

States of Matter

SM II

Mixtures of Gases

- (Vapor Pressure)
- Partial Pressure
- Dalton's Law (IGL)
- App^s of Dalton's Law

Ref 5: 4

Prob FUP: 5: 9, 10

E of C: 5: 45, 46, 50

Adv Rdg 5: 6

Gas Mixtures

Definitions:

1.) Mole Fraction, X_i , of component i

$$X_i = \frac{n_i}{n_{\text{tot}}} \quad ; \quad (\sum X_i = 1)$$

Ex. mix. of 2 mol He & 3 mol O₂

$$n_{\text{tot}} = 5 \text{ mol}$$

$$X_{\text{He}} = \frac{2 \text{ mol}}{5 \text{ mol}} = 0.4, \quad X_{\text{O}_2} = \frac{3 \text{ mol}}{5 \text{ mol}} = 0.6$$

2.) Partial Pressure (PP)

$$P_i = X_i P_{\text{tot}}$$

Ex. cont^d: if $P_{\text{tot}} = 2 \text{ atm}$,

$$P_{\text{He}} = 0.4 \times 2 \text{ atm} = 0.8 \text{ atm}$$

$$P_{\text{O}_2} = 0.6 \times 2 \text{ atm} = 1.2 \text{ atm}$$

Dalton's Law of Partial Pressures

$$P_{\text{tot}} = \sum P_i^*$$

where P_i^* = pressure of component i
if it were there alone in container
("alone pressure")

or equivalent

$$P_i = P_i^* \quad (\text{where } P_i = X_i P_{\text{tot}})$$

in words: the partial pressure of gas in a mixture
is the same as the "alone pressure"

or: partial pressure is not affected
by presence of other gases

Dalton's Law ...

also:

can apply IGL to individual components &
to mixture as a whole

$$P_i V = n_i R T,$$

$$P_{\text{tot}} V = n_{\text{tot}} R T$$

note: V is volume of container

Comment:

- applicable strictly only to ideal gases
(b/c no attraction/repulsion between molecules;
molecules far apart)
- in practice, used also
for non-ideal ("real") gases, **even for vapors**

Practice

Container (25 L) holds He & CH₄;

$$P_{\text{He}}^* = 85 \text{ kPa}, \quad P_{\text{CH}_4}^* = 25 \text{ kPa}, \quad T = 25^\circ\text{C}$$

0.35 mol Ar is added

a.) partial pressures & total pressure, if V, T const.

Assume: Dalton's Law valid throughout

$$P_{\text{He}} = P_{\text{He}}^* = \underline{85 \text{ kPa}}, \quad P_{\text{CH}_4} = P_{\text{CH}_4}^* = \underline{25 \text{ kPa}}$$

$$\begin{aligned} P_{\text{Ar}} &= P_{\text{Ar}}^* = \frac{n_{\text{Ar}} R T}{V} \\ &= \frac{(0.35 \text{ mol}) (8.31 \text{ kPaL/molK}) (298 \text{ K})}{25 \text{ L}} \\ &= \underline{35 \text{ kPa}} \end{aligned}$$

$$P_{\text{tot}} = (85 + 25 + 35) = \underline{145 \text{ kPa}}$$

Practice ...

b.) What is the mole fraction (X) of each gas?

can get from definition of partial pressures

$$P_i = X_i P_{\text{tot}}, \quad X_i = \frac{P_i}{P_{\text{tot}}}$$

(also, generally, PP ratios = X ratios)

$$X_{\text{He}} = \frac{85}{145} = \underline{0.59} \quad X_{\text{CH}_4} = \frac{25}{145} = \underline{0.17}$$

$$X_{\text{Ar}} = \dots = \underline{0.24}$$

c.) What are the partial pressures P_i, if in exp. a.),

P_{tot} remains constant at 110 kPa.

(V can change like in a cylinder/piston system)

(we know X_i; doesn't change when P_{tot} changes)

$$P_{\text{He}} = 0.59 \times 110 \text{ kPa} = \underline{65 \text{ kPa}}$$

$$P_{\text{CH}_4} = \dots = \underline{19 \text{ kPa}}$$

$$P_{\text{Ar}} = \dots = \underline{26 \text{ kPa}}$$

Collecting Gases over Liquids

see Pet. Fig. 6.15

“Gas” contains “desired gas” +
“vapor gas”

i. e., it is a mix. of gases

Let's assume Dalton's Law holds, then

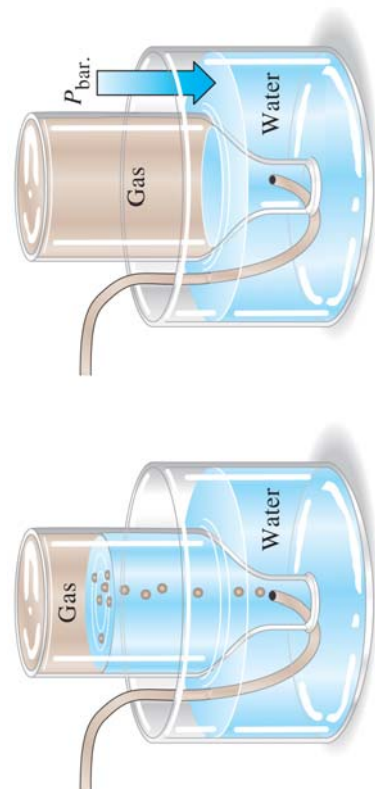
$$P_{\text{tot}} = P(\text{desired gas}) + VP(\text{of "liquid"})$$

VP is a function of T,

look up from Tables,

e.g., CDS, Table #9; if liquid = water

Pet. Fig. 6.15 Collecting Gases over Liquids



Practice

20 L of H₂ collected over water (i.e., “wet gas”);

P_{atm} = 93.0 kPa, T = 22 °C.

moles of H₂ ?

must deduct VP of H₂O from P_{tot} = P_{atm}

to get PP of H₂ acc. to Dalton's Law;

then apply IGL to get moles of H₂

$$P_{H_2} = P_{atm} - VP^{22^\circ C} \text{ of } H_2O \quad (\text{from CDS \#9})$$

$$= 93.0 \text{ kPa} - 19.8 \text{ torr} \left(\frac{101.3 \text{ kPa}}{760 \text{ torr}} \right)$$

$$= (93.0 - 2.6) \text{ kPa} = 90.4 \text{ kPa}$$

moles of H₂

$$n_{H_2} = \frac{P_{H_2}V}{RT} = \frac{(90.4 \text{ kPa})(20 \text{ L})}{(8.31 \text{ kPa}\cdot\text{L}/\text{mol}\cdot\text{K})(295 \text{ K})}$$

$$= \underline{0.74 \text{ mol } H_2}$$

Stoichiometry w/ PP's

(assuming Dalton's Law is valid)

- convenient for gas rxns

(even if solids and/or liquids are present,

as long as their vapor pressure is negligible and as long as

they are not limiting reactants, often identified as “in xs”)

- can use PP's in reaction tables

(instead of moles (n) or conc. (c))

b/c PP ∝ n

Ex.

Consider the reaction NO_{2(g)} → N₂O_{4(g)}, unbalanced;

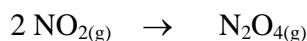
P_{initial} = 82 kPa; no initial N₂O₄;

P_{final} = 50 kPa

Determine final PP's of NO₂ and N₂O₄.

Stoichiometry ...

Ans. Balanced Equation



I	82	0
C	- 2x	+ x
F	82 - 2x	x

Dalton's: P_{tot} = P_{NO₂} + P_{N₂O₄}

$$= (82 - 2x) + x = 50$$

$$= 82 - x = 50$$

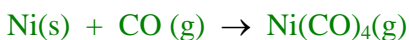
$$x = 82 - 50 = \underline{32 \text{ kPa}}$$

$$P_{N_2O_4} = x = \underline{32 \text{ kPa}}$$

$$P_{NO_2} = 82 - (2 \times 32) = \underline{18 \text{ kPa}}$$

Extra Practice in PP Stoichiometry

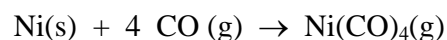
Process in Nickel Refining:



(Ni(s) in xs, can be ignored since it's a solid, presumably w/t vapor pressure)

Initially no product present. Total pressure goes from 10 atm to 4atm. What are the final partial pressures?

Ans. Balanced Equation



Reaction Table:

I	10	0
C	- 4x	+ x
F	10 - 4x	x

Dalton's: 4 (atm) = 10 - 4x + x

$$= 10 - 3x$$

$$3x = 10 - 4 = 6 \quad x = 2$$

$$P_{CO} = 10 - 4(2) = \underline{2 \text{ kPa}}, \quad P_{Ni(CO)_4} = \underline{2 \text{ kPa}}$$