Physical Chemistry

Second Stage

Almustaqbal College

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- **Chemistry :** Is the scientific discipline involved with compounds composed of atoms, i.e. elements, and molecules, i.e. combinations of atoms: their composition, structure, properties, behaviour and the changes they undergo during a reaction with other compounds.

- **Physical chemistry :** is the study of the fundamental physical principles that govern the way that atoms, molecules, and other chemical systems behave. Physical chemists study a wide array of topics such as the rates of reactions (kinetics), the way that light and matter interact (spectroscopy), how electrons are arranged in atoms and molecules (quantum mechanics), and the stabilities and reactivities of different compounds and processes (thermodynamics).

Ideal gas equation

- The equation of ideal gas can be written as below

$$\boxed{PV = nRT}$$

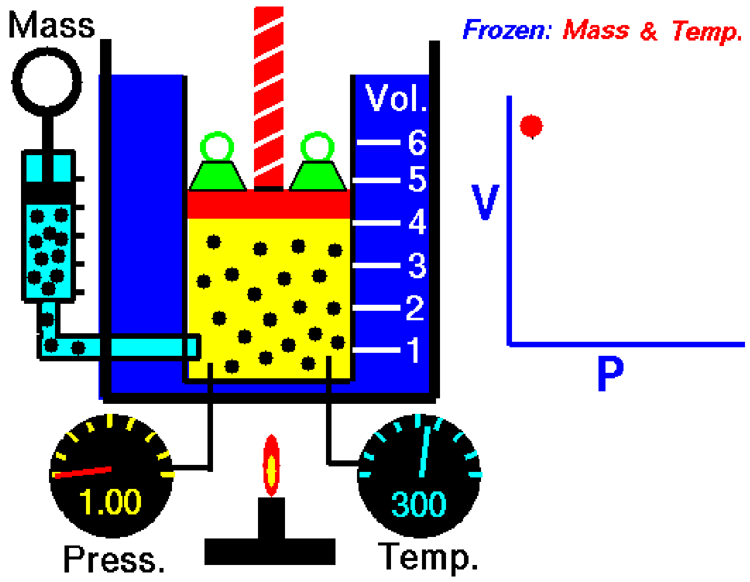
*Boyle's Law

According to Boyle's Law, the pressure (P) of a given mass of gas is inversely proportional to its volume (V), provided that the temperature of the gas remains constant.

$$V \,\alpha\, \frac{}{P}$$

$$PV = \text{constant}$$

$$P_1V_1 = P_2V_2$$



- **Example:** In an industrial process, a gas confined to a volume of 1 L at a pressure of 20 atm is allowed to flow into a 12-L container by opening the valve that connects the two containers. What is the final pressure of the gas?

*solution

Set up the problem by setting up the known and unknown variables. In this case, the initial pressure is 20 atm (P_1), the initial volume is 1 L (V_1), and the new volume is 1L + 12 L = 13 L (V_2), since the two containers are connected. The new pressure (P_2) remains unknown.

$P_1V_1 = P_2V_2$

(20 atm)(1 L) = (P_2)(13 L).

20 atom = (13) P_2.

P_2 = 1.54 atm.

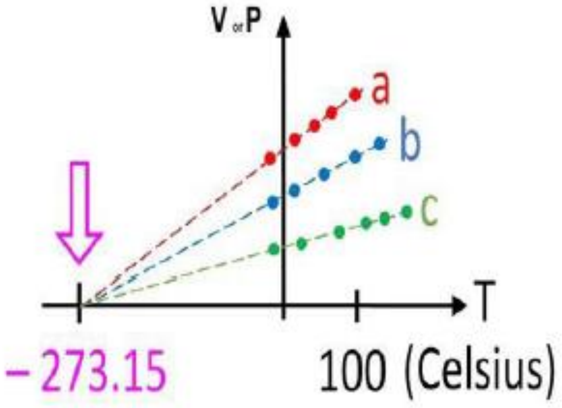
The final pressure of the gas is 1.54 atm.

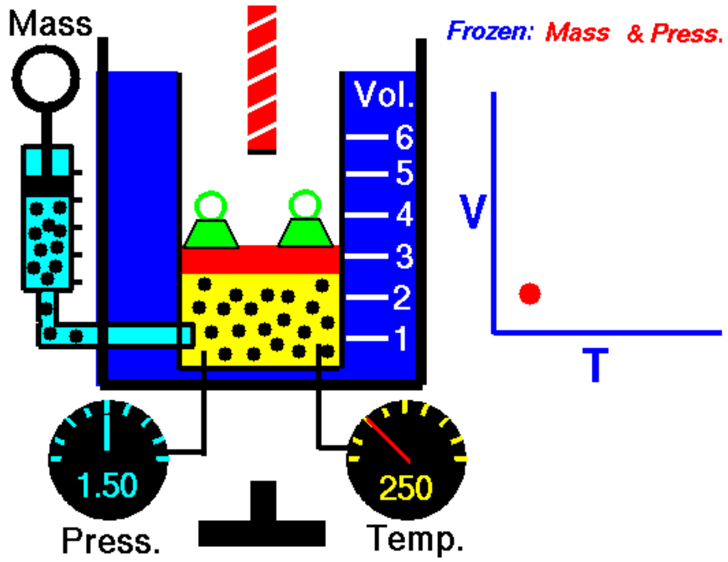
*Charles' Law

describes the relationship between volume and temperature of gases at constant pressure and mass. With the same amount of gas he found that as the volume increases the temperature also increases.

$$V \alpha T$$

$$\frac{V1}{T1} = \frac{V2}{T2}$$



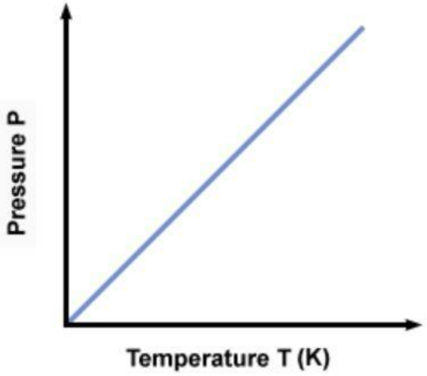


*Gay-Lussac's Law

The pressure and absolute temperature (K) of a gas are directly related at constant mass & volume.

$$P \alpha \mathrm{T}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$



Example: A balloon is filled to a volume of 2.20L at a temperature of 22°C. The balloon is then heated to a temperature of 71°C. Find the new volume of the balloon.

***Solution**

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \rightarrow \therefore V_2 = \frac{V_1 \times T_2}{T_1}$$

$$V_2 = \frac{2.20L \times 344K}{295K} \rightarrow \therefore V_2 = 2.57\ L$$

Example: The gas in an aerosol can is under a pressure of 3.00atm at a temperature of 25°C. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of 845°C?

***Solution**

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow \therefore\ P_2 = \frac{P_1 \times T_2}{T_1}$$

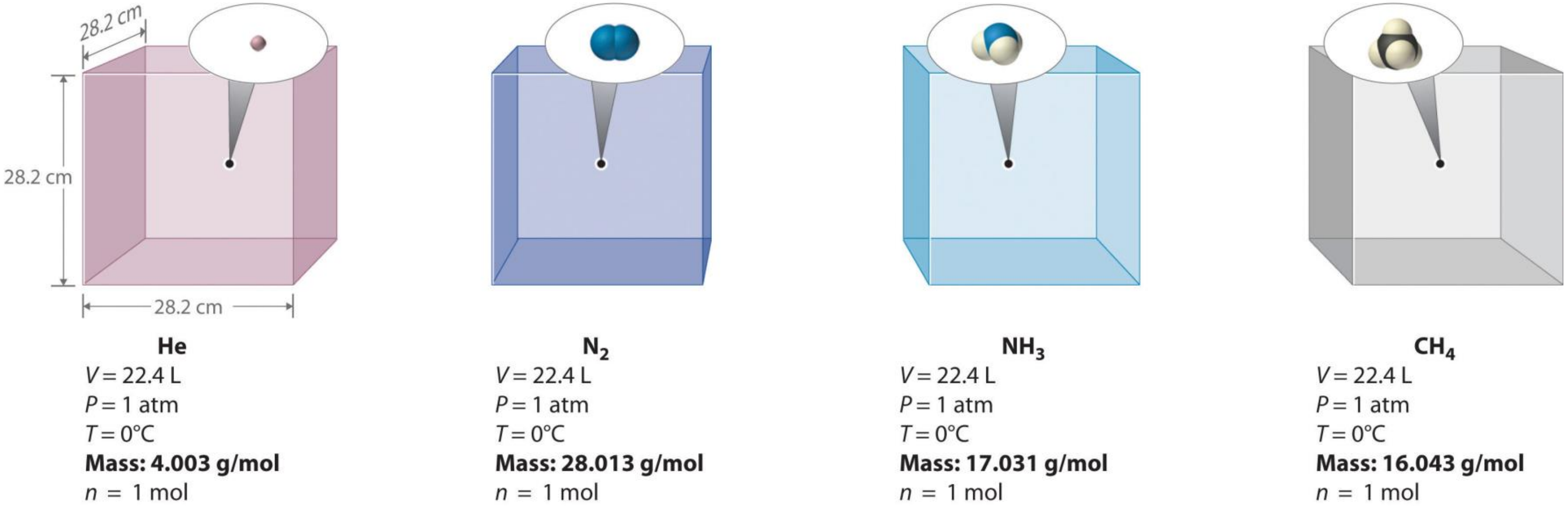
$$P_2 = \frac{3\ atm \times 1118K}{298K} \rightarrow\ \therefore P_2 = 11.3atm$$

*Avogadro's Principle

Equal volumes of gases contain equal numbers of moles at constant temp & pressure its true for any ideal gas.

$$V \, \alpha \, n$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$



So $\boldsymbol{V \alpha \frac{nT}{P}}$

- $\boldsymbol{PV = nRT \ldots\ldots\ldots \text{ ideal gas}}$
- $\boldsymbol{\therefore V = \frac{nRT}{P}}$
- $\boldsymbol{n = m/M_{wt}}$ $\boldsymbol{\rightarrow \therefore PM_{wt} = (V/m)RT}$

$$\boldsymbol{\therefore M_{wt} = \frac{\rho RT}{P}}$$

Example: A balloon has been filled to a volume of 1.90L with 0.0920mol of helium gas. If 0.0210mol of additional helium is added to the balloon while the temperature and pressure are held constant, what is the new volume of the balloon?

* **Solution**

Note that the final number of moles has to be calculated by adding the original number of moles to the moles of added helium.

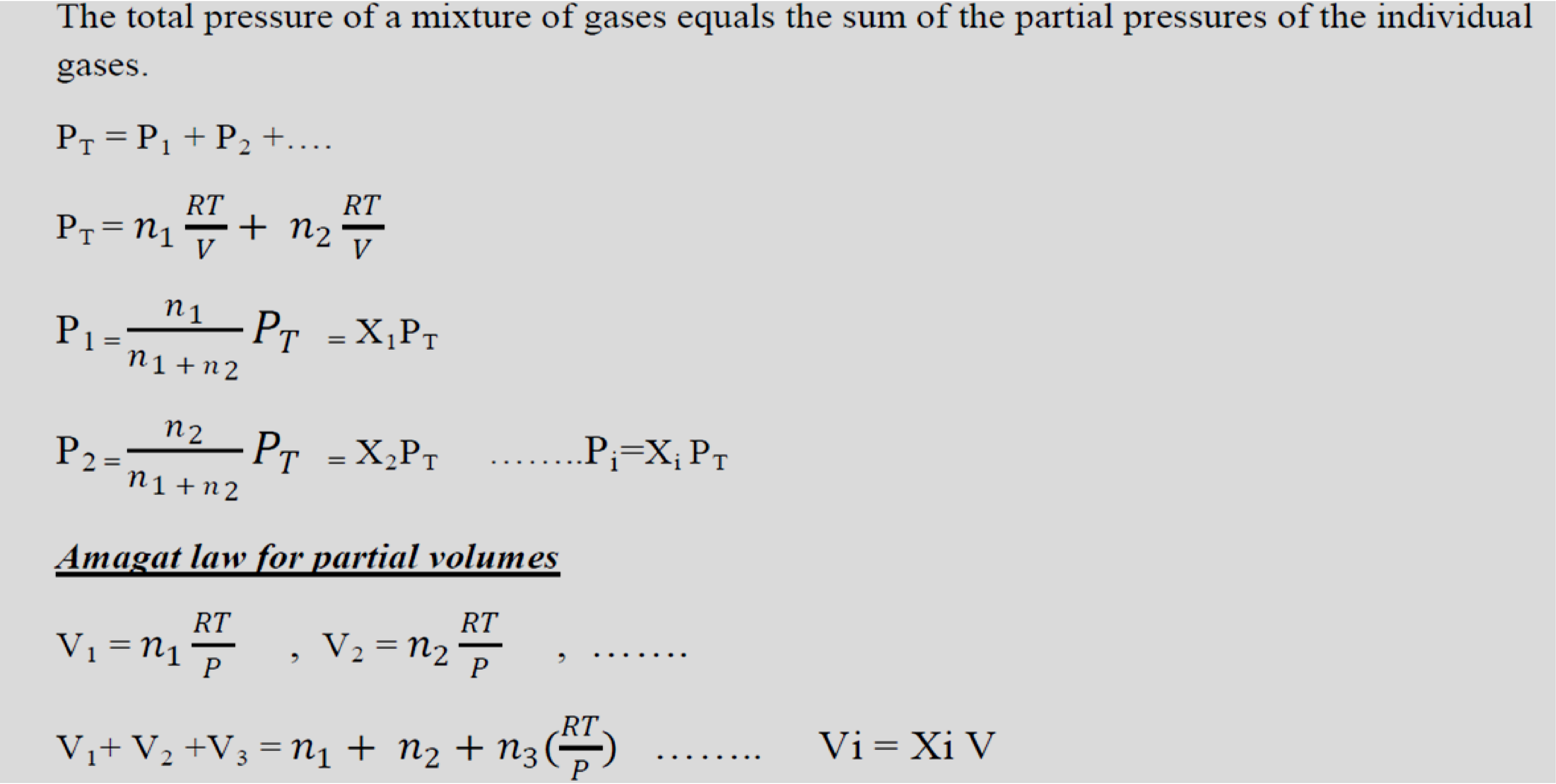
$$n_2 = 0.0920 + 0.0210 = 0.1130\,mol$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \rightarrow \therefore V_2 = \frac{V_1 \times n_2}{n_1}$$

$$V_2 = \frac{1.90L \times 0.1130\,mol}{0.0920\,mol} \rightarrow \therefore V_2 = 2.33L$$

*Dalton’s Law of Partial Pressures

Dalton’s Law, or the Law of Partial Pressures, states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the gases in the mixture.



The total pressure of a mixture of gases equals the sum of the partial pressures of the individual gases.

$$P_T = P_1 + P_2 + \ldots.$$

$$P_T = n_1\frac{RT}{V} + n_2\frac{RT}{V}$$

$$P_1 = \frac{n_1}{n_1 + n_2} P_T = X_1 P_T$$

$$P_2 = \frac{n_2}{n_1 + n_2} P_T = X_2 P_T \qquad \ldots\ldots..P_i = X_i\, P_T$$

Amagat law for partial volumes

$$V_1 = n_1\frac{RT}{P} \quad , \quad V_2 = n_2\frac{RT}{P} \quad , \quad \ldots\ldots$$

$$V_1 + V_2 + V_3 = n_1 + n_2 + n_3\left(\frac{RT}{P}\right) \quad \ldots\ldots. \qquad Vi = Xi\ V$$

Example: 24.0 L of nitrogen gas at 2 atm and 12.0 L of oxygen gas at 2 atm are added to a 10 L container at 273 K. Find the partial pressure of nitrogen and oxygen and then find the total pressure.

- **Solution**
- Find the number of moles of oxygen and nitrogen using PV=nRT which is n=PV/RT
  - oxygen: ((1 atm)(12L))/(0.08206 atm L mol^{-1} K^{-1})(273 K)=0.536 moles oxygen
  - nitrogen: ((1 atm)(24.0L))/(0.08206 atm L mol^{-1} K^{-1})(273 K)=1.07 moles of Nitrogen
  - add to get n_{tot}: .536 mol_{Oxygen}+1.07 $mol_{Nitrogen}$=1.61 moles total

- Use PV=nRT or P=(nRT)/V to find the total pressure
  - Ptot=((1.61 mol_{total})(0.08206 atm L mol^{-1} K^{-1})(273 K))/(10.0 L)=3.61 atm

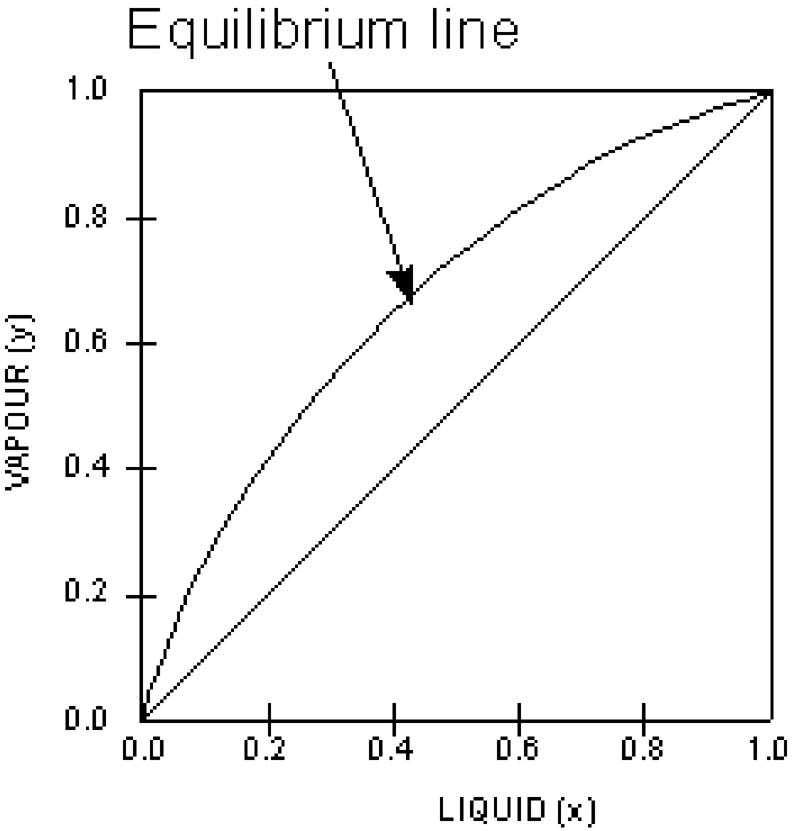
- $P_A/P_{tot}=n_A/N_{tot}$ can be rearranged to $P_{A=(}P_{tot)(}n_A/N_{tot)}$ to find the partial pressures
  - P_{oxygen}=(3.61 atm_{total})(.536 mol_{Oxygen}/1.61 mol_{total})=1.20 atm_{Oxygen}
  - $P_{nitrogen}$=3.61 atm_{total}-1.20 atm_{Oxygen}=2.41 $atm_{Nitrogen}$

Phase Equilibrium and Phase Diagrams

- Why it’s important (Some properties that might be difficult to predict using a “common sense” without the knowledge of the phase diagrams)
- **example 1**: Melting temperature of a mixture AB (solution) of two components A and B could be either lower or higher than the melting point of each component.
- **example 2**: Upon cooling to a lower temperature a phase transformation of a material could cause expansion, which could cause internal stresses and failure (e.g. tin food cans will crumble at low T)
- **example 3**: No abrupt liquid-to-solid transformation when two components are present (soid + liquid in a temperature range)
- **example 4**: Chip-Solder-Joint-Failure, for example: T_{melt} (Sn) = 232 C, T_{melt} (Pb) = 327 C, but but T_{melt} ($Sn_{0.62}Pb_{0.38}$) = 183 C, so this is a common soldering alloy.
- **example 5**: Tmelt (Au) = 1064 C, Tmelt (Si) = 2550 C, but T_{melt} ($Au_{0.97}Si_{0.03}$) = 363 C, so thin layer of gold is used to attach Si chip to a ceramic substrate (shock protection)
- **example 6**: Mechanical properties (hardness and tensile strength) of an alloy could be substantially higher than that of the individual components (e.g. hardness (AgCu) about twice the harness of Ag or Cu)

Vapor–liquid equilibrium

- In thermodynamics and chemical engineering, the vapor–liquid equilibrium (VLE) describes the distribution of a chemical species between the vapor phase and a liquid phase. The concentration of a vapor in contact with its liquid, especially at equilibrium, is often expressed in terms of vapor pressure, which will be a partial pressure (a part of the total gas pressure) if any other gas(es) are present with the vapor.
- For each component in a binary mixture, one could make a vapor–liquid equilibrium diagram. Such a diagram would graph liquid mole fraction on a horizontal axis and vapor mole fraction on a vertical axis.



The Clausius-Clapeyron Equation

The vaporization curves of most liquids have similar shape. The vapour pressure steadily increase as the temperature increases. A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the pressure P, enthalpy of vaporization, ΔH_{vap}, and temperature T are related.

$$P \; = \; A\,\exp(-\,\Delta H_{vap}\,/\,R\,T)$$

where R (= 8.3145 J mol^{-1} K^{-1}) and **A** are the gas constant and unknown constant. This is known as the **Clausius- Clapeyron equation**. If P_1 and P_2 are the pressures at two temperatures T_1 and T_2, the equation has the form:

$$\boxed{\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

The Clausius-Clapeyron equation allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

Example : The vapor pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol-1. Estimate the vapor pressure at temperature 363 and 383 K respectively.

- **Solution**

Using the Clausius-Clapeyron equation,

$$\boxed{\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

we have:

P_{363} = 1.0 exp (- (40700/8.3145)(1/363 - 1/373) = 0.697 atm

P_{383} = 1.0 exp (- (40700/8.3145)(1/383 - 1/373) = 1.409 atm

Note that the increase in vapor pressure from 363 K to 373 K is 0.303 atm, but the increase from 373 to 383 K is 0.409 atm. The increase in vapor pressure is not a linear process.

Example : The vapor pressures of ice at 268 and 273 are 2.965 and 4.560 torr respectively. Estimate the heat of sublimation of ice.

***Solution**

The enthalpy of sublimation is ΔH_{sub}. Use a piece of paper and derive the Clausius- Clapeyron equation so that you can get the form:

$$\boxed{\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

ΔH_{sub} = R ln (P_{268} / P_{273}) (1/268 - 1/273)

= 8.3145*ln(2.965/4.560) / (1/268 - 1/273)

= 52370 J mol^{-1}

Note that the heat of sublimation is the sum of heat of melting and the heat of vaporization

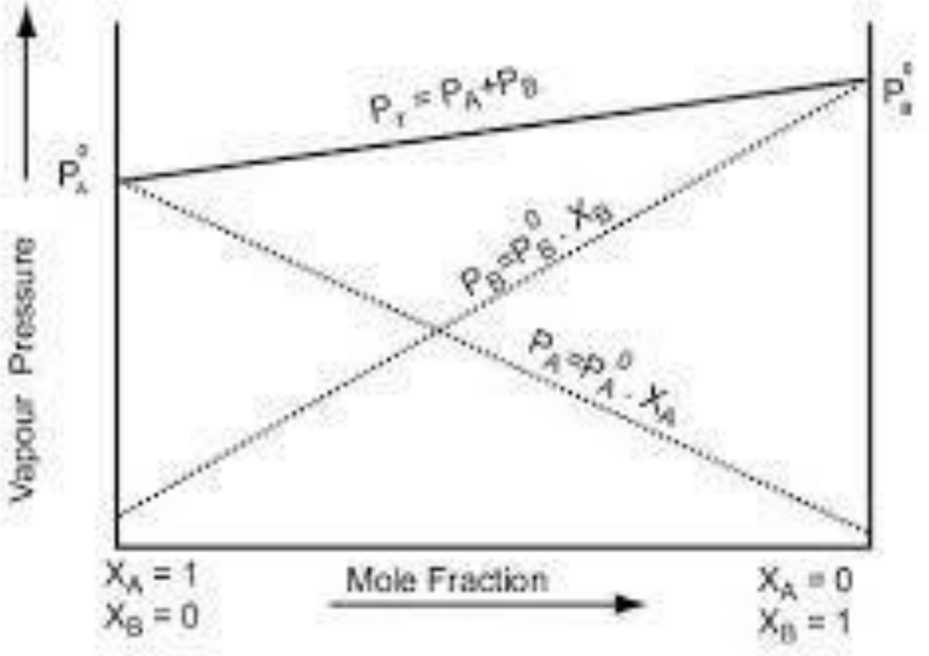
Raoult's law

In separation science, one often exploits the preference of a substance for one phase over another to separate a mixture. This is the principle behind distillation. We have seen that under ideal condition, the vapor pressure of a volatile liquid obeys Raoult's law. Say we have a liquid mixture containing two components 1 and 2. Let the mole fraction of 1 in the liquid be x_1 and the mole fraction of 2 be x_2. $x_1 + x_2 = 1$ necessarily. If at some temperature T, the vapor pressure of the pure component 1 is P 1 and that of the pure component 2 is P2 , then the partial pressures of the two substances in the vapor phase are described by Raoult's law if the solution is ideal:

$$\mathbf{P_1 = x_1P_1^* \qquad\qquad P_2 = x_2P_2^*}$$

The total pressure of the two vapors is

$$\mathbf{P = P_1 + P_2 = x_1P^*_1 + x_2P^*_2 = P_2 - x_1(P^*_2 - P^*_1\ )}$$



Vapour Pressure Diagram for Ideal Solution

Example : Calculate the vapor pressure of a mixture containing 252 g of n-pentane (Mw = 72) and 1400 g of n-heptane (Mw = 100) at 20°C. The vapor pressure of npentane and n-heptane are 420 mm Hg and 36 mm Hg respectively.

*__Solution__

According to Raoult's law, the vapor pressure exercised by a component of a mixture can be calculated as follows **$P = P^o x$**

where

P is the vapor pressure of the component in the mixture.

P^o is the vapor pressure of the pure component.

x is the molar fraction of the component in the mixture.

Calculation of molar fractions (x)

moles n-pentane = 252/72 = 3.5 moles n-heptane = 1400/100 = 14

Totals = 3.5 + 14 = 17.5 moles

$x_{\text{n-pentane}} = 3.5/17.5 = 0.2$ $x_{\text{n-eptane}} = 14/17.5 = 0.8$

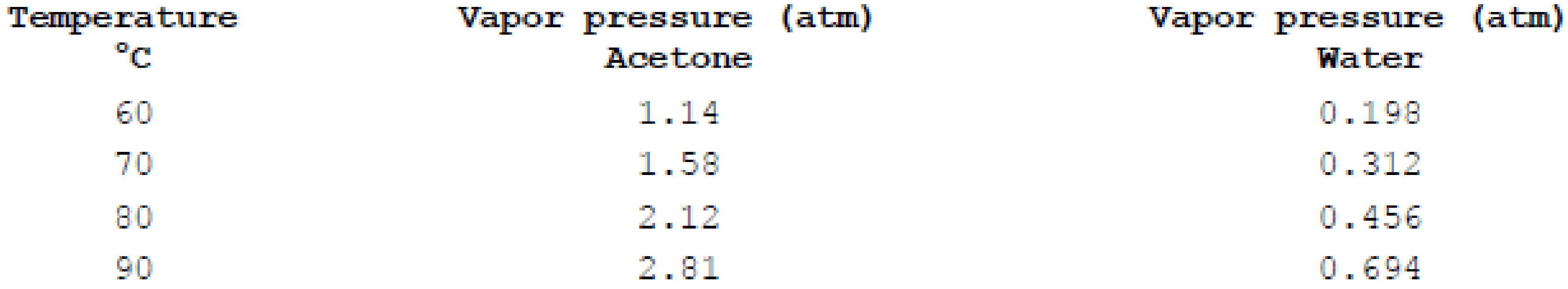
Thus:

$P_{\text{n-pentane}} = 0.2 \times 420 = 84$ mm Hg $P_{\text{n-eptane}} = 0.8 \times 36 = 28.8$ mm Hg

and the vapor pressure of mixture is

$P_{\text{mixture}} = 84 + 28.8 = 112.8$ mm

Example: Calculate the boiling point (at 1 atm) of a solution containing 116 g of acetone (Mw = 58) and 72 g of water (Mw = 18) by using the following table:



Temperature °C	Vapor pressure (atm) Acetone	Vapor pressure (atm) Water
60	1.14	0.198
70	1.58	0.312
80	2.12	0.456
90	2.81	0.694

*__Solution__

A liquid starts to boil when its vapor pressure matches the atmospheric pressure (1 atm inthis case). Thus, according to Raoult's law

$P = x_{acetone} P^{o}_{acetone} + x_{water} P^{o}_{water} = 1$ atm

From the given data we can calculate the molar fractions

Moles acetone = 116/58 = 2 moles water = 72/18 = 4

total moles = 6

xacetone = 2/4 = 1/3 xwater = 4/6 = 2/3

thus

$P = 2/3\ P^{o}_{acetone} + 1/3\ P^{o}_{water} = 1$ atm

By trials, using the table, we can find the values of vapor pressure which satisfies the above equation. The best result is obtained by using the values at 80°C :

P = 2/3 0.456 + 1/3 2.12 = 1.01 atm then the boiling point is about 80°C.

Ideal Solutions	**Non Ideal Solution**
1- The solutions which obey Raoult’s Law at every range of concentration and at all temperatures are Ideal Solutions.	1- The solutions which don’t obey Raoult’s law at every range of concentration and at all temperatures are Non-Ideal Solutions.
2-The enthalpy of mixing of two components should be zero, that is, $\Delta H_{mix} = 0$.	2- The enthalpy of mixing that is, $\Delta H_{mix} \neq 0$
3- The volume of the mixing is equal to zero that is, $\Delta V_{mix} = 0$.	3-The volume of mixing that is, $\Delta V_{mix} \neq 0$,
4-The solute-solute interaction and solvent-solvent interaction is almost similar to the solute-solvent interaction.	4- The solute-solute and solvent-solvent interaction is different from that of solute-solvent interaction.
5- Examples of Ideal Solutions • n-hexane and n-heptane • Bromoethane and Chloroethane • Benzene and Toluene • CCl4 and SiCl4 • Chlorobenzene and Bromobenzene • Ethyl Bromide and Ethyl Iodide • n-Butyl Chloride and n-Butyl Bromide	5- Examples of Non Ideal Solutions • Acetone and Carbon disulphide • Acetone and Benzene • Carbon Tetrachloride and Toluene or Chloroform • Methyl Alcohol and Water • Acetone and Ethanol • Ethanol and Water

Non-ideal solutions showing positive deviation from Raoult’s Law	**Non-ideal solutions showing negative deviation from Raoult’s Law**
1-Positive Deviation from Raoult’s Law occurs when the vapour pressure of the component is greater than what is expected in Raoult’s Law. 2- The solute-solvent forces of attraction is weaker than solute-solute and solvent-solvent interaction. 3- The enthalpy of mixing is positive that is, $\Delta H_{mix} > 0$ 4-The volume of mixing is positive that is, $\Delta V_{mix} > 0$ as the volume expands on the dissolution of components A and B 5- Examples of Positive Deviation • Acetone and Carbon disulphide • Acetone and Benzene • Carbon Tetrachloride and Toluene or Chloroform • Methyl Alcohol and Water • Acetone and Ethanol • Ethanol and Water	1- Negative Deviation occurs when the total vapour pressure is less than what it should be according to Raoult’s Law. 2- The solute-solvent interaction is stronger than solute-solute and solvent-solvent interaction. 3- The enthalpy of mixing is negative that is, $\Delta H_{mix} < 0$ 4- The volume of mixing is negative that is, $\Delta V_{mix} < 0$ as the volume decreases on the dissolution of components A and B. 5- Examples of Negative Deviation • Chloroform and Benzene • Chloroform and Diether • Acetone and Aniline • Nitric Acid (HNO3) and water • Acetic Acid and pyridine • Hydrochloric Acid (HCl) and water