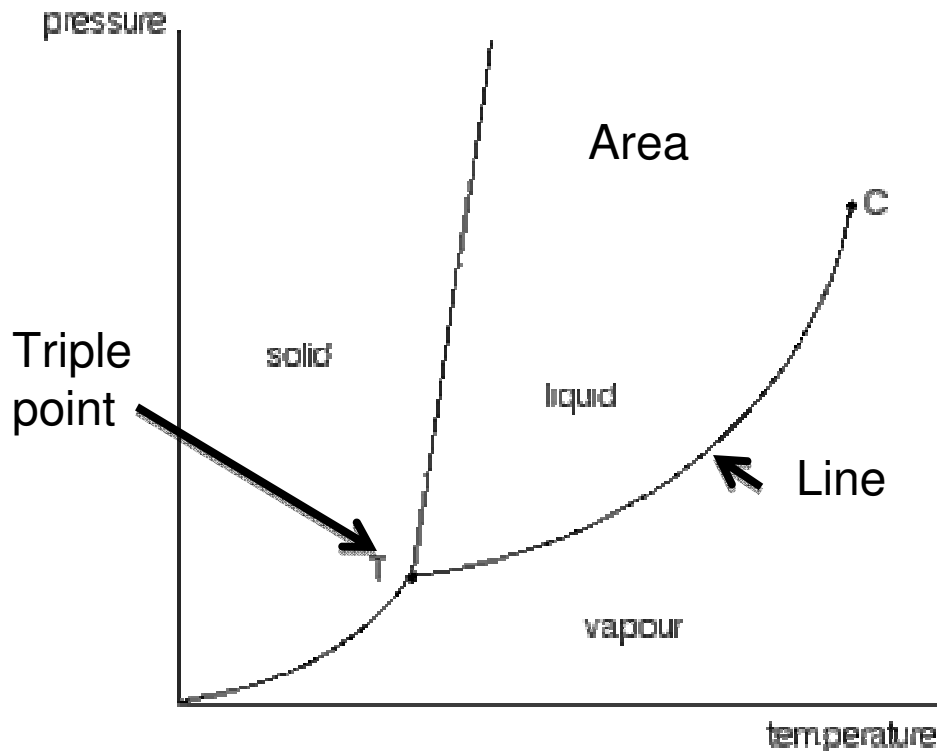
Case 3: three phases are present (solid, liquid and vapor for instance):

$$F = 3 - 3 = 0$$

Such a system is said to be “invariant” and is represented by a point in a plot of phase diagram (T-p), where the pressure and temperature are fixed by the equilibrium.

Phase diagrams

It is a graphical way to depict the effects of pressure and temperature on the phase of a substance. A phase diagram shows exactly what phases are present at any given temperature and pressure.



The phases will simply be the solid, liquid or vapor (gas) states of a pure substance.

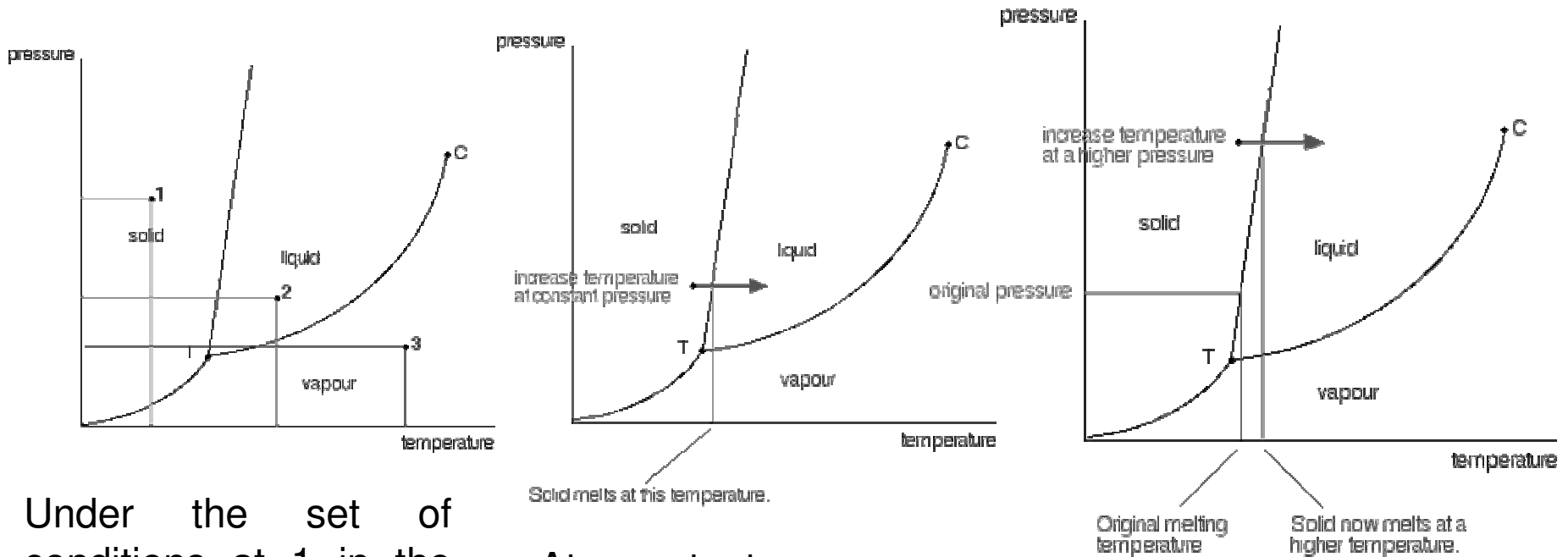
This phase diagram is characterized by area, line and triple point.

Area: it represents a one phase ($F = 2$), where the two variables T and p are necessary to define, like areas of solid, liquid, and vapor.

Line: it represents two phases ($F = 1$) in equilibrium. The system can be completely define by T or p .

Triple point (T): it represents three phases ($F = 0$) in equilibrium. The system can be completely define by T or p . It is only one point in the diagram. If T or p change, the two phase will dissappear.

The three areas



Under the set of conditions at 1 in the diagram, the substance would be a solid because it falls into that area of the phase diagram. At 2, it would be a liquid; and at 3, it would be a vapor (a gas).

Solid melts at this temperature.

At constant pressure, as the temperature increases to the point where it crosses the line, the solid will turn to liquid.

Original melting temperature

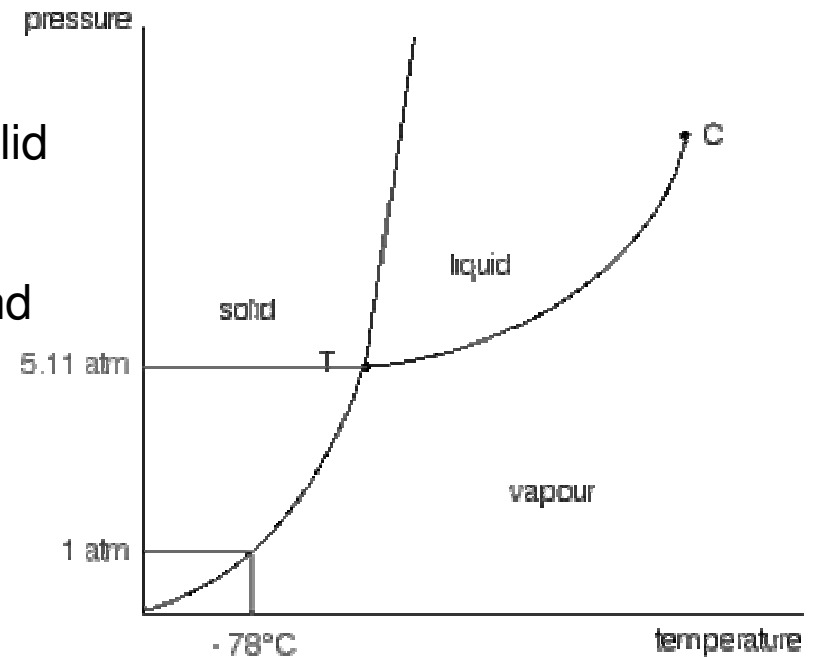
Solid now melts at a higher temperature.

If you repeated this at a higher fixed pressure, the melting temperature would be higher because the line between the solid and liquid areas slopes slightly forward.

Phase diagram of CO₂

It shows that there is equilibrium between solid and gas at 1 atm and -78°C.

Liquid CO₂ is produced only above 5.1 atm and -57°C.



The only thing special about this phase diagram is the position of the triple point which is well above atmospheric pressure. It is impossible to get any liquid carbon dioxide at pressures less than 5.11 atmospheres.

That means that at 1 atmosphere pressure, carbon dioxide will sublime at a temperature of -78°C.

This is the reason that solid carbon dioxide is often known as "dry ice". You can't get liquid carbon dioxide under normal conditions - only the solid or the vapor.

Existence of phases in a one-component system

When a solid is heated, the solid phase changes to liquid and then to gas.

To understand these processes, a plot of the chemical potential versus T at constant p for various phases is studied.

T_m is the melting point at which solid and liquid are at equilibrium at the same chemical potential.

T_b is the boiling point at which liquid and gas are at equilibrium at the same chemical potential.

Below T_m , the solid has the lowest μ and is therefore, the stable phase.

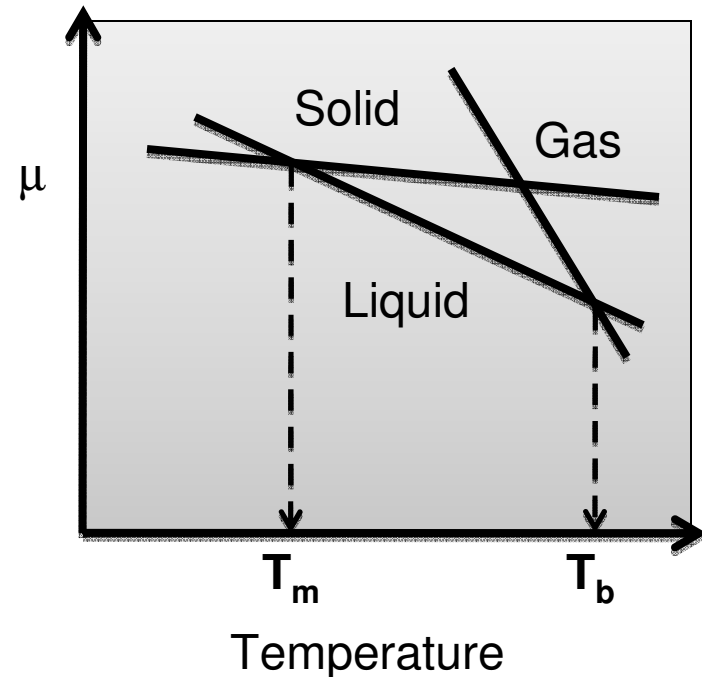
Between T_m and T_b the liquid is the stable phase.

The slope of the lines giving the molar entropy of the phases, where: $\left(\frac{d\mu}{dt}\right)_p = -S_m$

Since S is positive, the slopes are negative.

Since $S_m(g) > S_m(l) > S_m(s)$,

The slope is more negative for a gas than a liquid than a solid



For a single phase of a pure substance, μ is a function of T and p .

Thus, it is convenient to consider μ as a function of T at specified pressures.

At lower pressure, the plots of μ vs. T are displaced.

The effect of p on μ of a pure substance

at constant T is given by: $\left(\frac{d\mu}{dp}\right)_T = V_m$

μ decreases as the p is decreased at constant T .

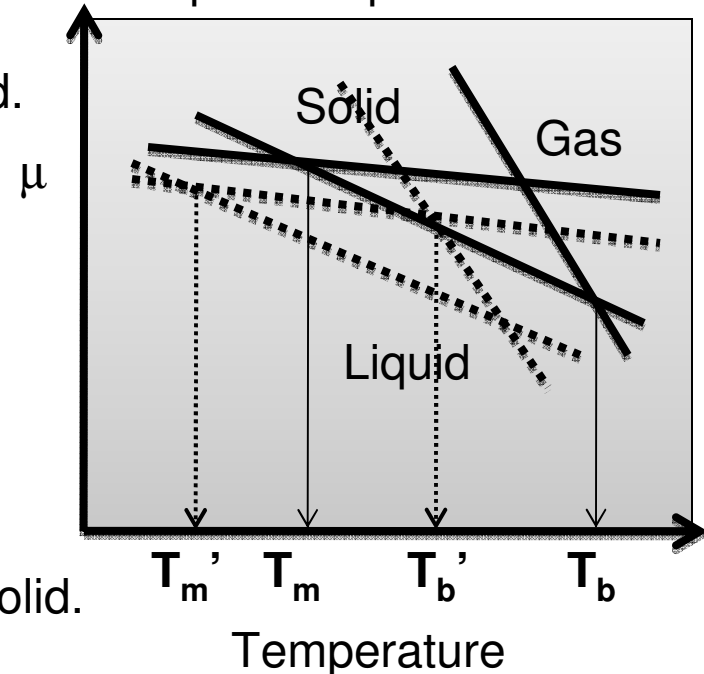
Since $V_m(g) \gg V_m(l), V_m(s)$,

The effects is much larger for gas than a liquid or solid.

Reducing the pressure lowers T_b and T_m , and the effect on T_b is much larger because of the large difference in molar volume of gas and liquid.

The range of T over which the liquid is the stable phase has been reduced.

At the same particular p , the solid, liquid, and gas lines will intersect at a point referred to as the “**triple point**”.



The Clapeyron Equation

Consider one component system with two phases α and β .

At equilibrium, T , p and μ are same in the two phases.

When T only changes or p only changes, one of the phases will disappear.

When both T and p change in such a way to keep μ is equal in the two phases, the two phases will continue to co-exist.

This is the co existence curve for the system $\alpha - \beta$.

Along the curve, $\mu_\alpha = \mu_\beta$

If T changes by dT , p will changes by dp .

At point 1: $\mu_{1\alpha} = \mu_{1\beta}$

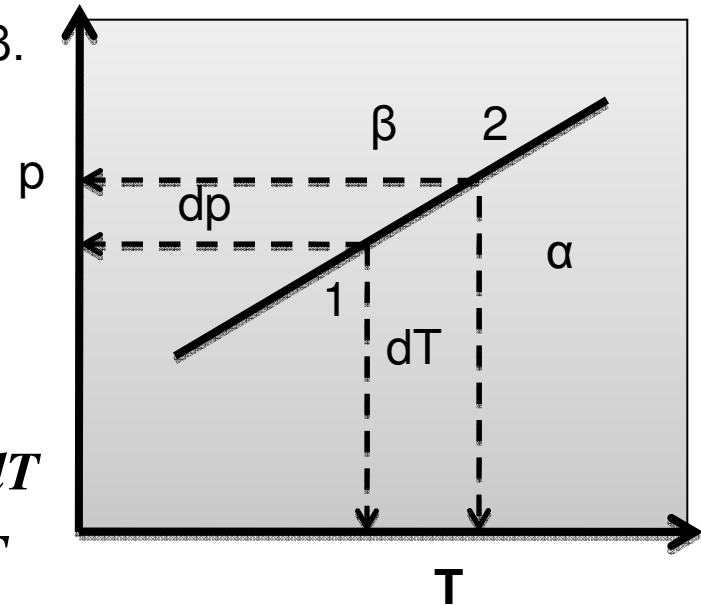
At point 2: $\mu_{1\alpha} + d\mu_\alpha = \mu_{1\beta} + d\mu_\beta$

$\therefore d\mu_\alpha = d\mu_\beta$ Since $d\mu = dG_m = V_m dp - S_m dT$

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

$\frac{dp}{dT} = \frac{S_{m,\beta} - S_{m,\alpha}}{V_{m,\beta} - V_{m,\alpha}} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \Delta V_m}$ This equation can be applied to vaporization, sublimation, fusion or transition between two phases.

Note that: $\Delta_{\text{sub}} H = \Delta_{\text{fus}} H + \Delta_{\text{vap}} H$



$\Delta_{\text{vap}}H$ of water = 40.69 kJ mol⁻¹, $V_{\text{m,g}} = 30.199 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, $V_{\text{m,l}} = 0.019 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ all at 100°C and 1 atm. What is the change in boiling points of water per Pascal.

Answer

$$\frac{dp}{dT} = \frac{\Delta H_{\text{m,vap}}}{T(V_{\text{m,g}} - V_{\text{m,l}})} = \frac{40.69 \text{ kJ mol}^{-1}}{(373.15\text{K})(30.199 - 0.019) \times 10^{-3} (\text{m}^3 \text{ mol}^{-1})}$$

Note: J = Pa m³ $\therefore \frac{dp}{dT} = 3613 \text{ Pa.K}^{-1} \quad \therefore \frac{dT}{dp} = 2.768 \times 10^{-4} \text{ K.Pa}^{-1}$

Calculate the change in pressure required to change the freezing point of water 1°C. At 0°C the heat of fusion of ice is 333.5 J g⁻¹, the density of water is 0.9998 g cm⁻³ and ice is 0.9168 g cm⁻³.

Answer

$$: \quad V_{\text{m,l}} = 1 / (0.9998 \text{ g cm}^{-3}) = 1.0002 \text{ cm}^3 \text{ g}^{-1} \quad V_{\text{m,ice}} = 1.0908 \text{ cm}^3 \text{ g}^{-1}$$

$$\Delta V_{\text{m}} = V_{\text{m,l}} - V_{\text{m,ice}} = 1.0002 \text{ cm}^3 \text{ g}^{-1} - 1.0908 \text{ cm}^3 \text{ g}^{-1} = -0.0906 \text{ cm}^3 \text{ g}^{-1}$$

$$= -0.0906 \times 10^{-6} \text{ m}^3 \text{ g}^{-1} = -9.06 \times 10^{-8} \text{ m}^3 \text{ g}^{-1}$$

$$\frac{dp}{dT} = \frac{\Delta H_{\text{m,fus}}}{T(V_{\text{m,l}} - V_{\text{m,ice}})} = \frac{333.5 \text{ J g}^{-1}}{(273.15\text{K})(-9.06 \times 10^{-8} \text{ m}^3 \text{ g}^{-1})} = -1.348 \times 10^7 \text{ Pa.K}^{-1}$$

$$= -134.8 \text{ bar.K}^{-1}$$

The Clausius-Clapeyron Equation

Clausius modified Clapeyron equation by neglecting the molar volume of liquid in comparison with molar volume of the gas.

$$\therefore \frac{dp}{dT} = \frac{\Delta_{vap}H}{TV_g} = \frac{P\Delta_{vap}H}{RT^2} \quad \therefore \frac{dp}{p} = \frac{\Delta_{vap}H}{RT^2} dT \quad \therefore \int \frac{dp}{p} = \frac{\Delta_{vap}H}{R} \int \frac{dT}{T^2}$$

$$\therefore \ln \frac{p}{p_o} = -\frac{\Delta_{vap}H}{RT} + C$$

By plotting $\ln \frac{p}{p_o}$ vs. $\frac{1}{T}$, ΔH can be calculated for vaporization or sublimation.

Also, by limits the integration: $\therefore \int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta_{vap}H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$

$$\therefore \ln \frac{p_2}{p_1} = \frac{\Delta_{vap}H(T_2 - T_1)}{RT_1T_2}$$

$$\Delta_{vap}H^o$$

Defects of this equation:

To represent p as a function of T over a wide range of T is necessary to consider as T dependence.

The vapor has been assumed to be an ideal gas.

Trouton's Rule:

The molar entropy of vaporization at the standard boiling point (the bp at 1 bar) is a constant and its value is about $88 \text{ JK}^{-1}\text{mol}^{-1}$.

$$\Delta_{vap} S \cong 88 \text{ JK}^{-1} \text{ mol}^{-1}$$

By using this rule $\Delta_{vap} H$ of a liquid can be estimated approximately:

$$\Delta_{vap} S = \frac{\Delta_{vap} H}{T_b}$$

Example: The boiling point of benzene is $80.1 \text{ }^\circ\text{C}$ at 1 atm. Estimate the vapor pressure at $25 \text{ }^\circ\text{C}$ using Trouton's rule.

The vapor pressure at $(80.1+273) 353.3 \text{ K}$ is 1.013 bar

According to Trouton's rule: $\Delta_{vap} H = (88 \text{ JK}^{-1}\text{mol}^{-1}) (353.3 \text{ K}) = 31.1 \times 10^3 \text{ J mol}^{-1}$

According to Clausius-Clapeyron equation $\therefore \ln \frac{p_2}{p_1} = \frac{\Delta_{vap} H (T_2 - T_1)}{RT_1 T_2}$

$$\therefore \ln \frac{1.013 \text{ bar}}{p_1} = \frac{(31.1 \times 10^3 \text{ J mol}^{-1})(353.3 \text{ K} - 298 \text{ K})}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(353.3 \text{ K})(298 \text{ K})} \longrightarrow P_1 = 0.143 \text{ bar}$$

Vapor-liquid Equilibrium of binary liquids mixtures

When a binary liquid mixture is in equilibrium with its vapor at constant T:

$$\therefore \mu_i(g) = \mu_i(l)$$

i.e. the chemical potential of each component is the same in the gas and liquid phase.

Assuming that the vapor is an ideal gas:

$$\therefore \mu_i(g) = \mu_i^o(g) + RT \ln \frac{p_i}{p^o}$$

And for a liquid mixture is:

$$\therefore \mu_i(l) = \mu_i^o(l) + RT \ln a_i$$

Where a_i is the activity

$$\therefore \mu_i^o(g) + RT \ln \frac{p_i}{p^o} = \mu_i^o(l) + RT \ln a_i$$

And for a pure liquid (its activity equal unity), $\therefore \mu_i^o(g) + RT \ln \frac{p_i^*}{p^o} = \mu_i^o(l)$

Where p_i^* is the vapor pressure of pure liquid i .

By subtract the last equation (for pure liquid) from that in a mixture

$$\therefore RT \ln \frac{p_i}{p_i^*} = RT \ln a_i \quad \boxed{\therefore a_i = \frac{p_i}{p_i^*}} \text{ This is for ideal behavior of the vapor.}$$

Raoult's Law

For a certain solution (ideal), the partial pressure of a component is equal to the mole fraction of that component times (x) the vapor pressure of the pure component.

$$p_i = x_i p_i^*$$

This law is correct when the components are quite similar.

Since the gas phase assumed to be an ideal gas:

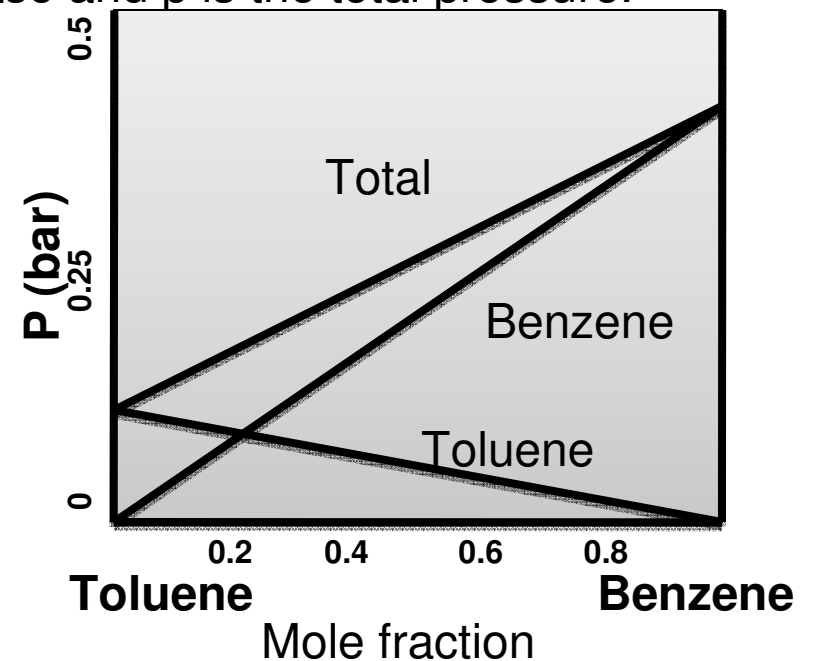
$$\therefore p_i = y_i P \quad \text{Dalton's Law}$$

Where, y_i is the mole fraction of i in the gas phase and p is the total pressure.

As shown in the figure, change of vapor pressure for benzene-toluene mixture, also with vapor pressure of both benzene and toluene solutions against the composition of solution.

The behavior of mixture follow the ideal solution behavior and Raoult's law.

For this solution, it is possible to calculate the composition of its vapor which in equilibrium with solution.



For a mixture of two liquid 1 and 2:

$$y_1 = \frac{p_1}{p} \quad \text{and} \quad y_2 = \frac{p_2}{p}$$

From Raoult's law: $y_1 = \frac{x_1 p_1^*}{p}$ and $y_2 = \frac{x_2 p_2^*}{p}$

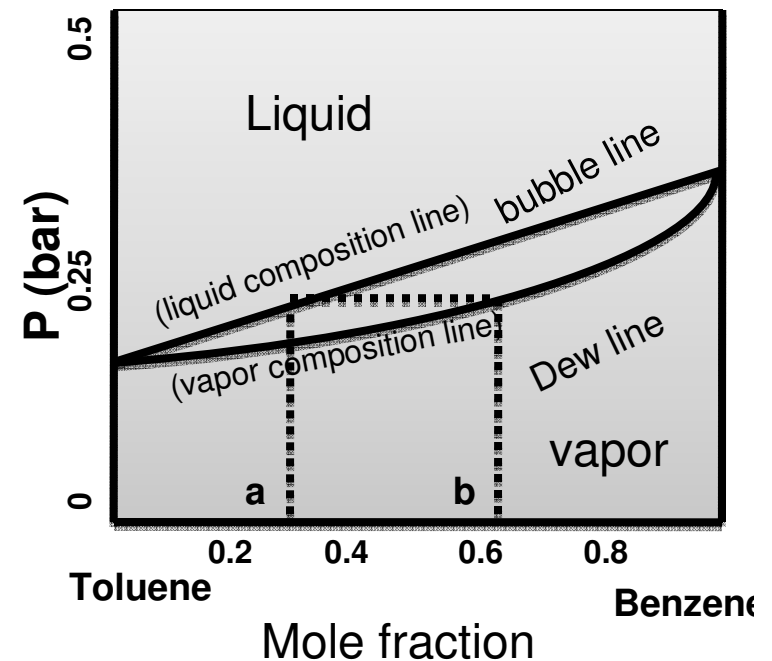
The relative mole fraction of components' in the vapor phase:

$$\frac{y_1}{y_2} = \frac{x_1 p_1^*}{x_2 p_2^*} \quad \text{and} \quad \frac{x_1}{x_2} = \frac{y_1 p_2^*}{y_2 p_1^*}$$

From this diagram:

-at any specific vapor pressure it can be determined
-the corresponding composition of liquid mixture.

- or at any specific composition of liquid mixture (a) can be determine the corresponding composition in vapor phase (b).



Example: At 60 °C the vapor pressures of pure benzene and toluene are 0.513 and 0.185 bar, respectively. For a solution with 0.6 mole fraction toluene. What are the partial pressures of components and what is the mole fraction of toluene in the vapor?

Answer:

$$p_1^* \text{ (benzene)} = 0.513 \text{ bar} \quad p_2^* \text{ (toluene)} = 0.185 \text{ bar} \quad x_2 = 0.6$$

$$y_2 = ??? \quad p_1 \text{ and } p_2 = ???$$

$$p_2 = x_2 p_2^* = 0.6 \times 0.185 \text{ bar} = 0.111 \text{ bar}$$

$$x_1 = 1 - x_2 = 1 - 0.6 = 0.4 \text{ bar}$$

$$p_1 = x_1 p_1^* = 0.4 \times 0.513 \text{ bar} = 0.205 \text{ bar}$$

$$P_{\text{total}} = p_1 + p_2 = 0.111 + 0.205 \text{ bar} = 0.316 \text{ bar}$$

$$y_2 = \frac{p_2}{P_{\text{total}}} = \mathbf{0.351}$$

Example: At 80 °C the vapor pressures of pure benzene and toluene are 100.4 kPa and 38.7 kPa, respectively.

a) Calculate the vapor composition and total pressure for solution at 80 °C consists of 0.5 benzene and 0.5 toluene mole fraction

b) Calculate the liquid composition at equilibrium for the mixture at 80 °C, where the vapor contains mole fraction of benzene 0.75.

Answer:

$$a) \quad \frac{y_1}{y_2} = \frac{x_1 p_1^*}{x_2 p_2^*} = \frac{(0.5)(100.4 \text{ kPa})}{(0.5)(38.7)} = 2.594$$

$$y_1 = y_2 (2.594) = (1 - y_1) (2.594) \quad y_1 = 0.722 \quad \text{and} \quad y_2 = 0.278$$

$$P_{\text{total}} = x_1 p_1^* + x_2 p_2^* = (0.5)(100.4 \text{ kPa}) + (0.5)(38.7 \text{ kPa}) = 69.55 \text{ kPa}$$

$$b) \quad \frac{y_1}{y_2} = \frac{x_1 p_1^*}{x_2 p_2^*} \quad \frac{x_1}{x_2} = \frac{y_1 p_2^*}{y_2 p_1^*}$$

$$\frac{x_1}{1 - x_1} = \frac{(0.75)(38.7 \text{ kPa})}{(0.25)(100.4 \text{ kPa})} = 1.156$$

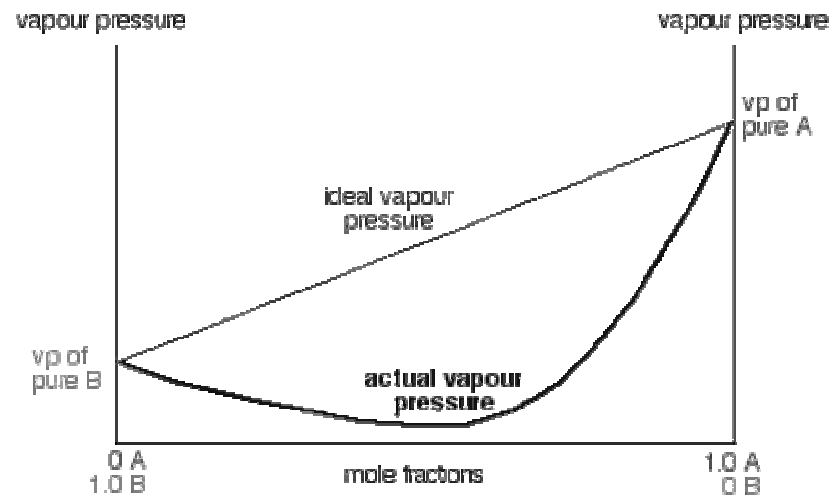
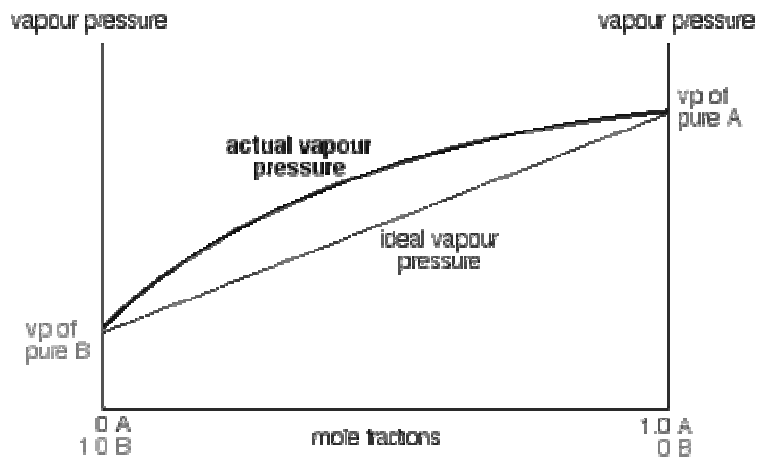
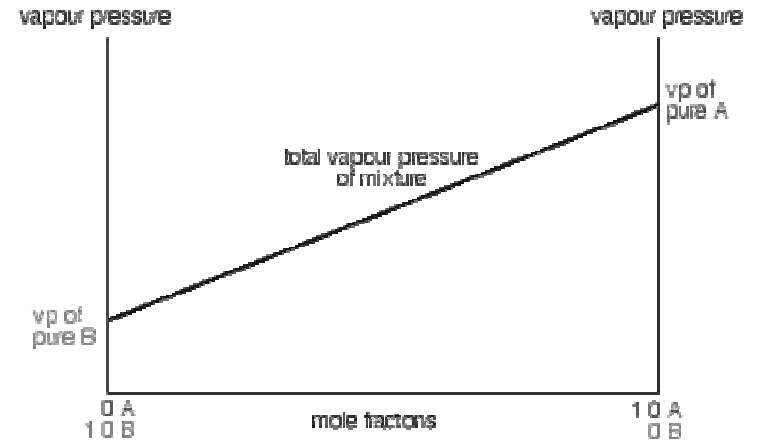
$$X_1 = 0.536 \quad \text{and} \quad X_2 = 1 - X_1 = 1 - 0.536 = 0.464$$

NON-IDEAL MIXTURES OF LIQUIDS

Deviations from Raoult's Law

By plotting the vapor pressure of an ideal mixture of two liquids against their composition, you get a straight line graph like this:

In this case, pure A has the higher vapor pressure and so is the more volatile component.



Positive deviations from Raoult's Law

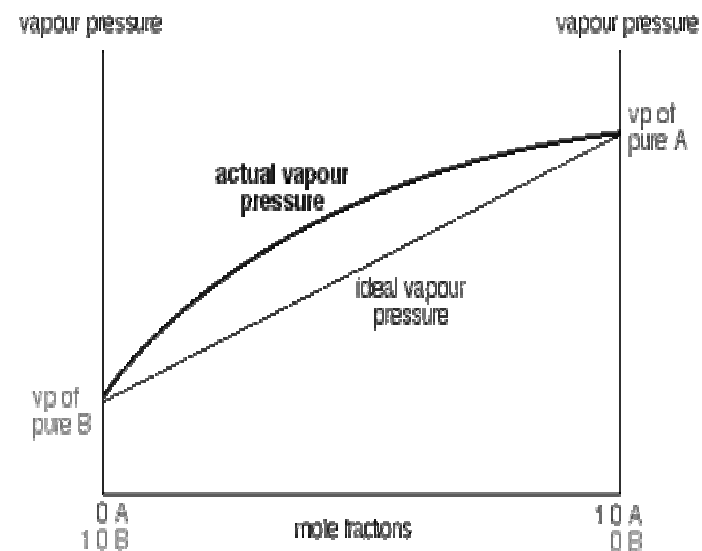
In mixtures showing a positive deviation from Raoult's Law, the vapor pressure of the mixture is always higher than you would expect from an ideal mixture, and hence have lower **BP**.

Because the vapor pressure is higher, the liquid is evaporating more easily than would be expected. This means that some of the intermolecular bonds in the liquid must have been broken when the liquids were mixed.

i.e., means that molecules are breaking away **more easily** than they do in the pure liquids, because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.

Example: mixture of ethanol and water. The ethanol molecules have an average of 1 hydrogen bond per molecule, whereas the water molecules have 2. The ethanol molecules interfere with the hydrogen bonds and therefore make the liquid more volatile.

Ethanol and benzene? the hydrogen bonding in the ethanol is reduced by the presence of the benzene.



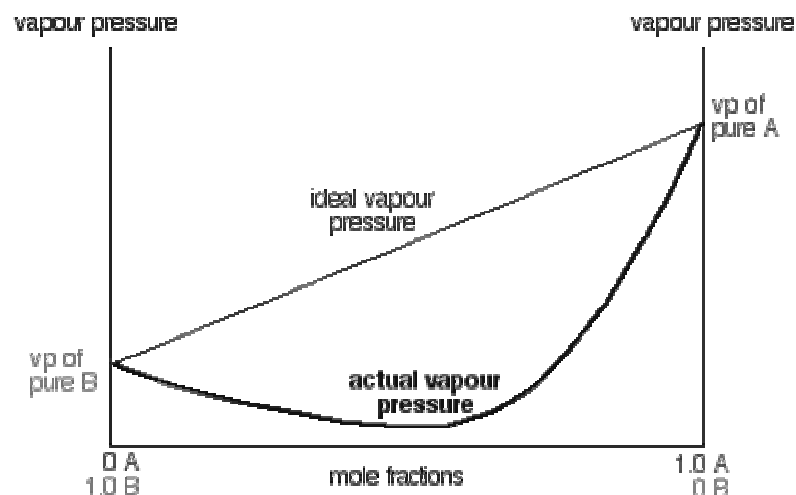
Negative deviations from Raoult's Law

In exactly the same way, having mixtures with vapor pressures which are less than would be expected by Raoult's Law.

These are cases where the molecules break away from the mixture **less easily** than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids.

i.e. the intermolecular forces increase when the liquids are mixed. This is generally because molecules where no hydrogen bonding is present are mixed to form a liquid with hydrogen bonds.

Example: Trichloromethane and ethoxyethane. CHCl_3 has a polar hydrogen atom but no lone pairs and therefore cannot form hydrogen bonds. $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$ has lone pairs on the oxygen but no polar hydrogen atom and therefore cannot form hydrogen bonds. When mixed, hydrogen bonds form, decreasing the vapor pressure.



Boiling point - composition diagrams

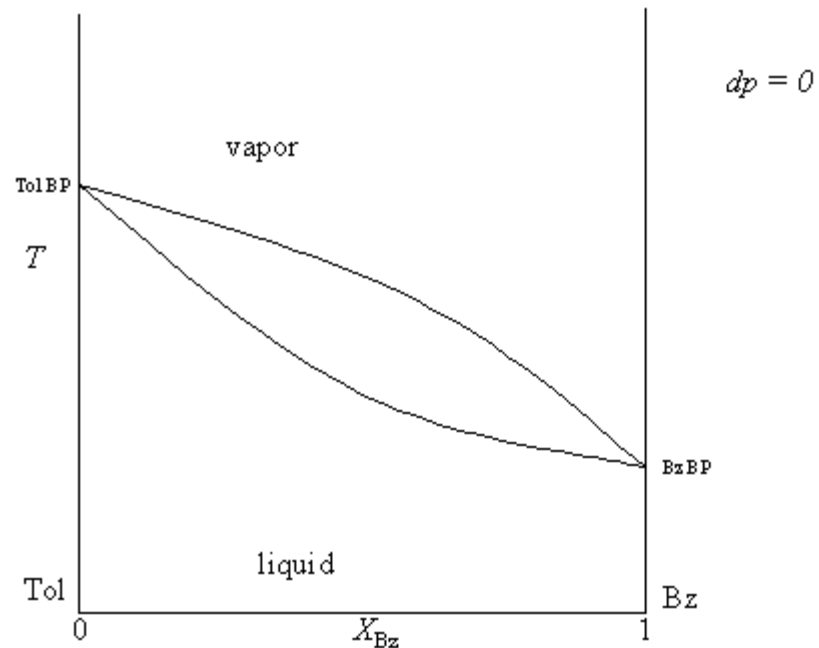
The BP of liquid mixture is the temperature at which the total pressure of liquid mixture equal to the atmospheric pressure.

At constant T , the VP of liquid mixture is changed with the composition of liquid, as it was shown before.

Also, at constant pressure (1 atm), the BP of liquid mixture is changed with liquid composition.

Ideal Mixtures

The vapor composition line is over the liquid composition line where more volatile component has higher content in the vapor.



The point on the lower curve at a mole fraction of benzene of about 0.33.

This point gives the boiling point of a mixture which is 0.33 mole percent benzene.

what is the composition of the vapor which is in equilibrium with the liquid at this temperature?

The vapor composition must lie

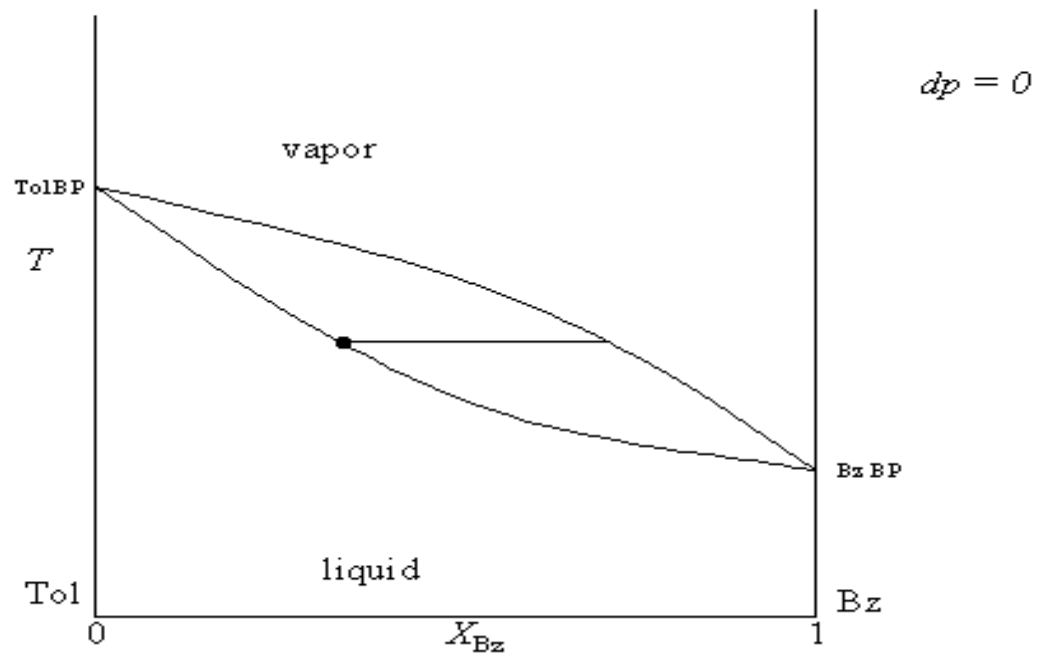
on a horizontal (constant temperature) line going through this point.

At any given temperature and pressure the composition of the vapor must be richer in the more volatile component and benzene is the more volatile component.

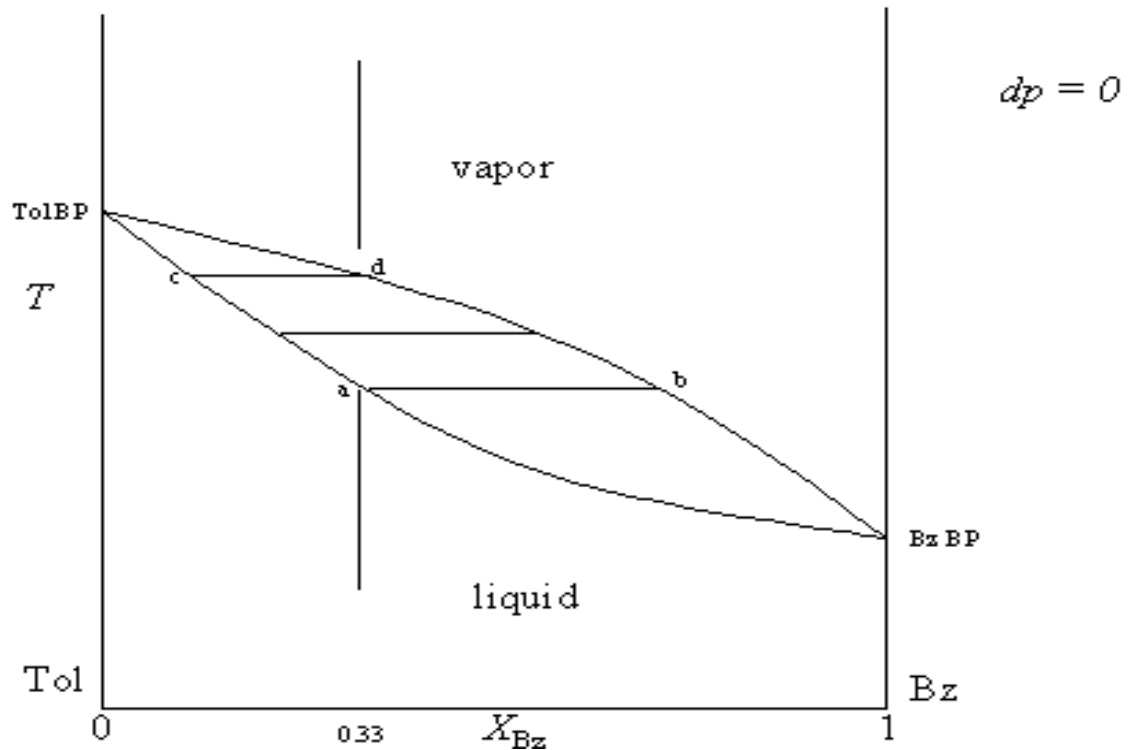
This line a **tie line** and it intersects the upper curve at the composition of the vapor in equilibrium with the liquid at the same temperature.

The region between the two curves is a two-phase region. In this region two phases, liquid and gas, are in equilibrium with each other.

Toluene – Benzene Mixture



If we heat a liquid mixture at a composition of about 0.33 mole fraction benzene the liquid will have the composition shown at point "a" when the liquid first begins to boil. The first vapor to come off will have the composition shown at point "b."



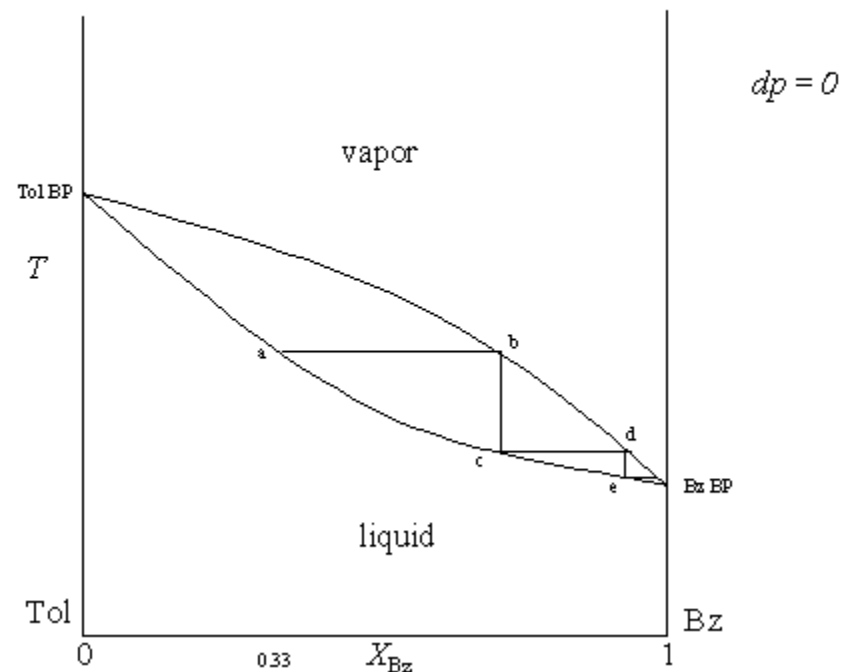
As we continue to heat the system the more volatile component will evaporate preferentially and the liquid phase will become richer in the less volatile component (toluene, here). As we continue to heat the mixture the toluene will gradually catch up to the benzene in the vapor phase. The very last bit of liquid to evaporate will have the composition shown at point "c," and the vapor will have the original composition that we started with, "d" (or "a"). Notice that as we heat the system the tie line "tracks" with the lower and upper curves to give the composition of liquid and vapor in equilibrium.

Fractional distillation

Boiling diagrams provide an explanation for fractional distillation.

Suppose we start with a liquid mixture with 0.33 mole fraction benzene.

As we heat the liquid it will begin to boil when the temperature reaches the temperature of point "a." The first vapor to come off has the composition shown at point "b." Capture the vapor, condense it, and heat it up. The new liquid will boil at point "c" giving a vapor with composition at point "d." Capture this vapor, cool it, and boil it at point, "e," and so on. by continuing this process the vapor can be made as pure in benzene as desired.



This is what fractional distillation does. There are more modern ways to separate mixtures, for example, chromatography, but fractional distillation still has industrial and some laboratory importance.

Boiling diagrams for non ideal solutions

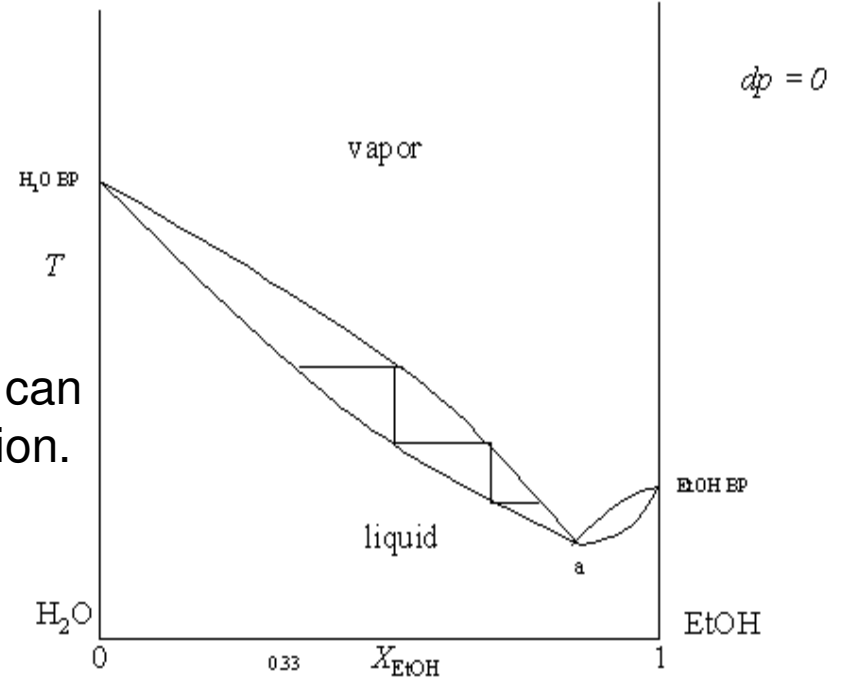
As was explained earlier, the solution with positive deviations from Raoult's law has a higher vapor pressure than would be given by Raoult's law.

That means that the solution would boil at a lower temperature than would be expected from Raoult's law.

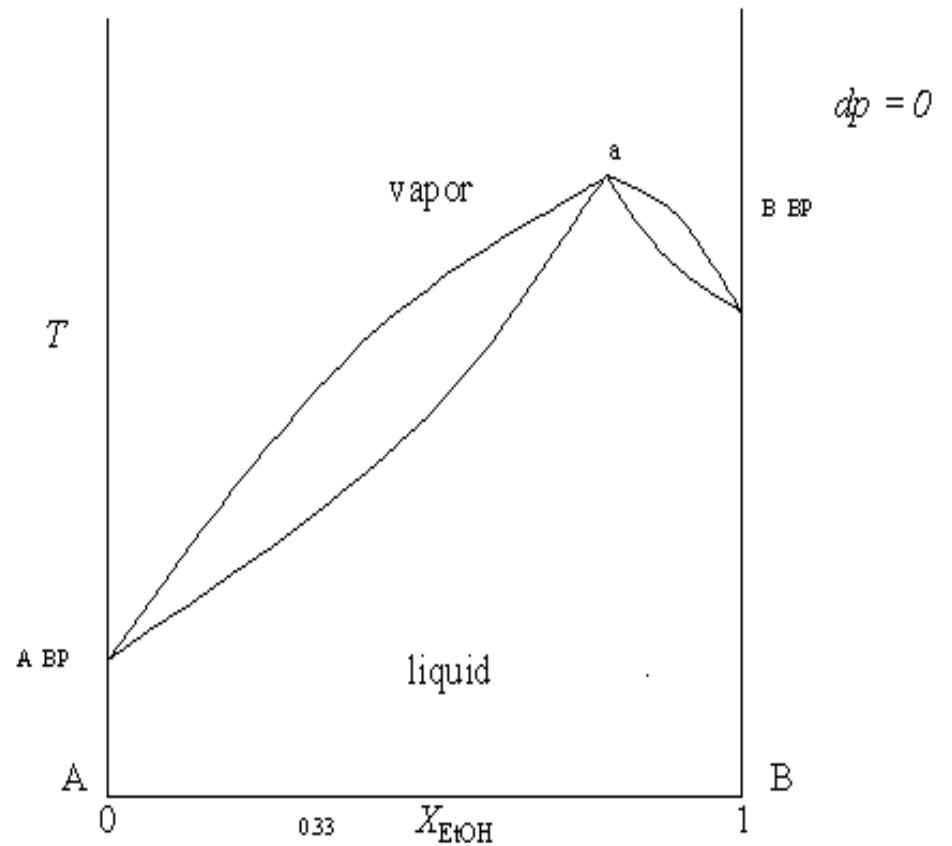
A boiling diagram for such a substance might look like the following:

Point "a" denotes a constant boiling mixture called an "azeotrope." (low boiling azeotrope)

When a system is azeotrope, its components can not be separated by simple fractional distillation.



In a mixture with negative deviations from Raoult's law the vapor pressure is lower than would be expected from Raoult's law which will produce boiling points higher than expected and a high boiling azeotrope.



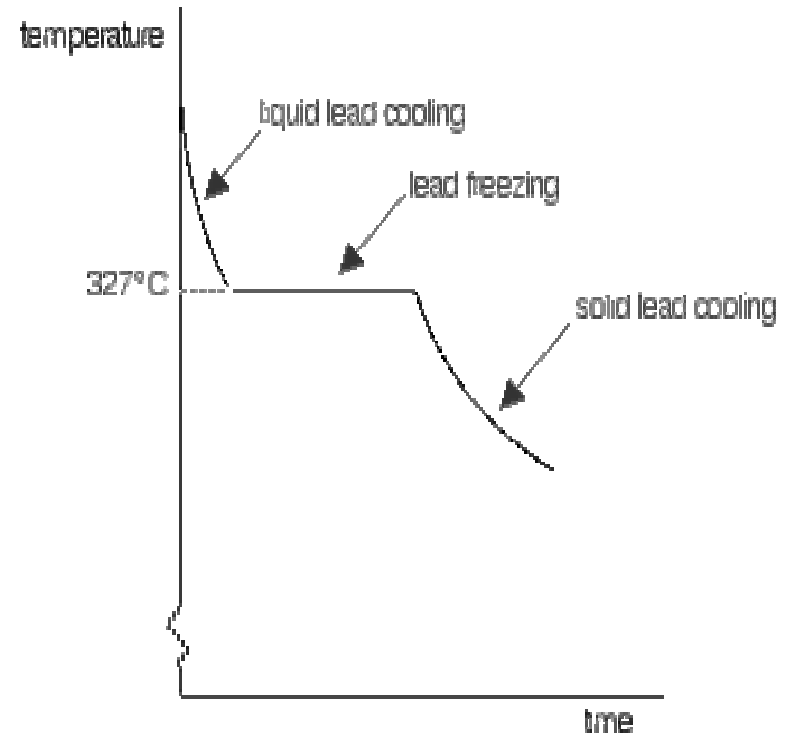
When a system is azeotrope, its components can not be separated by simple fractional distillation.

Cooling curves for pure substances

If there is pure molten lead and it was allowed to cool down until it has all solidified. Plotting the temperature of the lead against time, will give a typical cooling curve for a pure substance.

Throughout the whole experiment, heat is being lost to the surroundings - and yet the temperature doesn't fall at all while the lead is freezing. This is because the freezing process liberates heat at exactly the same rate that it is being lost to the surroundings.

Energy is released when new bonds form - in this case, the strong metallic bonds in the solid lead.



Cooling curves for tin-lead mixtures

If you add some tin to the lead, the shape of the cooling curve changes. If you cool a liquid mixture containing about 67% lead and 33% tin by mass, the cooling curve will be looking like this....

Comments:

Adding the tin to lead, lowers its freezing point.

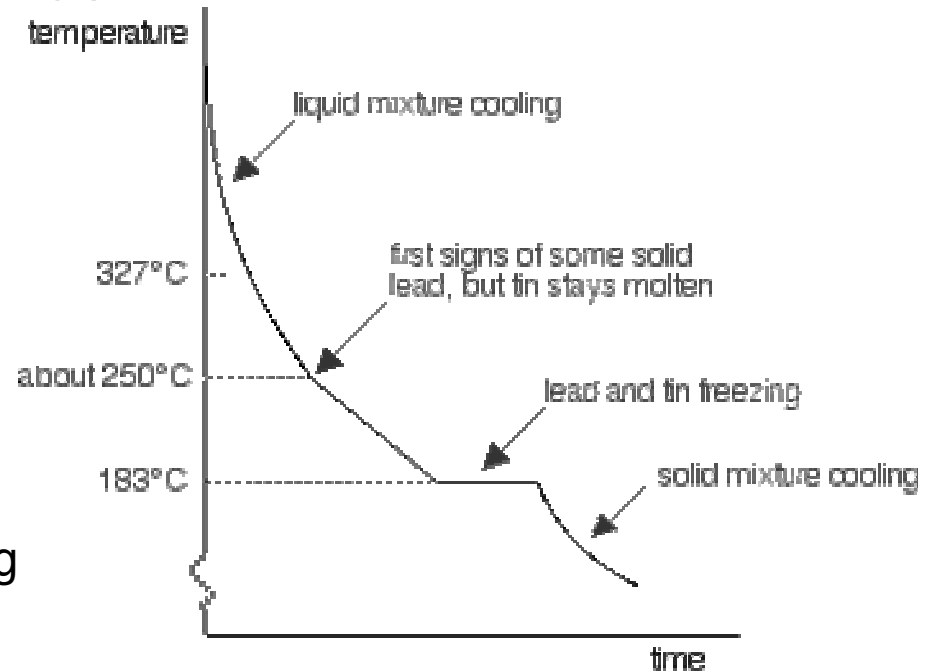
Freezing starts for this mixture at about 250°C. You would start to get some solid lead formed - but no tin. At that point the rate of cooling slows down - the curve gets less steep.

The temperature does stop falling at 183°C. Now both tin and lead are freezing. Once everything has solidified, the temperature continues to fall.

Changing the proportions of tin and lead

If you had less tin in the mixture, the overall shape of the curve stays much the same, but the point at which the lead first starts to freeze changes.

The less tin there is, the smaller the drop in the freezing point of the lead.



For a mixture containing only 20% of tin, the freezing point of the lead is about 275°C. That's where the graph would suddenly become less steep.

BUT . . . you will still get the graph going horizontal (showing the freezing of both the tin and lead) at exactly the same temperature: 183°C.

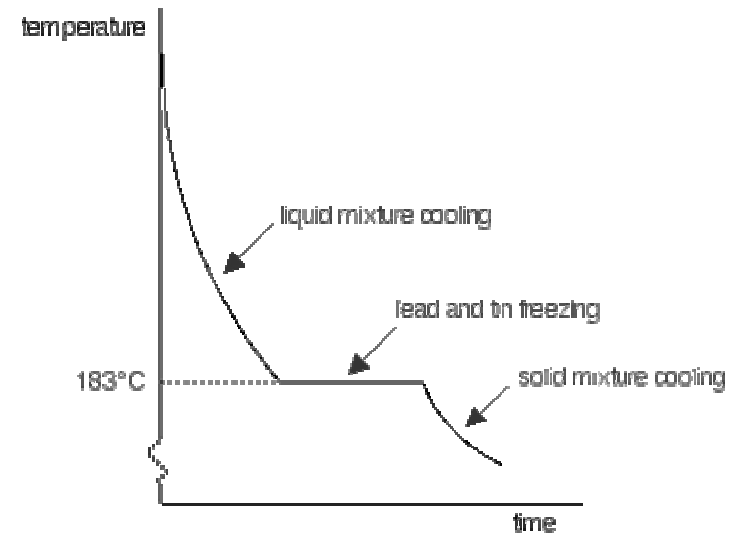
As you increase the proportion of tin, the first signs of solid lead appear at lower and lower temperatures, but the final freezing of the whole mixture still happens at 183°C.

That continues until you have added enough tin that the mixture contains 62% tin and 38% lead. At that point, the graph changes.

This particular mixture of lead and tin has a cooling curve which looks exactly like that of a pure substance rather than a mixture. There is just the single horizontal part of the graph where everything is freezing.

However, it is still a mixture. If you use a microscope to look at the solid formed after freezing, you can see the individual crystals of tin and lead.

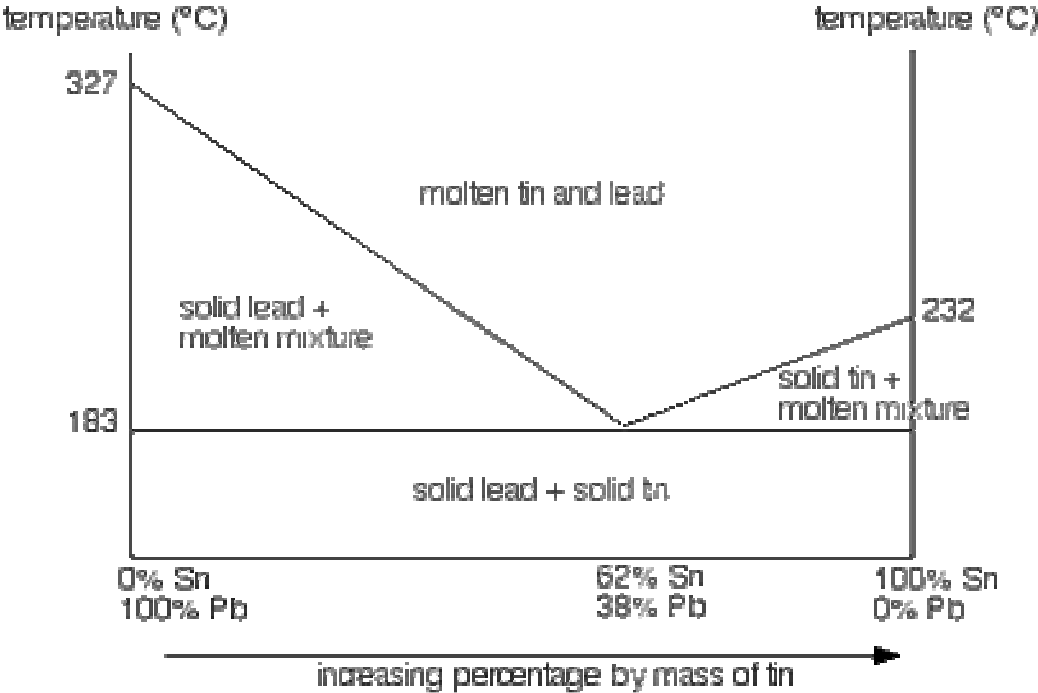
This particular mixture is known as a ***eutectic mixture***. The word "eutectic" comes from Greek and means "easily melted".

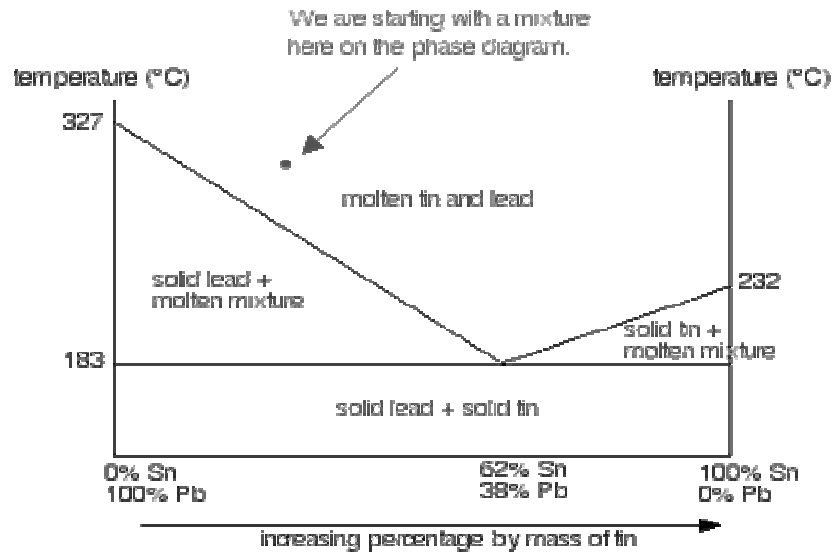


The eutectic mixture has the lowest melting point (which is, of course, the same as the freezing point) of any mixture of lead and tin. The temperature at which the eutectic mixture freezes or melts is known as the ***eutectic temperature***.

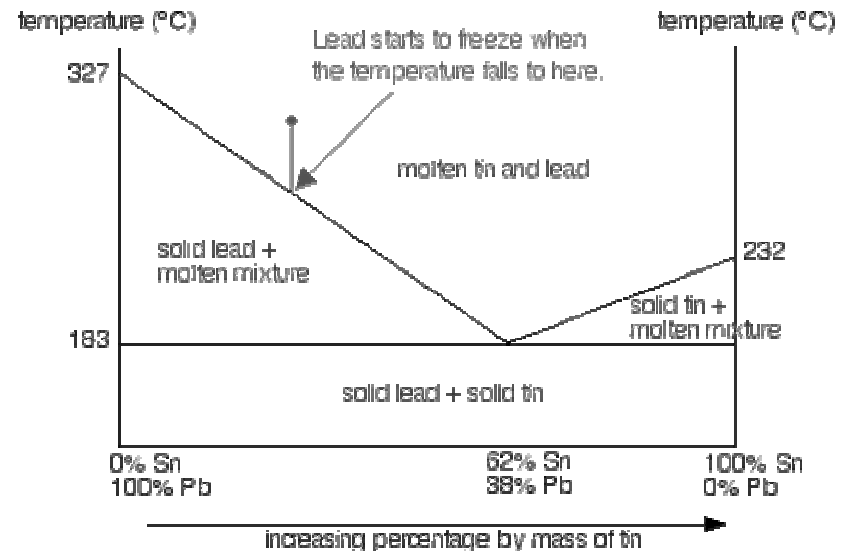
The phase diagram

Start from data obtained from the cooling curves. Draw a graph of the temperature at which freezing *first* starts against the proportion of tin and lead in the mixture. The only unusual thing is that you draw the temperature scale at each end of the diagram instead of only at the left-hand side.

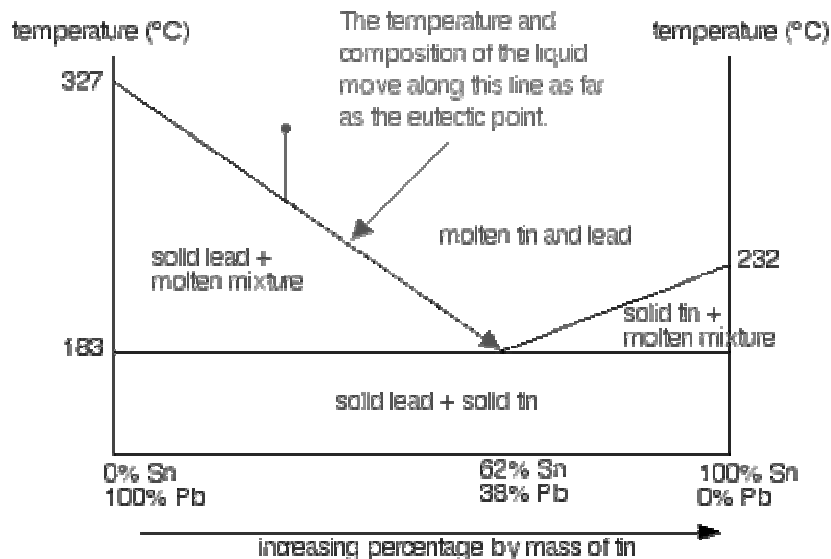




If there is a mixture of 67% lead and 33% tin. That's the mixture from the first cooling curve plotted above. Suppose it is at a temperature of 300°C.



if you cool that mixture. Eventually the temperature will drop to a point where it crosses the line into the next region of the diagram. At that point, the mixture will start to produce some solid lead - in other words, the lead (but not the tin) starts to freeze. That happens at a temperature of about 250°C.



When the first of the lead freezes, the composition of the remaining liquid changes. It obviously becomes proportionally richer in tin. That lowers the freezing point of the lead a bit more, and so the next bit of lead freezes at a slightly lower temperature - leaving a liquid still richer in tin.

This process goes on. The liquid gets richer and richer in tin, and the temperature needed to freeze the next lot of lead continues to fall. The set of conditions of temperature and composition of the liquid essentially moves down the curve - until it reaches the eutectic point.

Once it has reached the eutectic point, if the temperature continues to fall, you obviously just move into the region of a mixture of solid lead and solid tin - in other words, all the remaining liquid freezes.

Tin-lead mixtures as solder

Traditionally, tin-lead mixtures have been used as solder, but these are being phased out because of health concerns over the lead. This is especially the case where the solder is used to join water pipes where the water is used for drinking. New non-lead solders have been developed as safer replacements.

Typical old-fashioned solders include:

60% tin and 40% lead. This is close to the eutectic composition (62% tin and 38% lead), giving a low melting point. It will also melt and freeze cleanly over a very limited temperature range. This is useful for electrical work.

50% tin and 50% lead. This will melt and freeze over a wider range of temperatures. When it is molten it will start to freeze at about 220°C and finally solidify at the eutectic temperature of 183°C. That means that it stays workable for a useful amount of time. That's helpful if it is being used for plumbing joints.

Two component system (Solid – Liquid phases)

In these systems, the components are completely miscible in liquid phase and immiscible in the solid phase. So, that the pure solid phase separate out in cooling.

Cooling Curves

Cooling curve (Temperature vs. time at constant pressure) for the system bismuth-cadmium.

When molten solution of Bi or Cd is cooled, the plot has nearly constant slope.

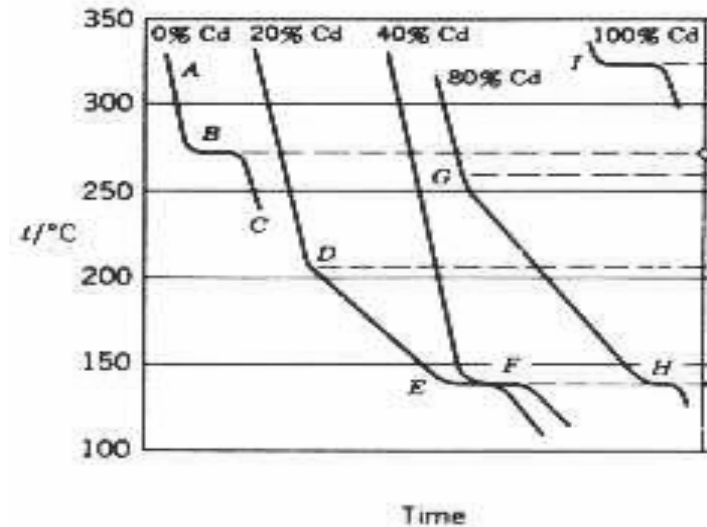
When solid crystallizes out, the plot becomes

horizontal results from a heat evolution, like at 273 and 323 °C for Bi and Cd, respectively.

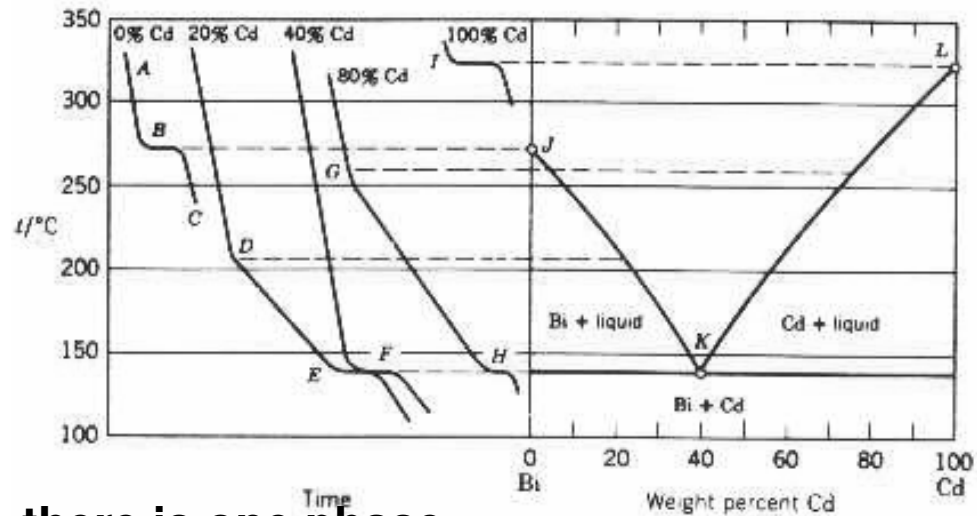
When a solution is cooled, there is a change in slope of the cooling curve at the temperature at which one of the components begins to crystalline out. Such changes in slope are evident in the cooling curve of 20% Cd and 80% Cd.

All the cooling curves of solutions show horizontal section at 140°C. At this temperature, both solid Cd and Bi crystallize out. **This is an eutectic temperature.**

The eutectic is not a phase, it is a mixture of two solid phases and has a fine grain structures.



Temperature – composition diagram of Bi-Cd



In the area above JKL, there is one phase:

$$F = 2 - P + 1 \quad \text{at constant pressure} \longrightarrow F = 3 - P \quad \text{at constant pressure}$$

$$\text{For a single phase, } P = 1 \qquad F = 2$$

Two degree of freedom are necessary, Temperature and mole fraction, to define any point in this area.

Along JK, Bi freezes out; along LK, Cd freezes out, there are two phases:

Solid and solution having a composition given by line JK and LK,

respectively

$$F = 2 - P + 1 \quad \text{at constant pressure} \longrightarrow F = 3 - P \quad \text{at constant pressure}$$

$$\text{For a two phases, } P = 2 \qquad F = 1$$

One degree of freedom is necessary, only Temperature or composition (mole fraction) of liquid can be specified.

At the eutectic point K, there are three phases:

Solid, Bi, Solid Cd, and liquid solution with 40% Cd.

$$F = 2 - P + 1 \text{ at constant pressure} \longrightarrow F = 3 - P \text{ at constant pressure}$$

$$\text{For a three phases, } P = 3 \qquad F = 0$$

Zero degree of freedom, there is only one temperature and only one composition (mole fraction) , at which the three phases coexist at equilibrium at a given constant pressure of liquid can be specified.

It is represent the lowest freezing point of whole solution series.

The eutectic mixture is a mechanical mixture and not a compound.

The area below the eutectic temperature K, is a two phase area:

Solid Bi and Solid Cd.

$$F = 2 - P + 1 \text{ at constant pressure} \longrightarrow F = 3 - P \text{ at constant pressure}$$

$$\text{For a two phases, } P = 2 \qquad F = 1$$

Only one temperature is needed to be specified (composition may not necessary because both Bi and Cd are present in pure components.

The addition of Cd lowers the freezing point of Bi along JK, and addition of Bi lowers the freezing point of Cd along LK.

OR, JK is the solubility curve for Bi in liquid Cd and LK is the solubility curve for Cd in liquid Bi

Calculation of the Solubility

To determine the molar mass of a solute B in a solvent A by the depression of the freezing point of A. Assume the solution is ideal and that pure crystalline A freezes out of solution,

Equation for the equilibrium is: $\mu_A^o(S, T) = \mu_A(1, T, x_A) = \mu_A^o(1, T) + RT \ln x_A$

Thus at T at which the two phases are in equilibrium,

$$\therefore \ln x_A = \frac{\mu_A^o(S, T) - \mu_A^o(1, T)}{RT} = -\frac{\Delta_{fus} G_A^o(T)}{RT}$$

$\Delta_{fus} G_A^o(T)$ Is the Gibbs energy of fusion of the solute at T.

$$\Delta_{fus} G_A^o(T) = \Delta_{fus} H_A^o - T \Delta_{fus} S_A^o = \Delta_{fus} H_A^o - T \frac{\Delta_{fus} H_A^o}{T_{fus,A}} = \Delta_{fus} H_A^o \left(1 - \frac{T}{T_{fus,A}}\right)$$

Substituting this equation in the above one:

$$\begin{aligned} \therefore \ln x_A &= -\frac{\Delta_{fus} G_A^o(T)}{R} = -\left(\frac{\Delta_{fus} H_A^o}{R}\right) \left(\frac{1}{T} - \frac{1}{T_{fus,A}}\right) = -\left(\frac{\Delta_{fus} H_A^o}{R}\right) \left(\frac{T_{fus,A} - T}{TT_{fus,A}}\right) \\ &= \left(\frac{\Delta_{fus} H_A^o}{R}\right) \left(\frac{T - T_{fus,A}}{TT_{fus,A}}\right) \end{aligned}$$

Example: Calculate the solubility in an ideal solution at 150 and 200°C. If $\Delta_{fus} H_{Bi} = 10.5 \text{ kJ mol}^{-1}$ at 273 °C and $T_{fus,Bi} = 273$

Increasing the temperature from 150 to 200, will increase the solubility.

Use the equation:
$$\ln x_{Bi} = \left(\frac{\Delta_{fus} H_A^o}{R} \right) \left(\frac{T - T_{fus,A}}{TT_{fus,A}} \right)$$

at 150 °C

$$\ln x_{Bi} = \left(\frac{10.5 \text{ Jmol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \right) \left(\frac{423 \text{ K} - 546 \text{ K}}{423 \text{ K} * 546 \text{ K}} \right)$$

$$x_{Bi} = 0.510$$

at 200 °C

$$\ln x_{Bi} = \left(\frac{10.5 \text{ Jmol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \right) \left(\frac{473 \text{ K} - 546 \text{ K}}{473 \text{ K} * 546 \text{ K}} \right)$$

$$x_{Bi} = 0.70$$

As expected, the solubility increases with increasing temperature.