The Equation of State

An equation that relates macroscopic variables (e.g., p, V, and T) for a given substance *in thermodynamic equilibrium*.

$$p = f (V,T,n)$$

•Equation of state is not a theoretical deduction *from* thermodynamics, rather an experimental addition *to* it. An equation of state is as accurate as the experiments that led to its formulation. It holds *only* within the range of measurement.

**perfect/ideal gas equation,** $pV = nRT$

perfect/ideal gas, a gas that obeys $pV = nRT$ exactly under all conditions.

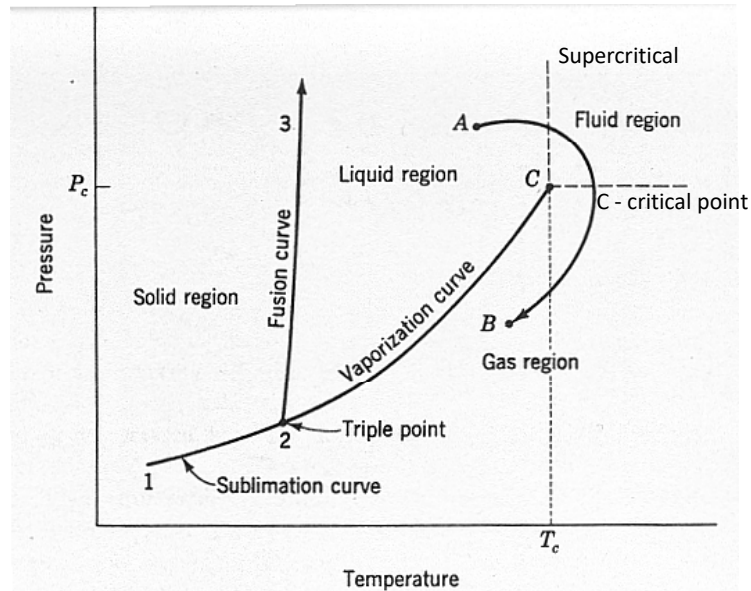**gas constant,** R (with $R = N_A k$, where N_A is Avogadro's constant and k is Boltzmann's constant).

Table 1.2 The gas constant

R	
8.314 47	$J\,K^{-1}\,mol^{-1}$
$8.205\,74 \times 10^{-2}$	$dm^3\,atm\,K^{-1}\,mol^{-1}$
$8.314\,47 \times 10^{-2}$	$dm^3\,bar\,K^{-1}\,mol^{-1}$
8.314 47	$Pa\,m^3\,K^{-1}\,mol^{-1}$
1 62.364	$dm^3\,Torr\,K^{-1}\,mol^{-1}$
1.987 21	$cal\,K^{-1}\,mol^{-1}$

The Equation of State (Ideal Gas)
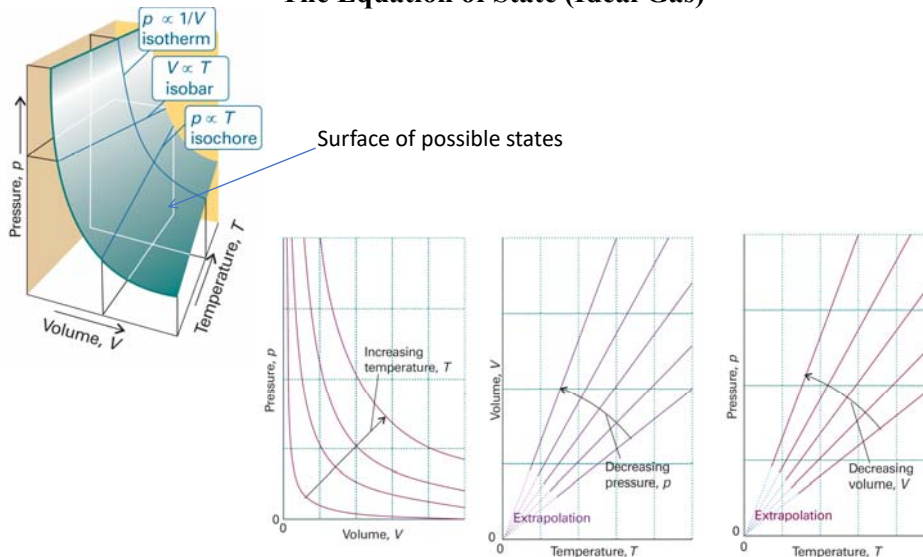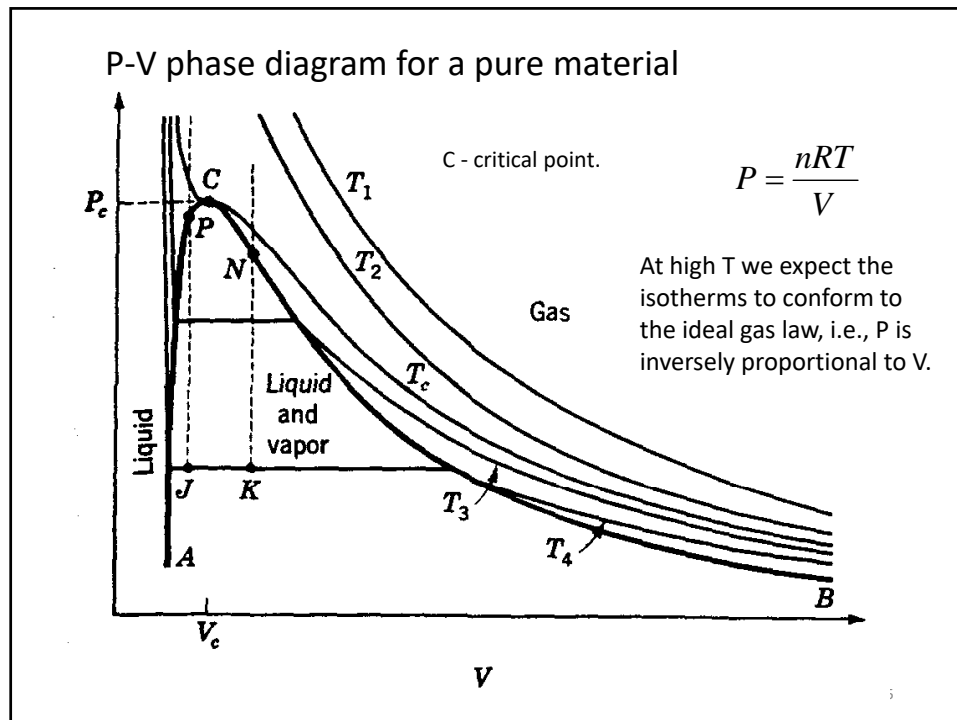
P-T phase diagram for a pure material

The Equations of State

Equations that relate the pressure, temperature, and specific volume of a substance. They predict the P-V-T relationship of a "**gas**" reasonably well within selected regions.
The most well-known is the: **Ideal gas equation:**

$$pV = nRT$$

- Gases do not always obey the ideal gas law.
    - At modest temperatures but high pressures, the molecules get close enough together that intermolecular attractive forces become significant.
        - Two things can happen –
            - At low temperatures the gas can turn into a liquid
            - At higher temperatures the gas stays a gas but behaves a lot like a liquid this state is called a supercritical fluid

P-V phase diagram for a pure material

C - critical point.

$$P = \frac{nRT}{V}$$

At high T we expect the isotherms to conform to the ideal gas law, i.e., P is inversely proportional to V.

[Figure: P-V phase diagram showing isotherms T_1, T_2, T_c, T_3, T_4, with labeled points C, P, N, J, K, A, B, critical pressure P_c and critical volume V_c, regions labeled Liquid, Liquid and vapor, and Gas. Axes labeled P (vertical) and V (horizontal).]

THE P-V DIAGRAM

- We can use the lever rule on a P-V diagram to determine the proportion of vapour vs. liquid at any given pressure.

- The bending of the isotherms in the vapour field from the ideal hyperbolic shape as the critical point is approached indicates non-ideality.

- The P-V diagram illustrates the difficulty in developing an equation of state for all regions for a pure substance. However, this can be done for the vapour phase.

Schematic isotherms in the two-phase field for a pure fluid
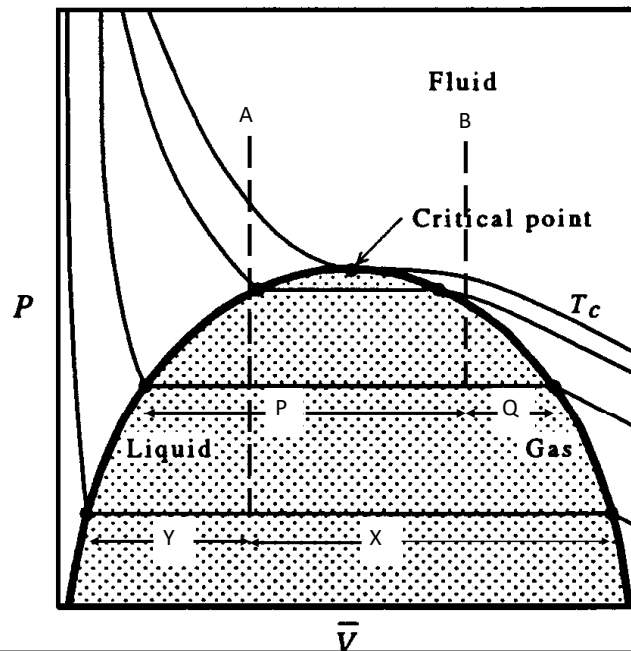
For fluid of density A, the proportion of vapor is Y/(X+Y) and the proportion of liquid is X/(X+Y).
For fluid of density B, the proportion of vapor is P/(P+Q) and the proportion of liquid is Q/(P+Q).

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van der Waals equation can be expressed as

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

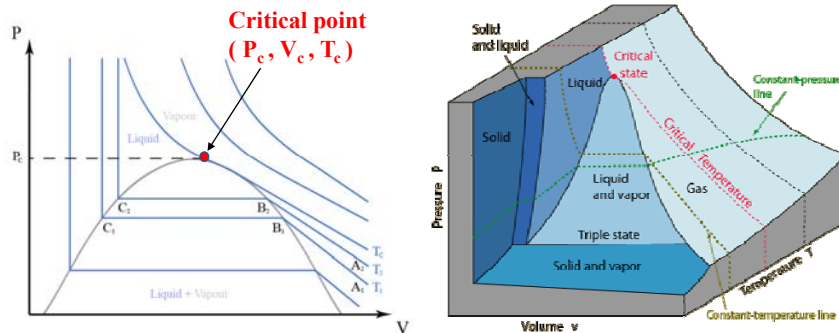→ Measure of the intermolecular attractive forces

Molar volume (V/n)

Volume occupied by one mole of gas molecules so, it is the excluded volume for finite size of molecules.

Is the correction term for the effect of intermolecular attractive forces on the gas pressure.

Excluded volume

Wall

Wall

(a) Low pressure   (b) High pressure
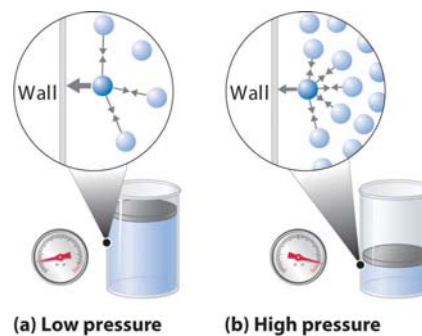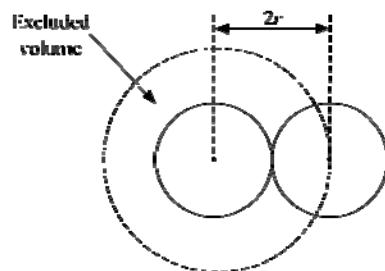
P-V isotherm for van der Waals gas

A critical point is the point of inflection beyond which phase equilibrium vanishes and only one phase exists. Which is defined by **Critical temperature (T_c), Critical pressure (P_c)** and **critical volume (V_c).**

Compressibility Factor

Compressibility factor, **Z**, is a measure of deviation from the ideal gas.

Where $\quad Z = \dfrac{Pv}{RT}, \; Pv = ZRT$

Note: Z = 1 for an ideal gas.
As Z approaches 1 for a gas at given conditions, the behaviour of the gas approaches ideal gas behaviour.

Although, different gases have very different specific properties at various conditions; ***all gases behave in a similar manner relative to their critical pressure, P_{cr} and critical temperature, T_{cr}.***

Hence, the gas pressures and temperatures are normalized by the critical values to obtain the *reduced pressure, P_r and temperature temparature, T_r.* defined as $P_r=P/P_{cr}$; $T_r=T/T_{cr}$
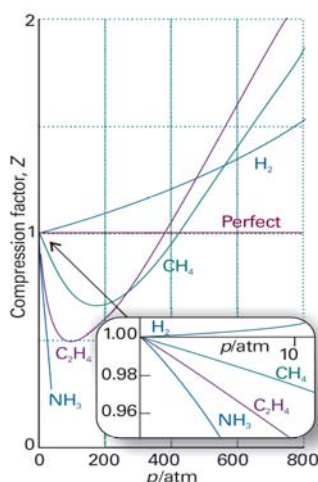
Deviation from ideality: REAL GAS

Compression/compressibility factor:

$$Z(p,T) = V_m/V_m^\circ$$

$$Z(p, T) = pV_m/RT$$

- At very low pressure and high temp.;
  $Z \sim 1$ (Perfect gas behavior)

- At high p, molecular volume significant, repulsion dominates
  $V_m > V_{m,ideal} \rightarrow Z > 1$

- At intermediate p, (& low temp), insignificant molecular volume; attraction dominates
  $V_m < V_{m,ideal} \rightarrow Z < 1$

Fig. 1.14 The variation of the compression factor, Z, with pressure for several gases at 0°C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

Compressibility Factor (Z)

Multiplication of the van der Waals equation by V_m/RT gives the compression factor or compressibility factor $Z=PV_m/RT$

$$\frac{PV_m}{RT} = Z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} = \frac{1}{1 - b/V_m} - \frac{a}{RTV_m}$$
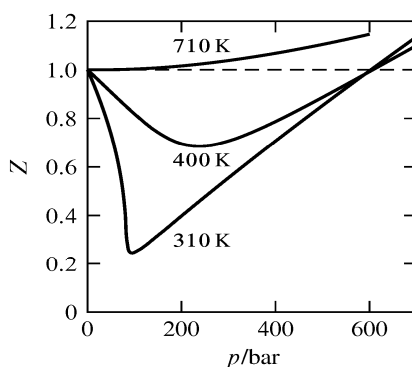
Z is a correction factor which describes the deviation of a real gas from ideal gas behaviour. The deviation from ideal behaviour becomes more significant the closer a gas is to a phase change, the **lower the temperature** or the **larger the pressure.**
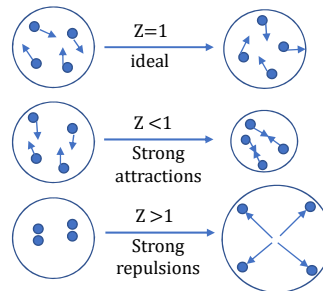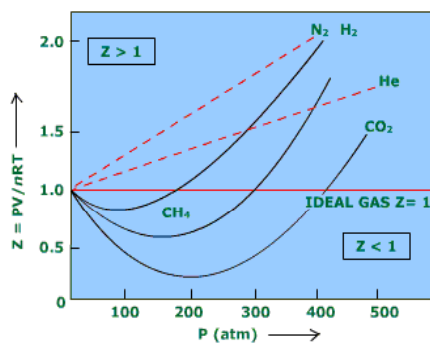
- Since $\dfrac{1}{1-b/V_m} > 1$, intermolecular repulsions (represented by b) tend to make $Z > 1$ and $P > P_{id}$.
- Since $-\dfrac{a}{RTV_m} < 1$, intermolecular attractions (represented by a) tend to make $Z < 1$ and $P < P_{id}$.

The Equation of state of a real gas (not at very high pressure) can be expressed as the following power series in $^1/_{V_m}$.

$$P = RT\left[1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \ldots\right]$$

→ **Virial Equation of state**

The coefficients B, C, . . . , which are functions of T only, are the second, third, . . . virial coefficients. They are found from experimental P-V-T data of gases.
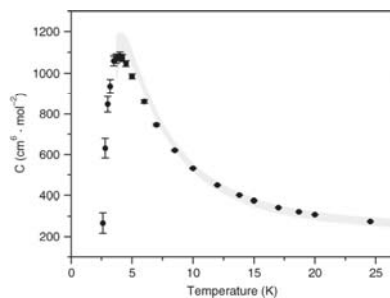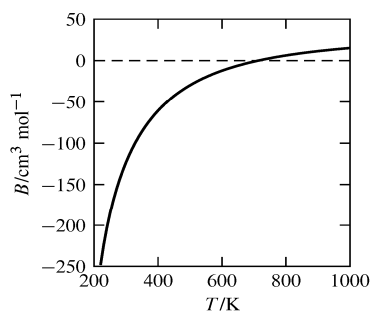
Condensation of a real gas

Critical Constants $(T_c; p_c; V_c)$**:**

Temperature at and above which the separation of liquid and gas surface ceases to exist.
At the critical point,

$$\frac{dp}{dV_m} = 0 \text{ and } \frac{d^2 p}{dV_m^2} = 0$$

T_c: Highest T at which condensation of a gas is possible.

p_c : Highest p at which a liquid boils when heated.

Fig. 1.15 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.04°C. The critical point is marked with a star.
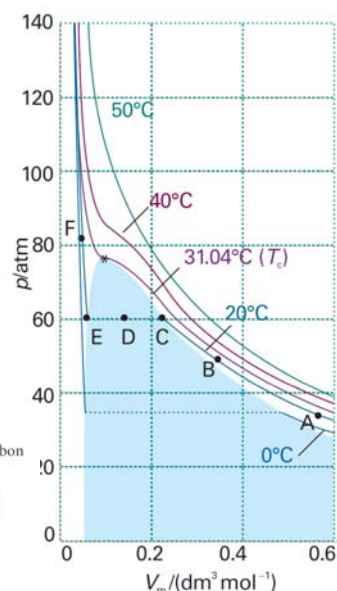
For any isotherm, at critical point $T=T_c$

$$\left(\frac{\partial P}{\partial V_m}\right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T=T_c} = 0$$

Now differentiating the Van der Waals equation, we get

$$\left(\frac{\partial P}{\partial V_m}\right)_{T=T_c} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T=T_c} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4}$$

$$\text{Or,} \frac{RT}{(V_m - b)^2} = \frac{2a}{V_m^3} \qquad \text{Or,} \frac{2RT}{(V_m - b)^3} = \frac{6a}{V_m^4}$$

Exercise:
1. Find out the expressions for P_c, V_c and T_c in terms of constant a and b.
2. Derive the expression of **Reduced equation of state** of the form $\left(\tilde{P} + \frac{3}{\tilde{V}^2}\right)(3\tilde{V} - 1) = 8\tilde{T}$, Where $\tilde{P} = \frac{P}{P_c}$, $\tilde{V} = \frac{V}{V_c}$, $\tilde{T} = \frac{T}{T_c}$ are the 'reduced' quantities.

- The temperature at which it becomes impossible to ever form a liquid regardless of the pressure is called the critical temperature. (Tc)
- The pressure at which there is just last both vapor and liquid is called the critical pressure. (Pc)
- The critical temperature and pressure are key parameters for calculating the relationship between P, V, and T for non-ideal fluids using empirical Equations of State

- The values of a and b are different for different chemical species, but they are related in <u>the same way</u> to the Tc and Pc values of the chemical species.
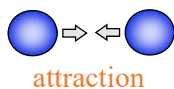- Critical properties are tabulated.

$$a = \frac{27\,R^2 T_c^{\,2}}{64\,P_c}, b = \frac{1}{8}\frac{RT_c}{P_c}$$

The van der Waals model of real gases
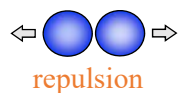
repulsion

$$V_{eff} = V - nb$$

$$p = \frac{nRT}{V}\quad\text{(Ideal gas equation)}$$

attraction

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

The van der Waals equation of state for real gases

- At high temperature and large volume, vdW equation reduces to ideal gas law.
- Liquid and gases coexist when attractive and repulsive forces balance

- Critical Constants and vdW parameters: V_c=3b, p_c=a/27b^2, T_c=8a/27Rb, Z_c=$p_c V_c/RT_c$=3/8 (the critical compression factor)

$$\frac{dp}{dV_m} = 0 \text{ and } \frac{d^2 p}{dV_m^2} = 0$$
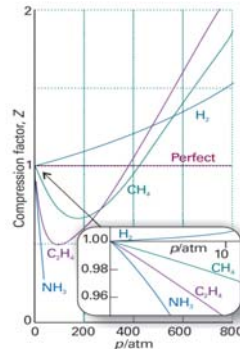
The Principle of Corresponding States

Real gases at same reduced volume and
reduced temperature exert same reduced
pressure and have same compressibility factor.

Reduced Variables:

$V_r = V_m / V_c$
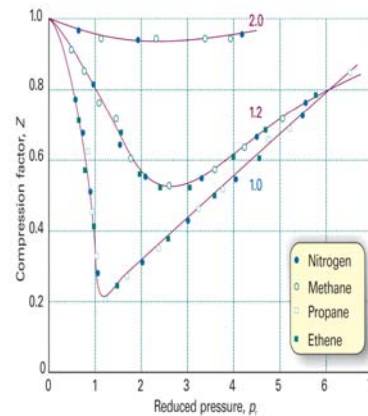$T_r = T / T_c$
$p_r = p / p_c$

Fig. 1.19 The compression factors of four of the gases shown in Fig. 1.14 plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. The use of reduced variables organizes the data on to single curves.

Limitations:
Polar or non-spherical molecules.

Mixture of Gases

☐ **Partial pressure:** of a gas (i), in a mixture of any gases

  $p_i = x_i \, p$, x_i=Mole fraction of the component.

☐ **Dalton's law:** The pressure exerted by a mixture of (ideal)
  gases is the sum of the partial pressures that each one would
  exert if it occupied the container alone.

  $$p = \sum_i p_i$$

☐ **vapour pressure,** the pressure of a vapour in equilibrium
  with its condensed phase.

The Gibbs Energy of Mixing of Ideal Gases

$$\mu_i(T) = \mu_i^{\,o}(T) + RT \ln p_i \qquad p_i = \text{partial pressure of } i^{\text{th}} \text{ gas in bar.}$$

Before mixing:

$$G_{\text{before mixing}} = \sum_i n_i\left(\mu_i^{\,o}(T) + RT \ln p\right)$$

After mixing:

$$G_{\text{mixture}} = \sum_i n_i\mu_i = \sum_i n_i\left(\mu_i^{\,o}(T) + RT \ln p_i\right)$$

$$= \sum_i n_i\left(\mu_i^{\,o}(T) + RT \ln x_i p\right)$$

Dalton's law of partial pressure, $p_i = x_i p$

$$\boxed{\Delta G_{mix} = nRT \sum_i x_i \ln x_i}$$

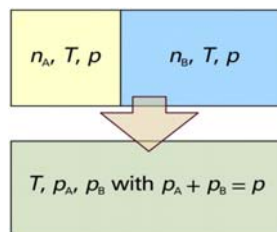Gibbs free energy of mixing of ideal gases is always negative, and hence spontaneous

---

The Enthalpy of Mixing of Ideal Gases

$$\Delta G_{mix} = nRT \sum_i x_i \ln x_i$$

$$\Delta S_{mix} = -\left(\frac{\partial(\Delta G_{mix})}{\partial T}\right)_{p,n} = -nR \sum_i x_i \ln x_i$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = 0$$

Ideal gases show no intermolecular interactions and hence change in enthalpy is zero

(isothermal) Pressure dependence of Chemical Potential

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} V dp \qquad G_2 = G_1 + \int_{P_1}^{P_2} V dp$$

for one component system, $\qquad \mu_2(T) = \mu_1(T) + \int_{P_1}^{P_2} V_m dp$

Case 1: <u>liquid or solid</u>; V weakly dependent on p

$$\mu_2(T) = \mu_1(T) + V_m(p_2 - p_1) \qquad \text{for one component system}$$

Case 2: <u>ideal gas</u>; V is dependent on p,

$$\mu_2(T) = \mu_1(T) + RT \ln \frac{p_2}{p_1}$$

$$\mu(T) = \mu^o(T) + RT \ln \frac{p}{p^o}$$
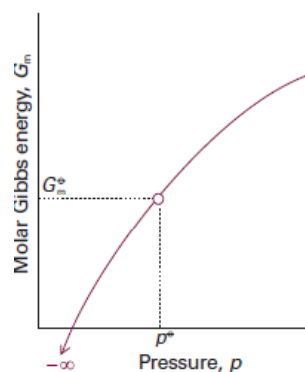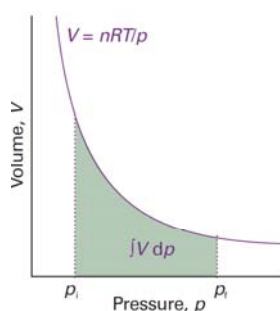
$$\mu(T) = \mu^o(T) + RT \ln p$$

μ^o = standard chemical potential, the chemical potential of the <u>pure gas</u> **at 1 bar** at temp T.

p expressed in bar.

Chemical Potential of an ideal gas

$$\mu_2 = \mu_1 + \int_{P_1}^{P_2} V_m dp \qquad\qquad \mu(T) = \mu^o(T) + RT \ln \frac{p}{p^o}$$

Activity and *Fugacity* (for a gas):

the apparent (or effective) concentration of a species as opposed to the actual concentration. They are a measure of the departure of a system from ideal behaviour and need to be taken into account even when dealing with relatively dilute solutions.

Activity (or fugacity) is related to concentration through the activity coefficient (γ_i).

$$\gamma_i = a_i / m_i$$

where a_i is the activity and m_i is the actual concentration.

Incorporating the chemical potential into the activity yields the following equation:

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

where μ_i^o is the chemical potential of component *i* in its standard state.

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Dependence of *G* on *p*

Real Gases.

For real gases we modify the expression for a perfect gas and replace the true pressure by a new parameter, *f*, which we call the fugacity.

$$G_m(p_f) = G_m{}^\theta + RT \ln \frac{f}{p^\theta}$$

The fugacity is a parameter we have simply invented to enable us to apply the perfect gas expression to real gases.

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Dependence of G on p

Real Gases.

We may then write $\quad \Delta G = RT \ln \dfrac{f_2}{f_1}$

We may show that the ratio of fugacity to pressure is called the fugacity coefficient:

$$\frac{f}{p} = \phi \qquad \text{Where } \phi \text{ is the fugacity coefficient}$$

Because we are expressing the behaviour of real gases in terms of perfect gases it is of little surprise that ϕ is related to the compression factor Z:

$$\ln \phi = \int_0^p \frac{Z-1}{p} dp$$

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Chemical Potential of Pure Real Gas

$$\mu(T) = \mu^o(T) + RT \ln f$$
$$= \mu^o(T) + RT \ln \phi p$$
$$= \mu^{\text{ideal}}(T) + RT \ln \phi$$

f = fugacity, an effective pressure in bar= $\phi\, p$

ϕ = fugacity coefficient

$$\ln \phi = \int_0^p \frac{Z-1}{p} dp \qquad Z = \text{Compressibility factor}$$
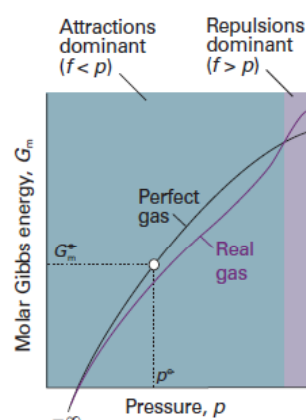
At low pressure,

$$Z < 1 \Rightarrow \ln \phi < 0 \Rightarrow \boxed{\mu^{\text{real}} < \mu^{\text{ideal}}}$$
$$\phi < 1 \Rightarrow f < p$$

At high pressure,

$$Z > 1 \Rightarrow \ln \phi > 0 \Rightarrow \boxed{\mu^{\text{real}} > \mu^{\text{ideal}}}$$
$$\phi > 1 \Rightarrow f > p$$

Vapour Pressure:

Vapour pressure or **equilibrium vapour pressure** is defined as the pressure exerted by a vapour in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system.

- **When the rate of condensation equals the rate of evaporation, the system reaches dynamic equilibrium**

Before reaching equilibrium:
rate of evaporation >
rate of condensation

After reaching equilibrium:
rate of evaporation =
rate of condensation
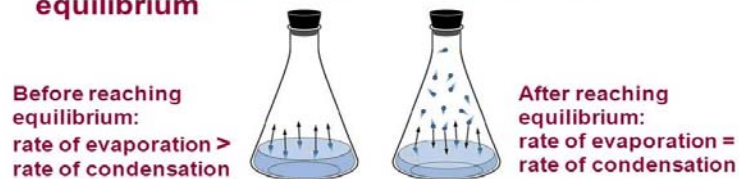
➢ *Vapour Pressure Depends on:-*
a) **Number of particles available at the surface**

b) **Propensity of each particle to leave the surface**

Effect of pressure on gas solubility

- The solubilities of solids and liquids are not affected appreciably by pressure

- When the pressure of a gas is increased, as in (b), the rate at which gas molecules enter the solution increases

- The concentration of solute molecules at equilibrium increases in proportion to the pressure

- So the solubility of a gas increases with pressure

(a)

(b)
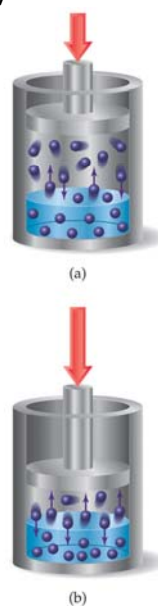
Pressure and Solubility of Gases

Solubility decreases as pressure decreases

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- Soft drink bottled under CO_2 pressure greater than 1 atm

- When the bottle is opened, partial pressure of CO_2 above the solution decreases

- Solubility of CO_2 decreases -> bubbles
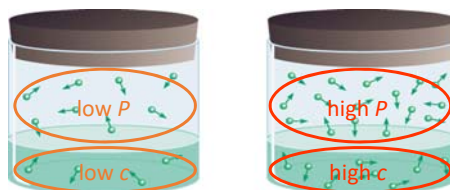
16

Pressure and Solubility of Gases

The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (***Henry's law***).

$$c = kP$$

c is the concentration (M) of the dissolved gas
P is the pressure of the gas over the solution
k is a constant (mol/L•atm) that depends only on temperature

1. Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 4.0 atm over the liquid at 25°C. The Henry's law constant for CO_2 in water at this temperature is 3.1×10^{-2} mol/L-atm.
2. Calculate the concentration of CO_2 in a soft drink after the bottle is opened and equilibrates at 25°C under a CO_2 partial pressure of 3.0×10^{-4} atm.

Blood gases and deep sea diving

- Solubility increases as pressure increases
- Divers who use compressed gases must be concerned about the solubility of the gases in their blood
- At depth, the blood contains higher concentrations of dissolved gases
- Ascension, if too rapid, will cause the blood to fizz similar to a soft drink when opened
- This is called decompression sickness, or "the bends", which is painful and can be fatal because the bubbles affect things like nerve impulses
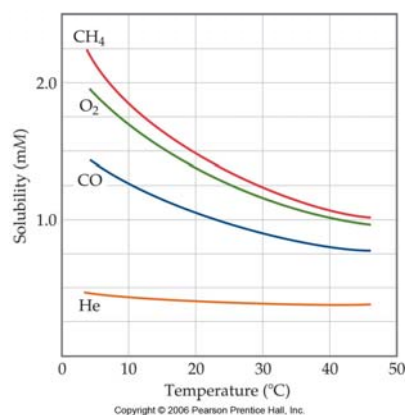

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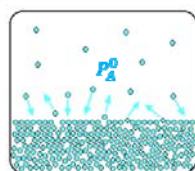
Temperature and Solubility

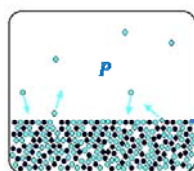Solubility of most solid solutes in water increases with increasing temperature
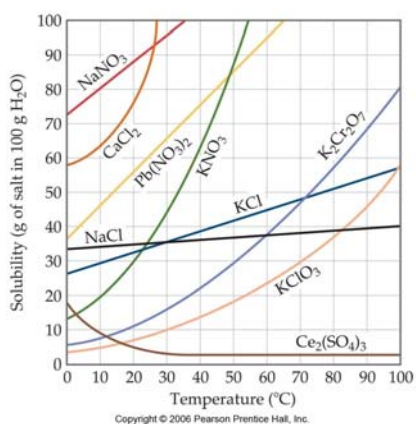
In contrast, solubility of gases in water decreases with increasing temperature

Raoult's law : solvent + non-volatile solute

Pure solvent

Solvent + Solute
(Non-volatile)

The decrease in vapor pressure is directly proportional to the mole fraction of solute in an ideal solution:

$$P = P_A^0 x_A,$$

x_A = mole fraction of solvent (A)

$$\Delta P = P_A^0 - P = P_A^0(1 - x_A) = P_A^0 x_B$$

Number of solvent molecules on the surface is less than that was in case of pure solvent therefore, the vapor pressure of the final solution is lower than that of the pure solvent.
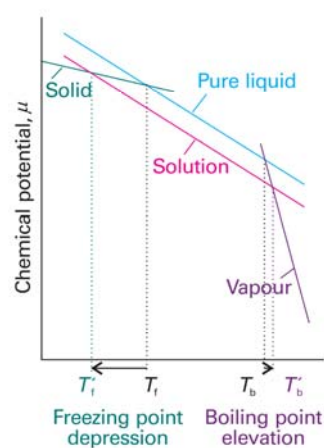
Because of solute-solvent intermolecular attractions, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapour phase.

Vapor pressure

Vapor pressure

Solvent alone

Solvent + solute

(a)

(b)
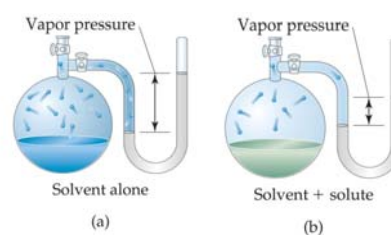
Effect of solute on boiling and melting points of solvent

$$\mu_A = \mu_A^* + RT \ln x_A$$

$$\mu_A = \mu_A^* + RT \ln a_A$$

Chemical potential, μ

Solid

Pure liquid

Solution

Vapour

T_f' T_f T_b T_b'

Freezing point depression

Boiling point elevation

Henry's Law

➢ The vapour pressure of a solute, P_2, in a solution in which the solute has a mole fraction of x_2 is given by:

$$P_2 = x_2 P_2*$$

where P_2* is the vapour pressure of the solute in a pure liquefied state.

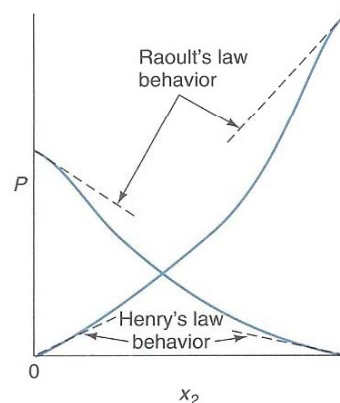➢ It is also found that *at the limits of infinite dilution, the vapour pressure of the solute obeys Henry's law*.

FIGURE 5.11
A hypothetical binary liquid mixture exhibiting negative deviation from Raoult's law, showing regions where Henry's and Raoult's laws are obeyed.

Partial Molar Quantities

➢ The method using partial molar quantities enables us to treat nonideal solutions. In this method we consider the changes in the properties of the system as its compositions change by adding or subtracting.

➢ The thermodynamic quantities, such as U, H, and G, are extensive functions and they depend on the P and T. For example, $G = G(P, T, n_1, n_2, n_3, …)$.

Partial Molar Volume

➢In this treatment, the volume is used as starting point to lead to the thermodynamic functions in terms of partial molar quantities.

$V*(H_2O) = 18$ mL

$V_{tot} = V_w + 18$ mL

$V_{tot} = V_w + 14$ mL

water

$V = V_w$

ethanol

$V = V_{eth}$
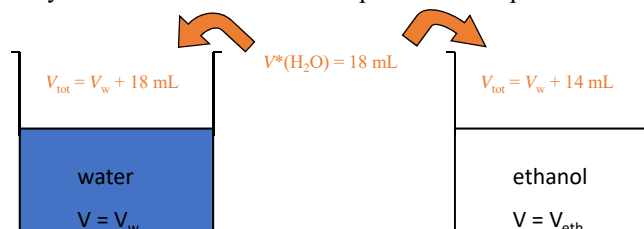
➢The volume occupied by H_2O molecules added is dependent on the nature of surrounding molecules.

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Thermodynamics of Simple Mixtures

Partial Molar Volume

1 mol of water added to a huge volume of water increases the volume by 18 cm^3. V_m=18 cm^3/mol

1 mol of water added to a huge volume of *ethanol* increases the volume by 14 cm^3. V_m=14 cm^3/mol

$$V_i = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_{j\neq i}} \quad \textit{Partial Molar Volume} \qquad \textit{Can be +ve, -ve, or 0!}$$

$$dV = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B$$

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A n_A + V_B n_B$$

$$G_{p,T} = n_1\mu_1 + n_2\mu_2 + \cdots = \sum_i n_i\mu_i$$

Gibbs-Duhem Equation

$$G_{p,T} = n_1\mu_1 + n_2\mu_2 + \cdots = \sum_i n_i\mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i$$

At thermal and mechanical equilibrium.

At constant *p* and *T*

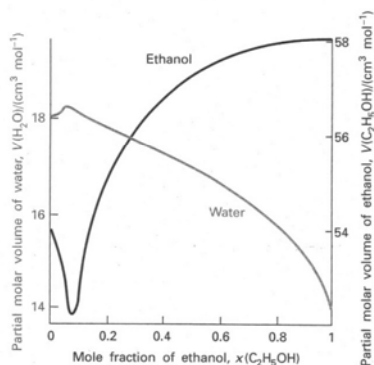$$\boxed{\sum_i n_i d\mu_i = 0}$$ **Gibbs-Duhem Equation**

For a binary mixture, $n_1 d\mu_1 + n_2 d\mu_2 = 0$

Hence, $d\mu_1 = -(n_2/n_1) d\mu_2$

If $n_2 > n_1$, a small change in μ_2 causes a large change in μ_1

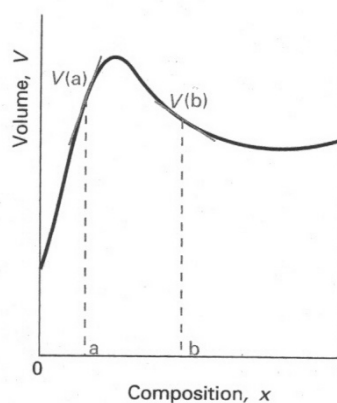| Chemical potential of one component of a mixture can not change independently of the chemical potentials of other components. |
| --- |

Partial Molar Quantities

Partial molar volume is defined as:

$$V_1 \equiv \left(\frac{\partial V}{\partial n_1} \right)_{T,P,n_2,n_3,\dots}$$

7.2 The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the composition. In general, partial molar quantities vary with the composition, as shown by the different slopes at the compositions a and b. Note that the partial molar volume at b is negative: the overall volume of the sample decreases as the component is added.

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Partial Molar Volumes

The partial molar volumes of acetone and chloroform in a solution mixture in which mole fraction of chloroform is 0.4693 are 74.166 cm³/mol and 80.235 cm³/mol, respectively. What is the volume of a solution of a mass 1.000 kg?

Application of Henry's Law

EXAMPLE 5.7 Dry air contains 78.084 mol % N_2 and 20.946 mol % O_2. Calculate the relative proportion of N_2 and O_2 dissolved in water under a total pressure of 1.000 bar. Henry's law constants, k', for N_2 and O_2 are 6.51×10^7 Torr and 3.30×10^7 Torr, respectively, at 25 °C.

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