Gases

Z Ch 5

"The particles of the air are in contact with each other, yet they do not fit closely in every part, but void spaces are left between them, as in the sand on the sea shore: the grains of sand must be imagined to correspond to the particles of air, and the air between the grains of sand to the void spaces between the particles of air. Hence, when any force is applied to it, the air is compressed, and, contrary to its nature, falls into the vacant spaces from the pressure exerted on its particles: but when the force is withdrawn, the air returns again to its former position from the elasticity of its particles, as is the ease with horn shavings and sponge, which, when compressed and set free again, return to the same position and exhibit the same bulk."

Hero of Alexandria, ~ AD 60

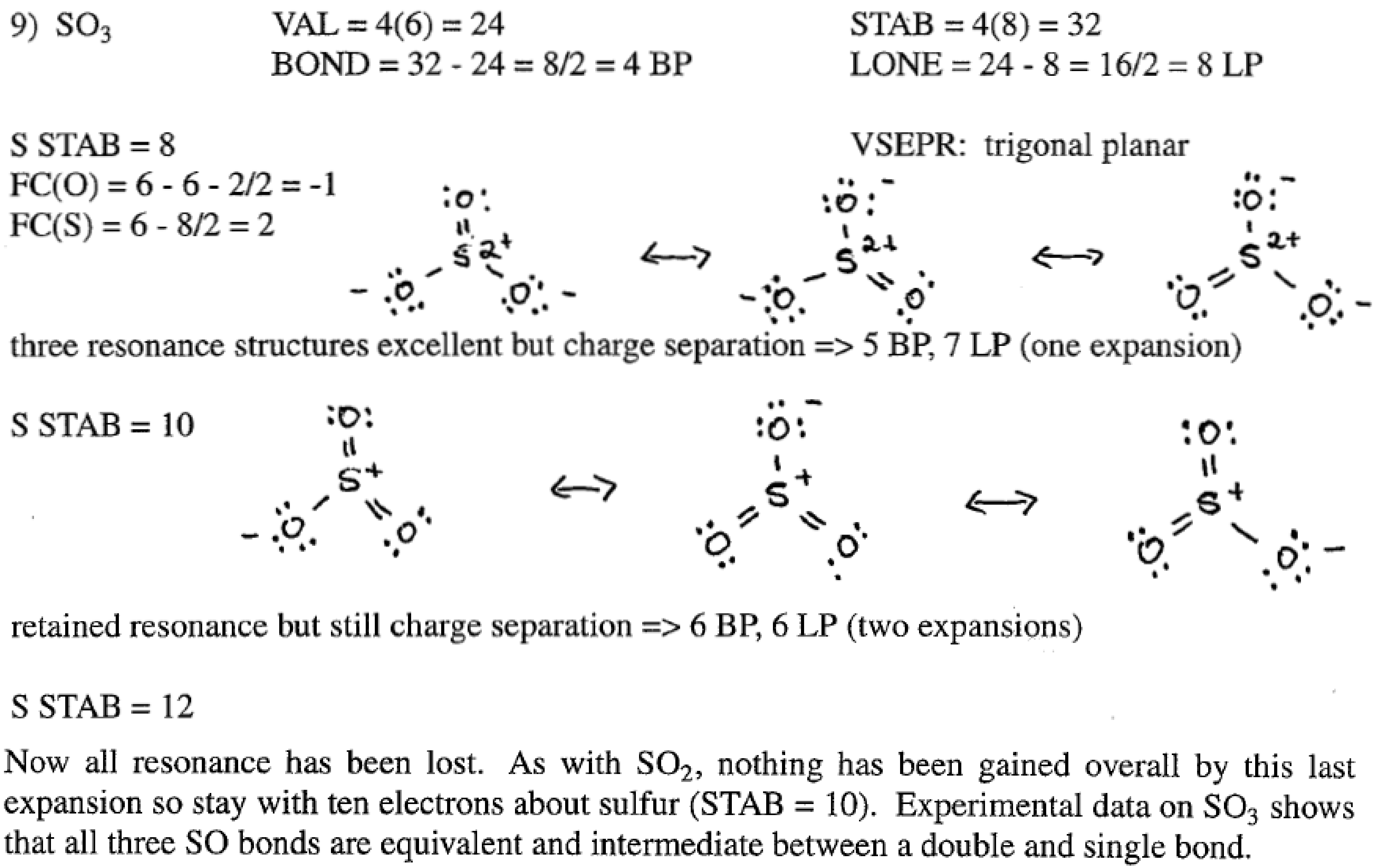
5.3 Ideal Gas Law
5.4 Gas Stoichiometry
5.5 Dalton's Law of Partial Pressures
5.6 Kinetic Molecular Theory of Gases
5.7 Effusion and Diffusion
5.8 Collisions of Gas Particles with Container Walls
5.9 Intermolecular Collisions
5.10 Real Gases

FRIDAY quiz
(VSE, intro gases)

LAB – Week 10
changed makeup lab week

Examples work out in detail on Blackboard – Week 6 Handout

Lewis Structures – When do You Stop VSE



9) SO_3

VAL = 4(6) = 24

BOND = 32 - 24 = 8/2 = 4 BP

STAB = 4(8) = 32

LONE = 24 - 8 = 16/2 = 8 LP

S STAB = 8

FC(O) = 6 - 6 - 2/2 = -1

FC(S) = 6 - 8/2 = 2

VSEPR: trigonal planar

three resonance structures excellent but charge separation => 5 BP, 7 LP (one expansion)

S STAB = 10

retained resonance but still charge separation => 6 BP, 6 LP (two expansions)

S STAB = 12

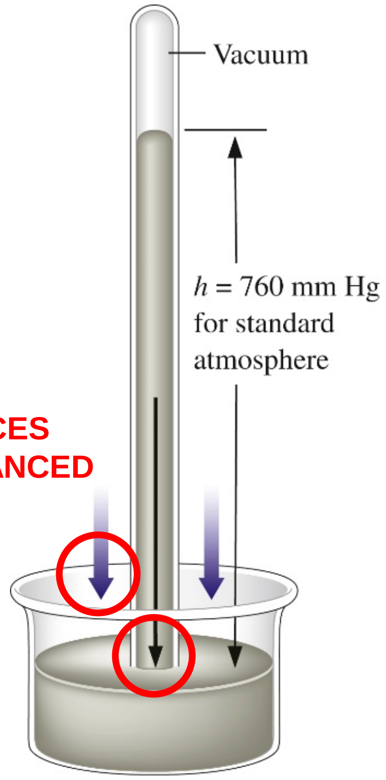
Now all resonance has been lost. As with SO_2, nothing has been gained overall by this last expansion so stay with ten electrons about sulfur (STAB = 10). Experimental data on SO_3 shows that all three SO bonds are equivalent and intermediate between a double and single bond.

REVIEW FROM FRIDAY

Torricelli's Barometer

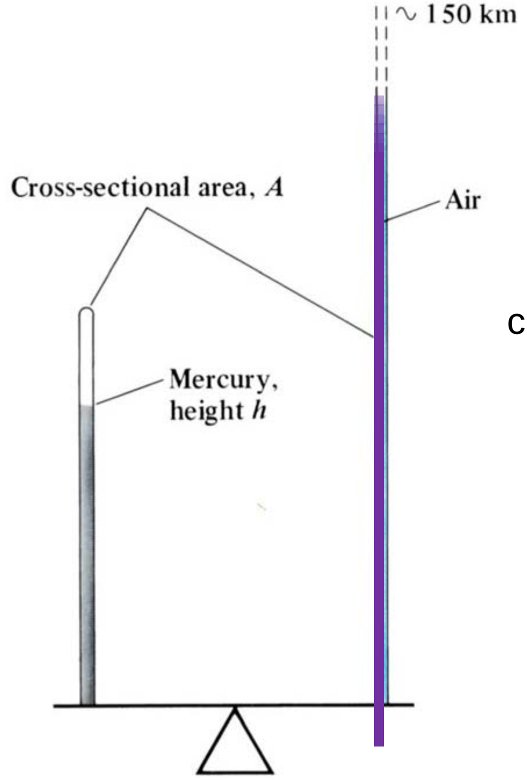
How is pressure measured? How do you measure atmospheric pressure, i.e., how does a barometer work? Consider a mercury barometer. Invert a glass tube that is completely filled with mercury in a dish of mercury. The mercury will flow out of the the glass tube until a certain height is reached.

Evangelista Torricelli, 1608-1648

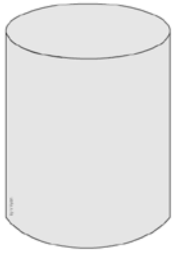


FORCES BALANCED

The height achieved is due to a balancing of forces on the surface of mercury, the weight of a column of air and the weight of the mercury column.

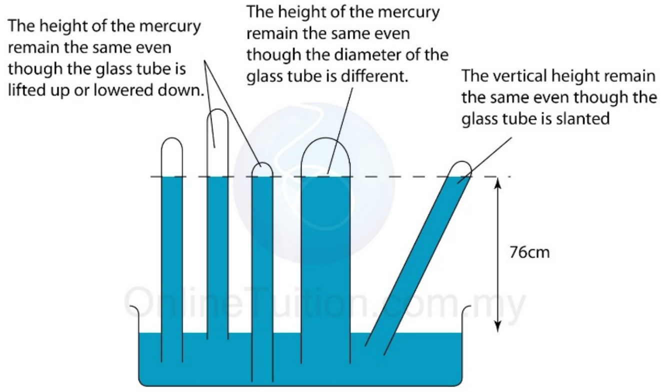


$P_{Hg} = F_{Hg}/A$ $F_{air}/A = P_{air}$



column cross section of area A

$$
\begin{aligned}
P &= F/A \\
&= mg/A \\
&= dVg/A \\
&= dAhg/A \\
\Rightarrow \mathbf{P} &= \mathbf{dgh}
\end{aligned}
$$

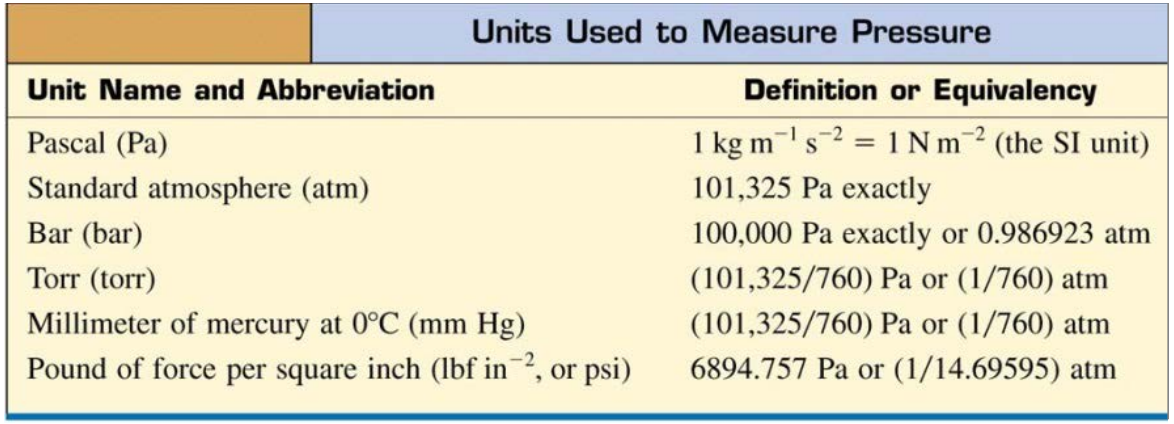


How is force related to height?

REVIEW FROM FRIDAY

Torricelli’s Barometer

1 **atm** = 760 **torr**
= 760 mm Hg (0°C)
= 29.92 in Hg (0°C)
= 101.325 kPa
= 14.69595 psi



Units Used to Measure Pressure

Unit Name and Abbreviation	Definition or Equivalency
Pascal (Pa)	$1\ \mathrm{kg\ m^{-1}\ s^{-2}} = 1\ \mathrm{N\ m^{-2}}$ (the SI unit)
Standard atmosphere (atm)	101,325 Pa exactly
Bar (bar)	100,000 Pa exactly or 0.986923 atm
Torr (torr)	(101,325/760) Pa or (1/760) atm
Millimeter of mercury at 0°C (mm Hg)	(101,325/760) Pa or (1/760) atm
Pound of force per square inch ($\mathrm{lbf\ in^{-2}}$, or psi)	6894.757 Pa or (1/14.69595) atm

EX 1. What is the pressure when the height of a column of mercury is 76.0000 cm? (d_{Hg} = 13.5951 g crn^{-3}, g = 9. 80665 m s^{-2})

$$P = dgh = (13.5951\ \mathrm{g} / \mathrm{cm}^{-3})\ (9.80665\ \mathrm{m} / \mathrm{s}^{2})\ (76.0000\ \mathrm{cm})$$

$$= (1.01325 \times 10^{4})\ (100\ \mathrm{cm} / \mathrm{m})^{2}\ (1\ \mathrm{kg} / 1000\ \mathrm{g})$$

$$= 1.01325 \times 10^{5}\ \mathrm{kg\ m^{-1}\ s^{-2}} = 101{,}325\ \mathrm{Pa} = \mathbf{101.325\ kPa}$$

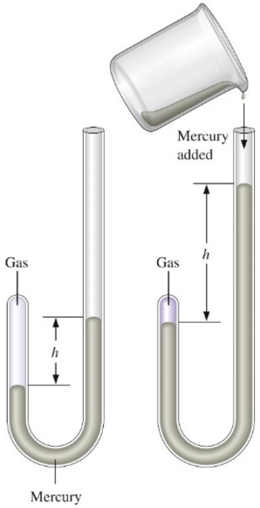
$$P = F / A = ma / A = \mathrm{kg\ m\ s^{-2}} / \mathrm{m^{2}} = \mathrm{kg\ m^{-1}\ s^{-2}}$$

REVIEW FROM FRIDAY

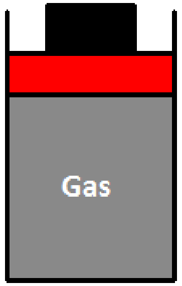
Gas Laws (Avogadro, Boyle, Charles – ABC)

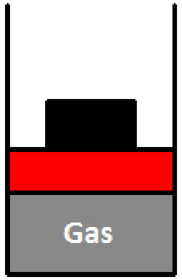
Robert Boyle, 1627-1691

$V \sim 1/P$



$T_1 = T_2 = 100\ K$



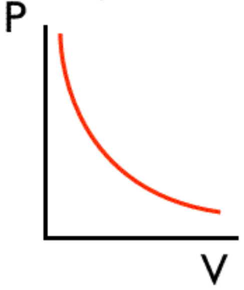


$p_1 = 2$
$v_1 = 5$

$p_2 = 5$
$v_2 = 2$

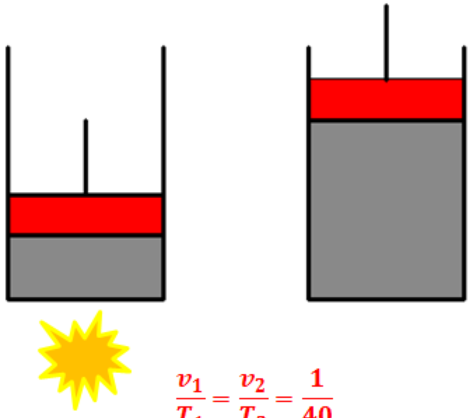
$p_1 v_1 = p_2 v_2 = 10$

Boyle's Law



PV=constant

$p_1 = p_2 = 1\ atm$

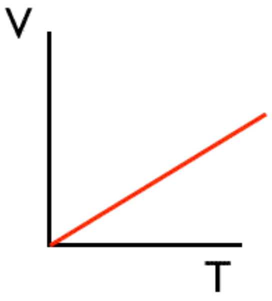


$v_1 = 5\ L$
$T_1 = 200\ K$

$v_1 = 10\ L$
$T_1 = 400\ K$

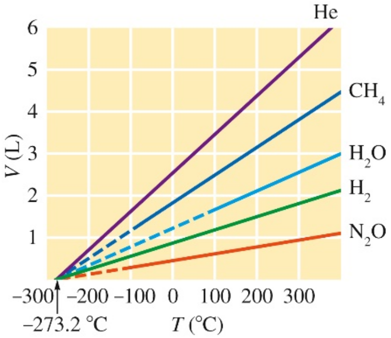
$$\frac{v_1}{T_1} = \frac{v_2}{T_2} = \frac{1}{40}$$

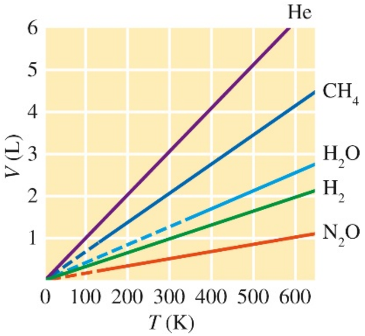
Charles' Law



$$\frac{V}{T} = constant$$

$V \sim T$





Jacques Alexandre César Charles, 1746-1823

REVIEW FROM FRIDAY

Charles Law and Absolute Zero

$$V = V_0 + \alpha V_0 t$$

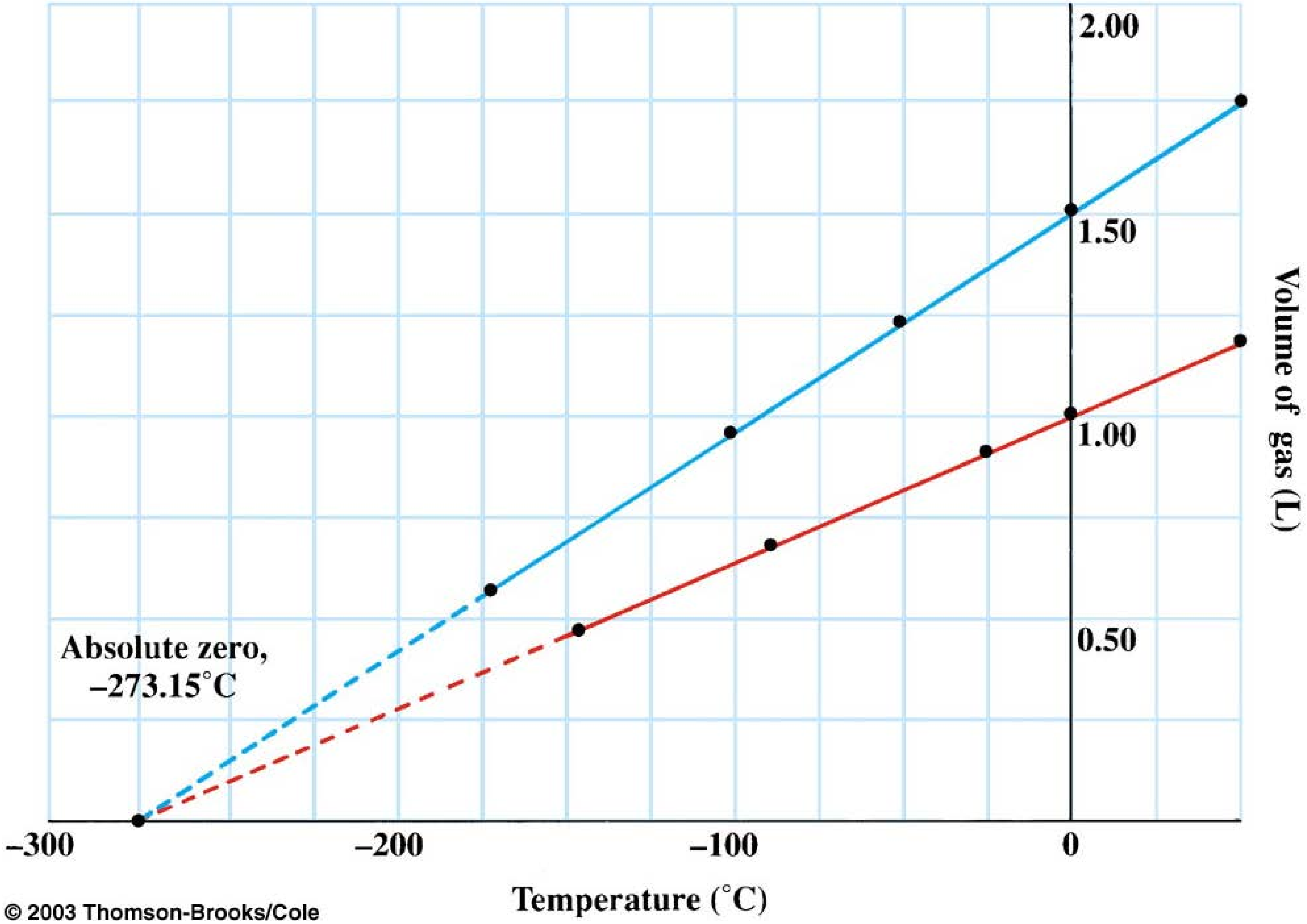
experimentally:

$$\alpha = 1/273.15\ (^{o}C)^{-1}$$

$$= V_0\left[1 + \frac{t}{273.15^{o}C}\right]$$

V = volume at 0^{o}C

α = coefficient of thermal expansion



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REVIEW FROM FRIDAY

Ideal Gas Law

Boyle: $V \sim 1 / P$

Charles: $V \sim T$ $V = CnT / P$ or $PV = nCT = nRT$

Gay-Lussac/Avogadro: $V \sim n$

EX 2. What is the volume occupied by one mole of an ideal gas at STP conditions?

$PV = nRT \Rightarrow V = nRT / P = (1.00)(0.0820574)(273.15) / (1 \text{ atm}) = 22.414 \text{ L}$

REVIEW FROM FRIDAY

Ideal Gas Law

EX 4. Hydrogen fills a 250-L reaction vessel at 100°C and 1.00 atm pressure. Determine the volume of the same quantity of hydrogen at 0°C and 1.50 atm.

$P_1 = 1.00$ atm	$P_2 = 1.50$ atm	*n* constant
$T_1 = 100\ ^oC$	$T_2 = 0^oC$	
$V_1 = 250$ L	$V_2 = ?$	

$$PV = nRT \Rightarrow \quad P_1V_1 / T_1 = nR = P_2V_2 / T_2$$

$$V_2 = P_1V_1T_2 / P_2T_1$$

$$V_2 = (1.00)(250)(273.15) / (1.50)(273.15 + 100)$$

$$= \mathbf{122\ L}$$

Density and Molar Mass

definitions: density $d = m / \boldsymbol{V}$, molar mass $M = m / \boldsymbol{n}$

$$P\boldsymbol{V} = \boldsymbol{n}RT \quad => \quad n / V = P / RT$$

$$d = m / V = (n / V)\, M = M\, P / RT \;\; => \;\; M = dRT / P$$

EX 5. Composition of liquid is 25.23% S, 74.77% F. It boils at 29°C where density of vapor is 9.95 g L^{-1} at 738 mm Hg. What is its molecular formula? $M_S = 32.066$, $M_F = 18.998$ g/mol

Assume 100 g mol S = 25.23 / 32.066 = 0.7868 mol F = 74.77 / 18.998 = 3.9356

mol F / mol S = 5.001 / 1

so empirical formula = SF_5 (M = 127.056)

$$M = dRT / P = (\,9.95\,)(\,0.0820574\,)\,(\,29 + 273.15\,) / 738/760$$

$$= 254.05 \;\; => \;\; \text{mol / emp} = 254.05 / 127.056 \sim 2 \;\; => \;\; S_2F_{10}$$

Gas Stoichiometry

EX 7. Calcium hydride (M_{CaH2} = 42.0938 g/mol) reacts with water to form hydrogen gas. Grams of CaH_2 needed to generate 64.5 L of H_2 gas if pressure of H_2 is 814 torr at 32°C?

$$CaH_2(s) \quad + \quad 2\,H_2O(l) \quad \rightarrow \quad Ca(OH)_2(aq) \quad + \quad 2\,H_2(g)$$

x g

64.5 L
814 torr
32^oC

$$n_{CaH2} = \tfrac{1}{2}\, n_{H2} \qquad (\, PV = nRT \,) \;\; => \;\; = \tfrac{1}{2}\, (\, PV \,/\, RT \,)_{H2}$$

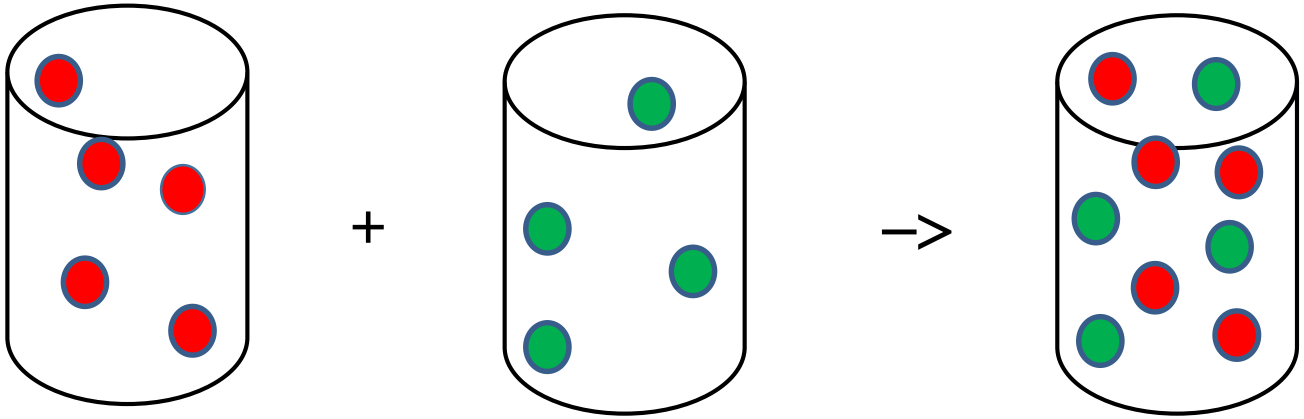
$$m = nM = MPV \,/\, 2RT$$

$$M = dRT \,/\, P$$

= (42.0938)(814/760)(64.15) / 2(0.0820574)(32 + 273.15)

= **58.1 g**

Dalton’s Law of Partial Pressures



at same *V*, *T*

$P = nRT / V$ $\qquad$ $P = nRT / V$

$$\begin{aligned} P_{\text{TOT}} &= P + P \\ &= (n + n)\, RT / V \\ &= n_{\text{TOT}}\, RT / V \end{aligned}$$

gases act independently

$$P / P_{\text{TOT}} = n / n_{\text{TOT}} = \underset{\text{mole fraction}}{X} \quad \Rightarrow \quad P = X\, P_{\text{TOT}}$$

Collecting Gas Over Water

EX 9. 15.00 g sodium azide decomposed by heating and the nitrogen gas which evolves is collected over water at 25°C at a barometric pressure of 745 mm Hg. What volume of dry gas is collected if the vapor pressure of water at 25°C is 24 mm Hg? M_{NaN3} = 65.011 g/mol

$$2\ NaN_3(s) \rightarrow 2\ Na(s) + 3\ N_2(g)$$

15.00 g 745 mm (wet), 25^{o}C

$P_{TOT} = P_{N2} + P_{H2O}$ (Dalton's Law) P_{N2}(dry) = 745 -24 = 721 mm

$n_{N2} = 3/2\ n_{NaN3} = 3/2\ 15.00/65.011 = 0.3460$

$PV = nRT$ =>

$V = nRT / P$ = (0.3460)(0.082058) (25 + 273.15) / 721/760 = **8.92 L**