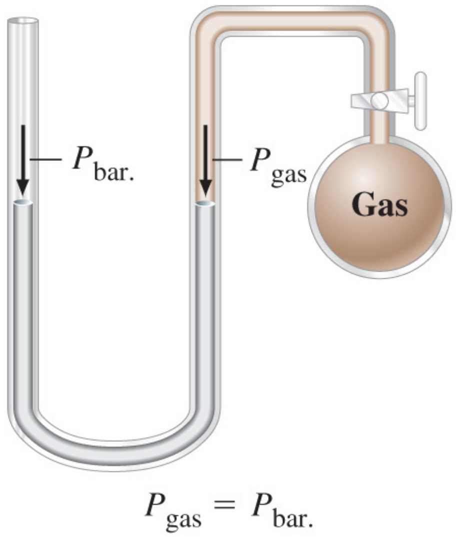
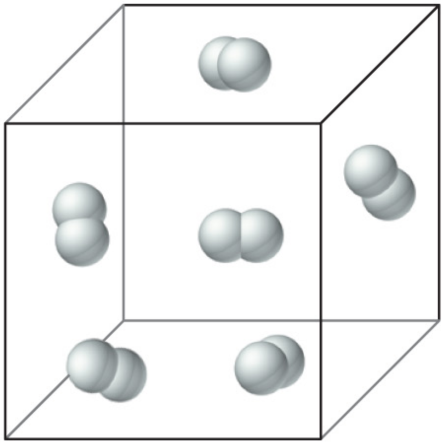
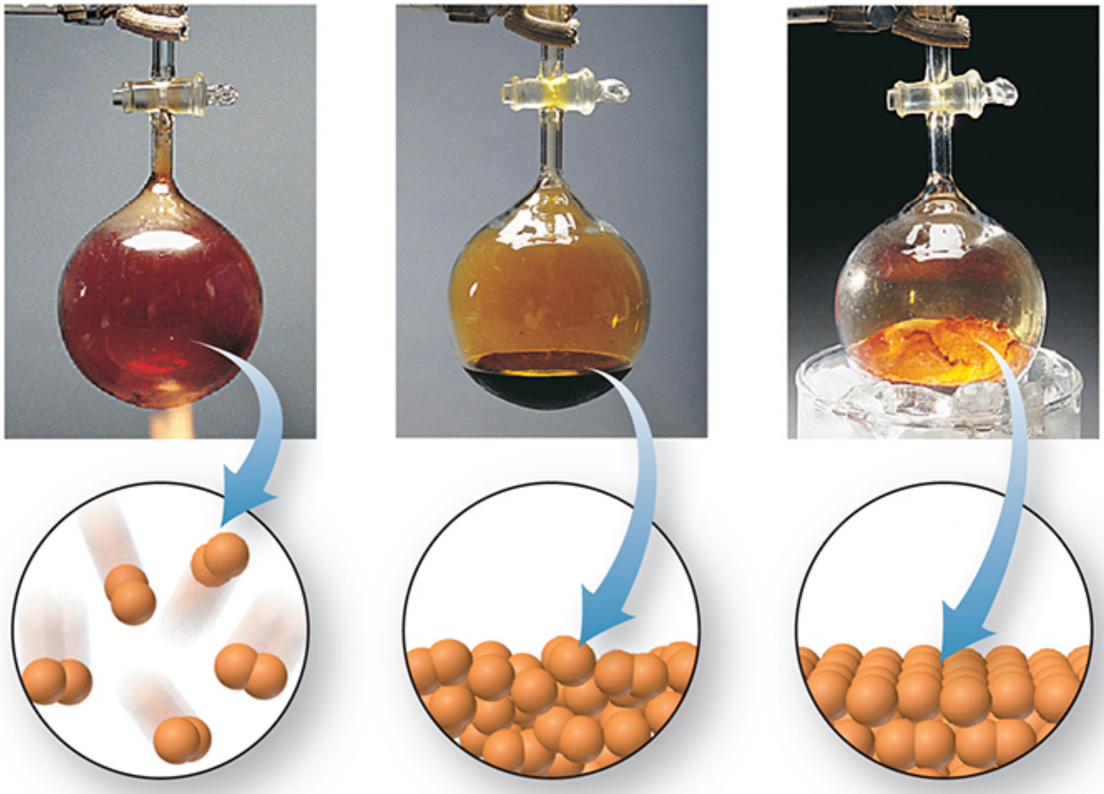
Chapter 4:
Gases and the KMT





The Three States of Matter



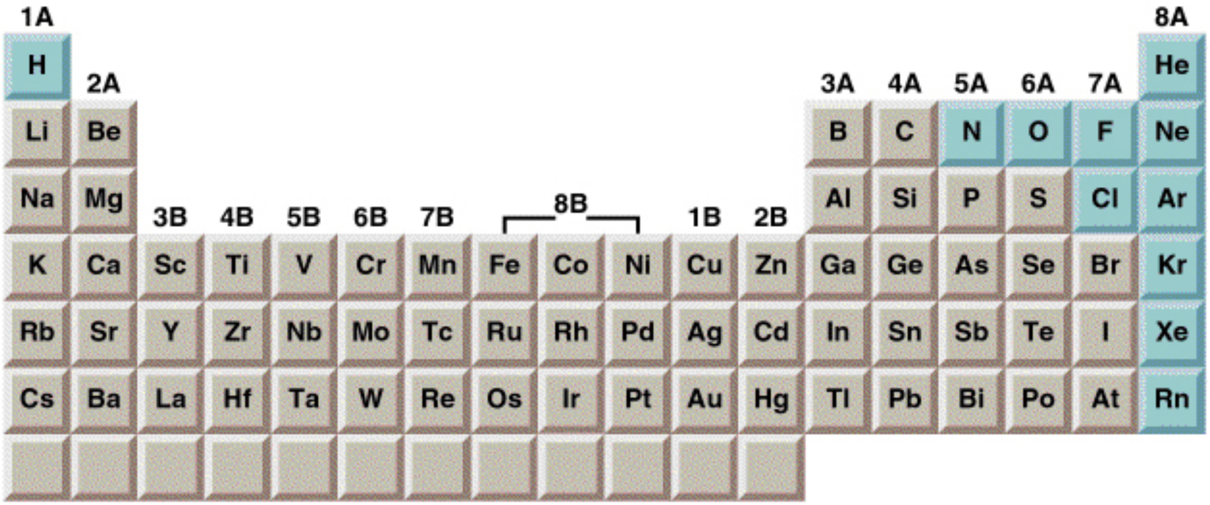
Gas: *Particles are far apart, move freely, and fill the available space.*

Liquid: *Particles are close together but move around one another.*

Solid: *Particles are close together in a regular array and do not move around one another.*

Gases and the Periodic Table

- 11 elements exist naturally as gases (25°C and 1 atm)
- diatomic gases: H_2, N_2, O_2, F_2, Cl_2
- monatomic gases: He, Ne, Ar, Kr, Xe, Rn
- oxygen has two forms: O_2 (common) and O_3 (rare)



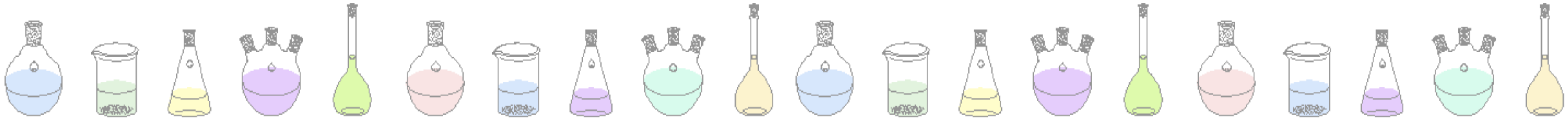
1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Gas or Vapour?

- a **gas** is a substance which is normally _____________ under regular temperature and pressure conditions
- a **vapour** is the gaseous form of a substance which is normally _______________________ under regular temperature and pressure conditions

water vapour
at 25°C

gaseous oxygen
at 25°C



The Concept of Pressure

P (Pa) = ______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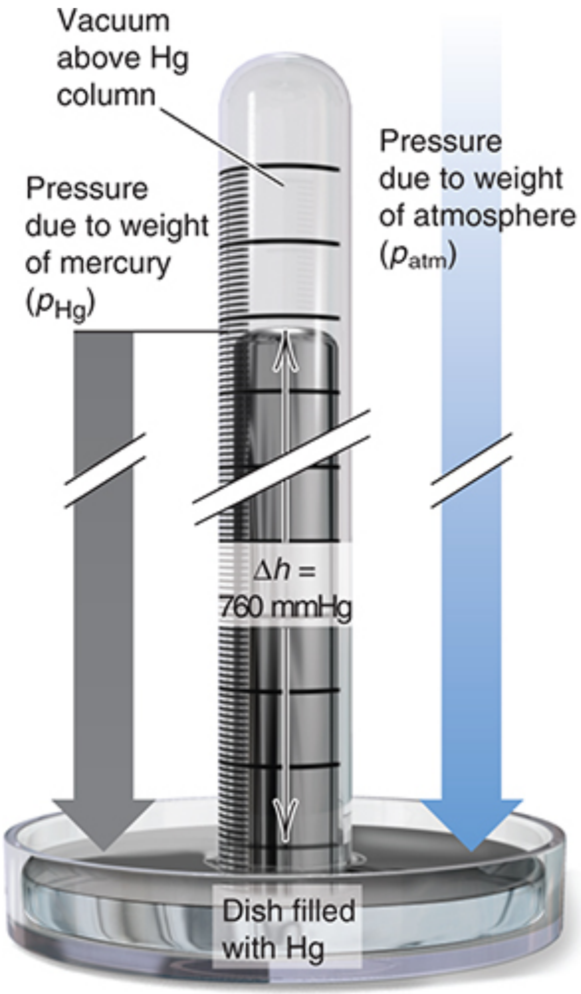
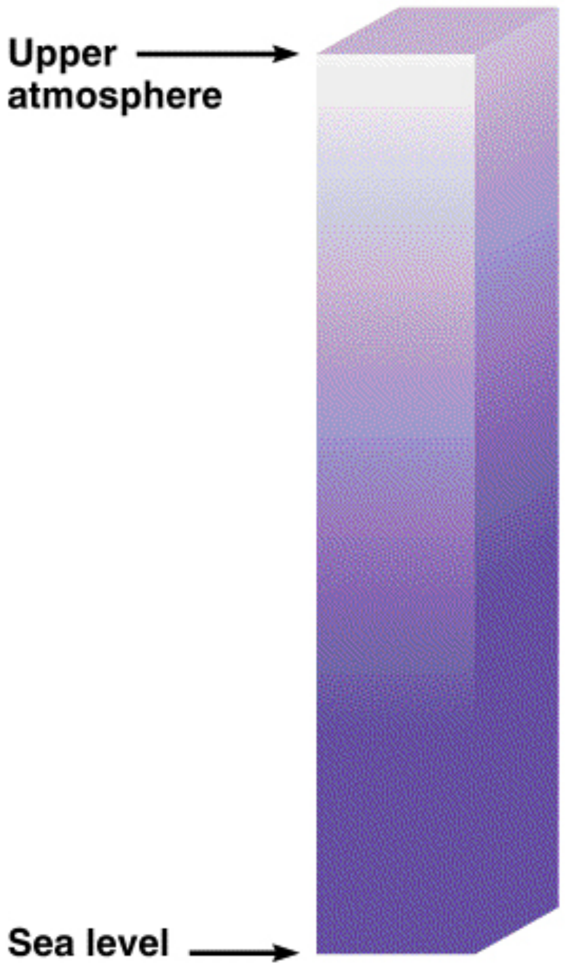
The Concept of Pressure



- The pressure exerted by a gas is measured with a BAROMETER
- Hg rises in tube until force of Hg (down) balances the force of atmosphere (pushing up).

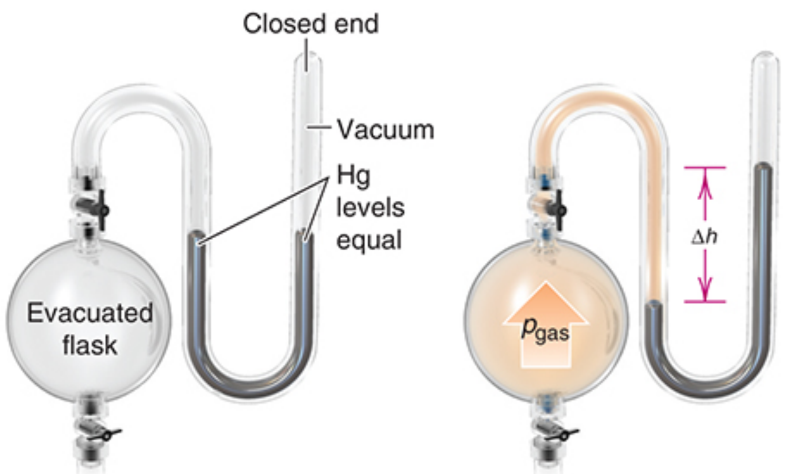
Atmospheric Pressure

- atmospheric pressure is the pressure exerted by the column of air situated above a surface
- we do not feel this pressure because we are physiologically adapted to it!



Manometers

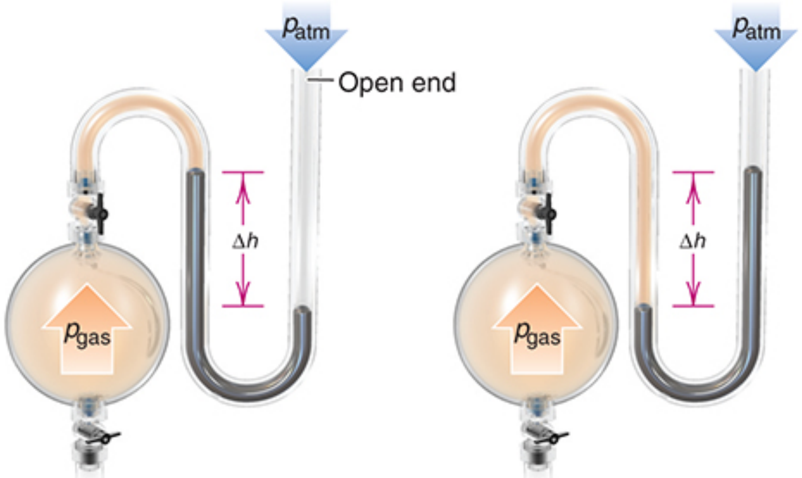
Closed-end manometer



The Hg levels are equal because both arms of the U tube are evacuated.

A gas in the flask pushes the Hg level down in the left arm, and the difference in levels, Δh, equals the gas pressure, p_{gas}.

Open-end manometer

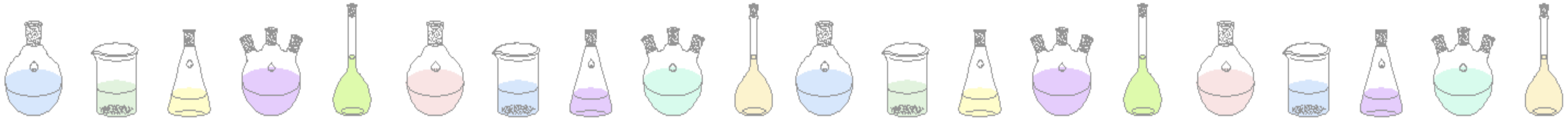


When p_{gas} *is less than* p_{atm}*, subtract Δh from* p_{atm}:

$p_{gas} < p_{atm}$
$p_{gas} = p_{atm} - \Delta h$

When p_{gas} *is greater than* p_{atm}*, add Δh to* p_{atm}:

$p_{gas} > p_{atm}$
$p_{gas} = p_{atm} + \Delta h$



Common Pressure Units

Name	**Unit**	**P_{atm} =**
Atmosphere	atm	1
Millimetres of Hg	mmHg	760
Torr	Torr	760
Pascal	Pa	101 325
Kilopascal	kPa	101.325
Bar	bar	1.01325
Millibar	mbar	1013.25

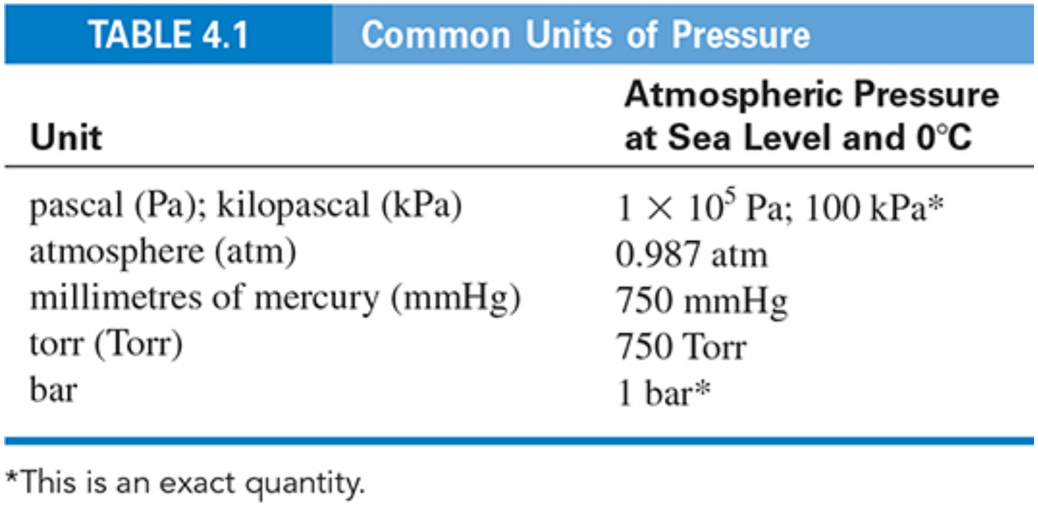


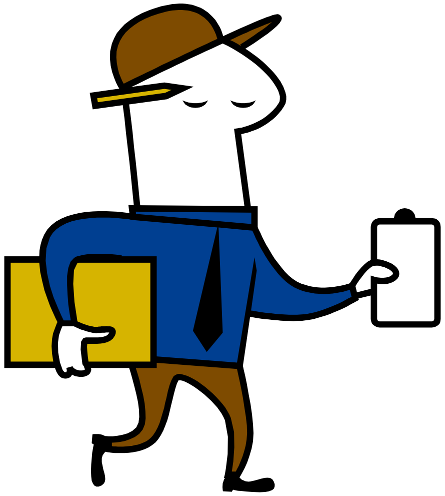
TABLE 4.1 Common Units of Pressure

Unit	**Atmospheric Pressure at Sea Level and 0°C**
pascal (Pa); kilopascal (kPa)	1×10^5 Pa; 100 kPa*
atmosphere (atm)	0.987 atm
millimetres of mercury (mmHg)	750 mmHg
torr (Torr)	750 Torr
bar	1 bar*

*This is an exact quantity.

IDEAL GAS LAW

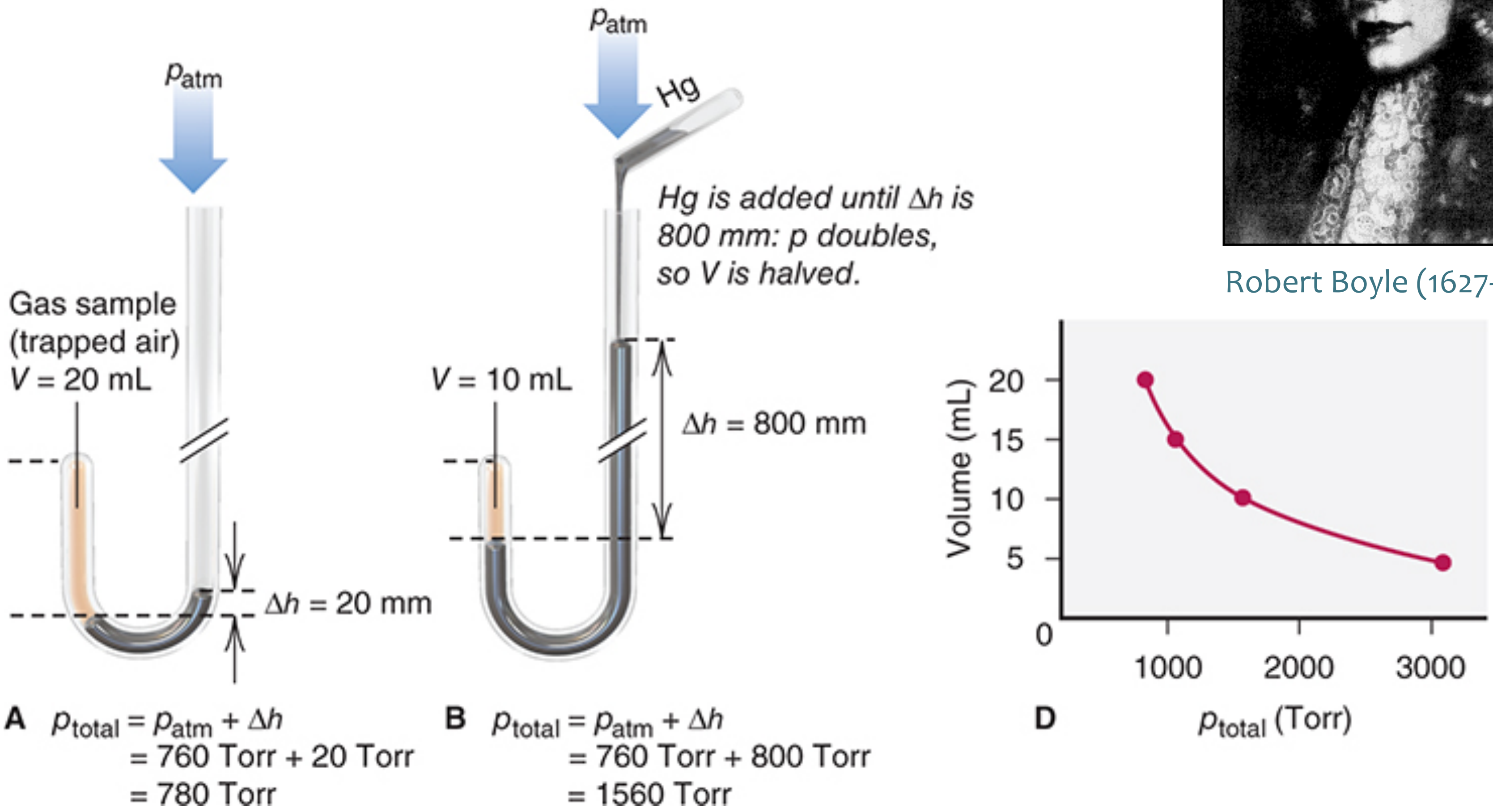
$$PV = nRT$$



- Brings together gas properties.
- Can be derived from experiment and theory.

Boyle’s Law

Robert Boyle (1627-1691)



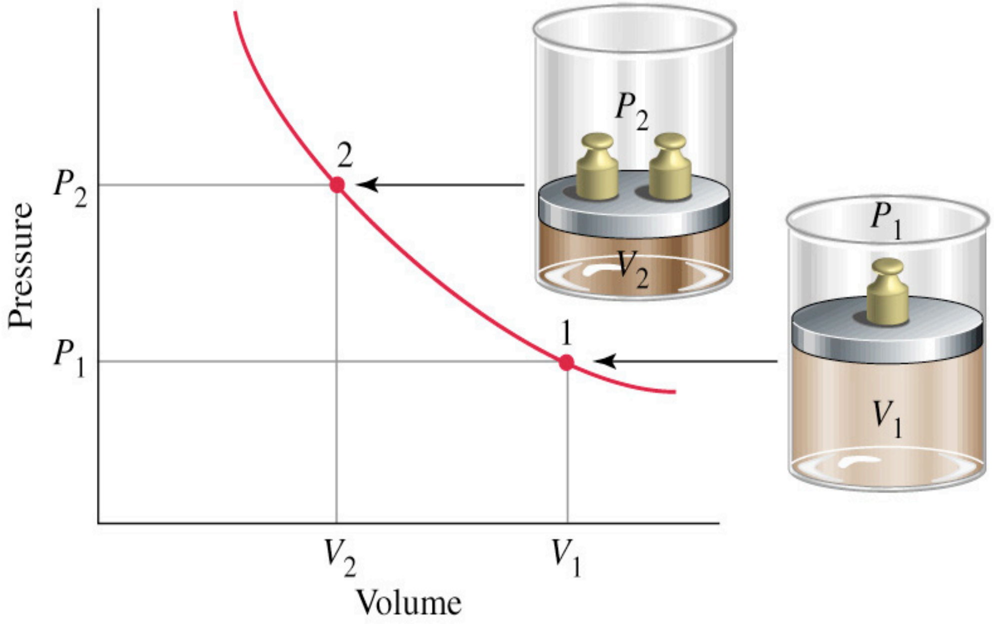
A $p_{total} = p_{atm} + \Delta h$
$= 760$ Torr $+ 20$ Torr
$= 780$ Torr

B $p_{total} = p_{atm} + \Delta h$
$= 760$ Torr $+ 800$ Torr
$= 1560$ Torr

Boyle's Law

At a constant temperature:

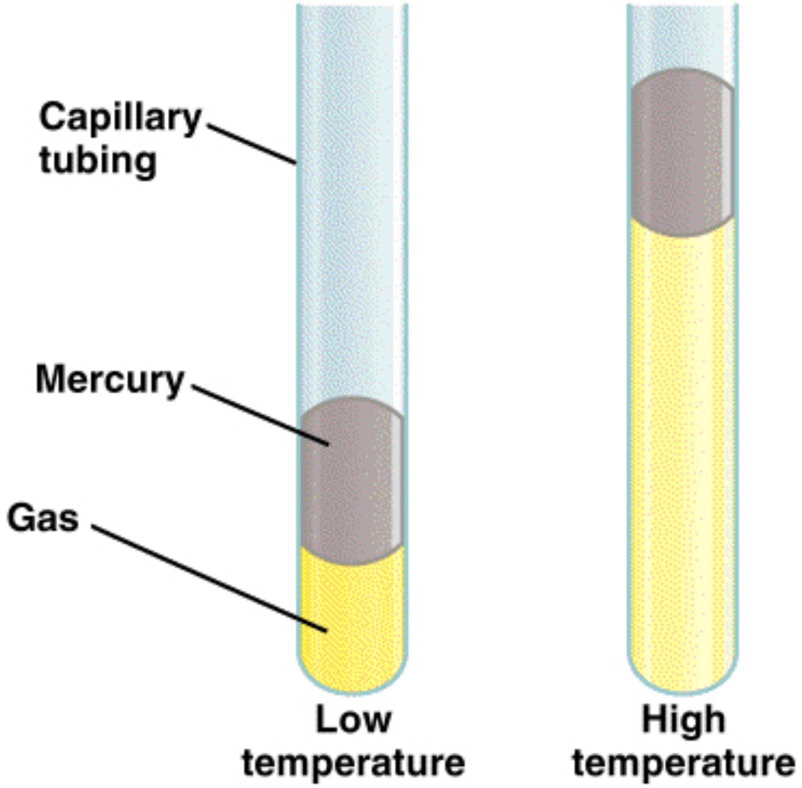
$$\boxed{P \propto \frac{1}{V}}$$ or $$P = \text{constant} \bullet \frac{1}{V}$$



$$PV = \text{constant}$$

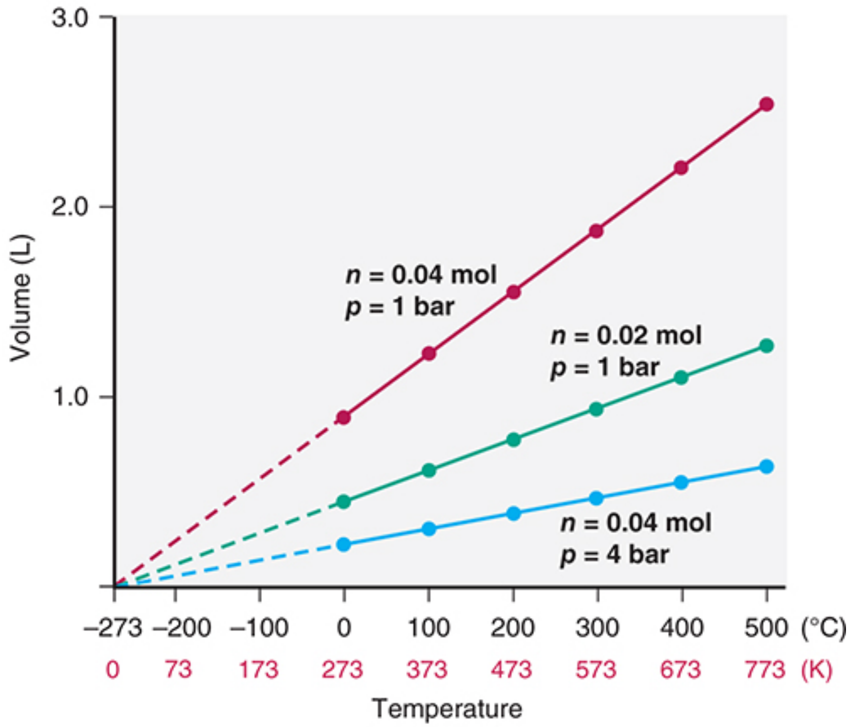
$$P_1V_1 = \text{constant} = P_2V_2$$

Charles's Law



Jacques Charles (1746-1823)

Charles's Law

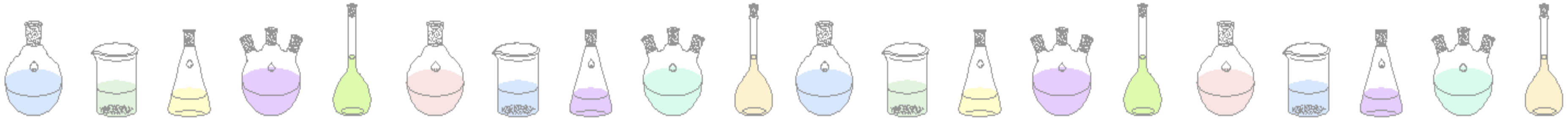


- extrapolation of all lines to V = 0 gives an intercept at

  T = -273.15°C

- Kelvin later proposed that -273.15°C is the lowest temperature attainable, or absolute zero

Temperature Scale: absolute temperature units of Kelvin (K):
T (Kelvin) = 273.15 + T (Celsius)



Charles's Law

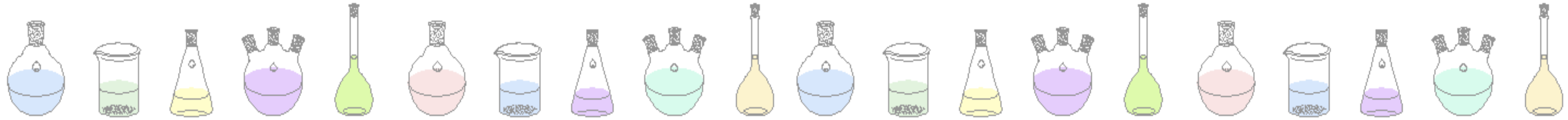
$$\boxed{V \propto T}$$

$$\text{or} \quad V = \text{constant} \bullet T$$

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

$$\frac{V_1}{T_1} = \text{constant} = \frac{V_2}{T_2}$$

NOTE: these formulas only work when temp is in Kelvins!!

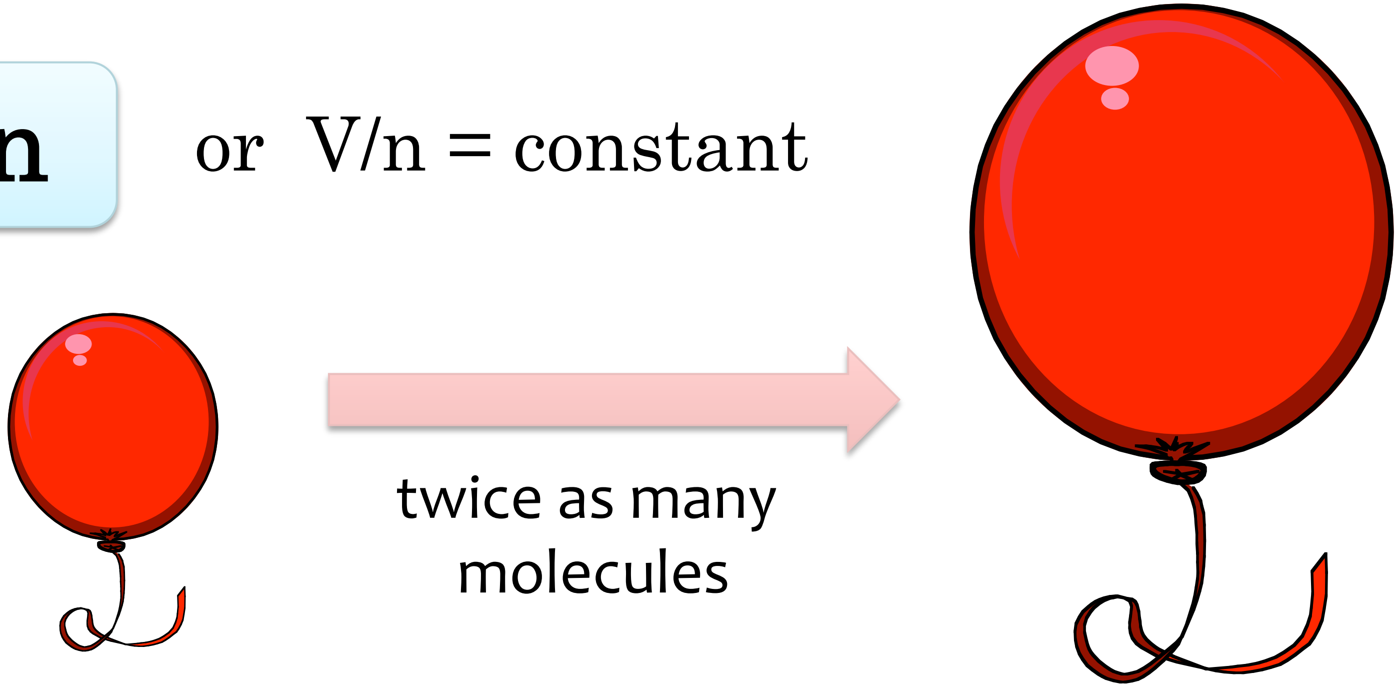


Avogadro's Hypothesis

- Equal volumes of gases at the same T and P have the same number of molecules.

$$\boxed{V \propto n}$$

or $V/n = \text{constant}$



twice as many molecules

The Gas Constant

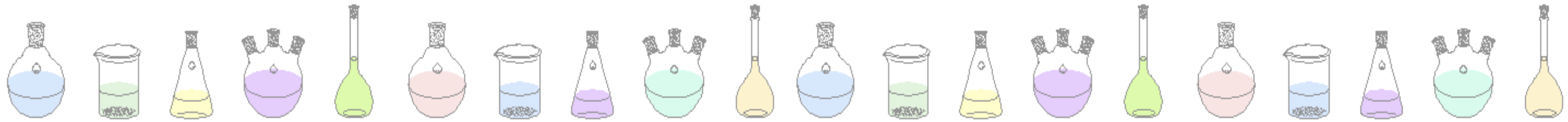
Combining all of these laws leads to:

- Boyle’s law: $V \propto 1/P$
- Charles’s law: $V \propto T$
- Avogadro’s law: $V \propto n$

The proportionality constant, **R** $= 0.08206$ ________________

$= 0.083145$ ______________

$= 8.3145$ ________________

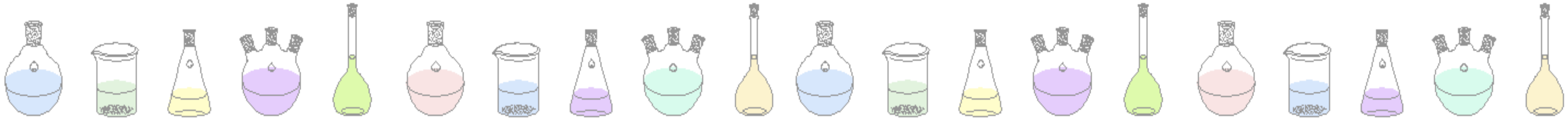


The Ideal Gas Law

- an ideal gas is a gas whose P, V, and T obey the ideal Gas Law

1. no attraction or repulsion between the molecules of an ideal gas
2. the volume occupied by the gas molecules themselves is negligible with respect to the gas container (i.e., the space in the container is empty)

- this approximation of an ideal gas works best at high temperature and low pressure



Standard Temperature and Pressure

- STP: reference point for normal temperature and pressure conditions

$$P = 1\ \text{bar} = 0.987\ \text{atm}$$

$$T = 0^{\text{o}}\text{C} = 273.15\ \text{K}$$

- experiments revealed that, at STP, the space occupied by one mole of gas is:

$$1\ \text{mol gas} = \underline{\hspace{3cm}}\ \text{L}$$

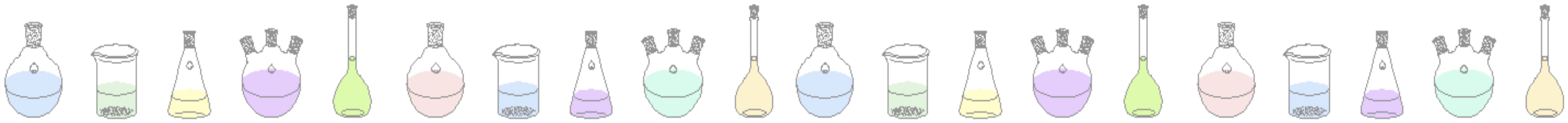
molar volume

Example: Integrative Problem

2008 Exam:

TV news reports often state that “10 000 gallons of air are required to combust each gallon of gasoline”. Suppose the average molecular formula of gasoline is equivalent to *iso*-octane (C_8H_{18}). If the mole fraction of oxygen in air is 0.195, calculate the actual volume of air (at 25.0°C and 1.00 bar) needed for the complete combustion of gasoline.

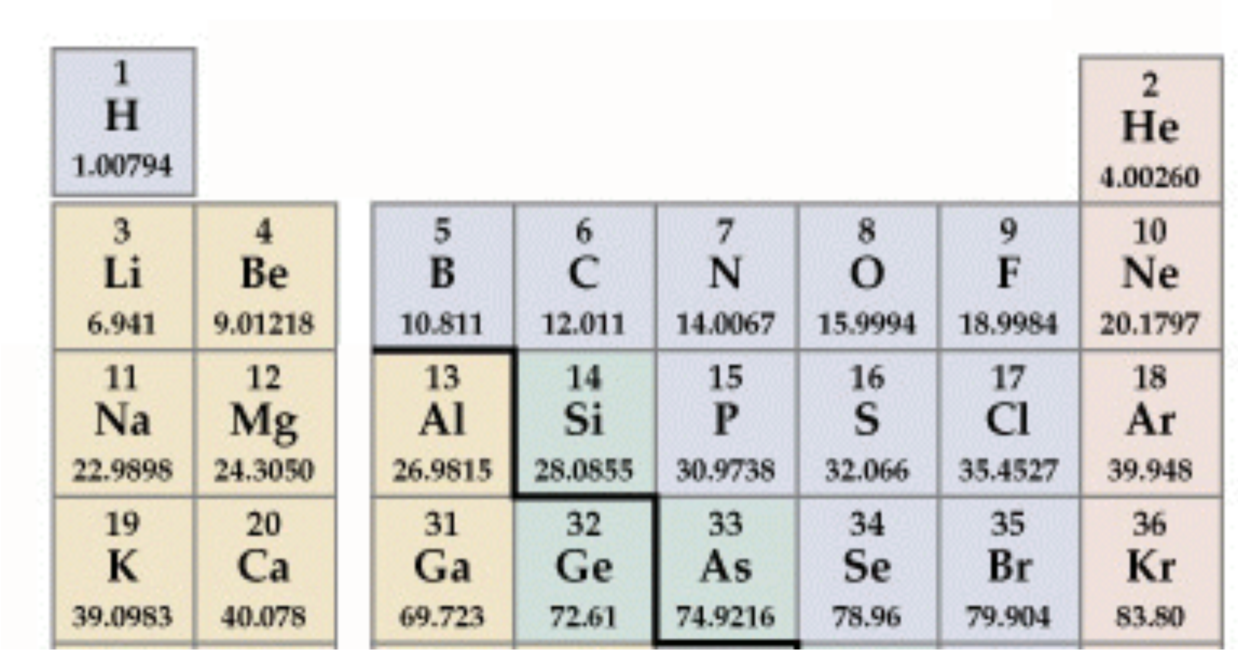
Note: 1 gallon = 3.78 L, density of C_8H_{18} = 0.701 g/mL



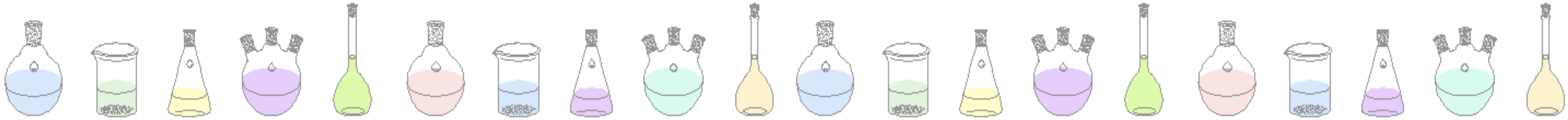
Your Turn…

Without doing detailed calculations, which of the following gases has the greatest density at STP?

A. O_2
B. N_2
C. Kr
D. CH_4
E. I'm not sure



1 H 1.00794							2 He 4.00260
3 Li 6.941	4 Be 9.01218	5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80



Example : Finding the MM of a Gas

A glass vessel weighs 40.1305 g when clean, dry and evacuated; it weighs 138.2410 g when filled with water (d = 0.9970 g/cm^3) and 40.2959 g when filled with propylene gas at 740.3 mm Hg and 24.0°C. What is the molar mass of propylene?

Another form of PV=nRT

- a modified version of the Ideal Gas Law is useful to measure changes in P, V, and T:

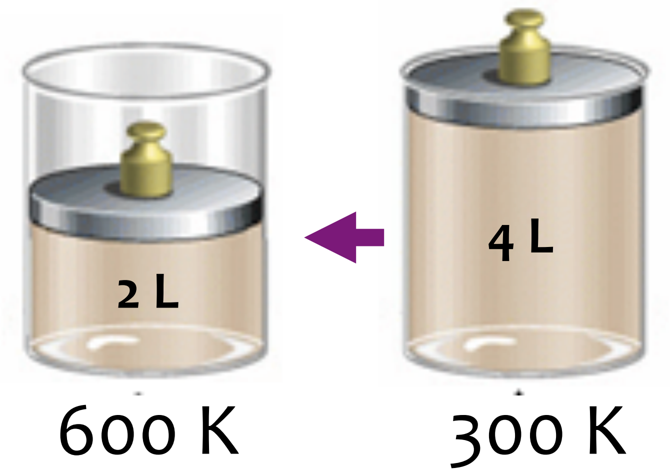
$$\frac{P_1V_1}{n_1T_1} = R = \frac{P_2V_2}{n_2T_2} \quad \therefore \quad \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

- in cases where *the number of moles of gas is constant:*

Your Turn…

You take a 4.0 L volume of gas at 300 K. You compress the gas to a 2.0 L volume and simultaneously heat the vessel to 600 K. The pressure of the gas…

A. Doubles
B. Quadruples
C. Halves
D. Remains the same
E. I'm not sure



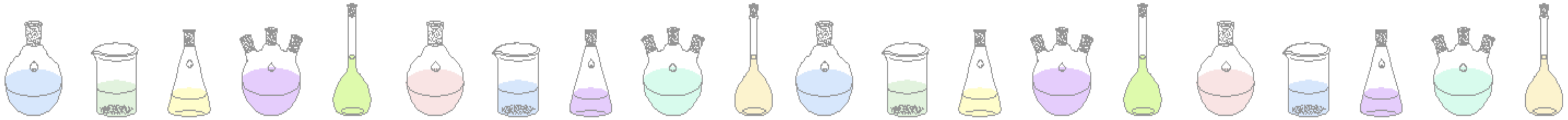
Example : Using the Ideal Gas Law

32.5 g of a gas were placed in an evacuated constant volume container, where T = 22°C and P = 1 atm. The container was heated to 212°C and, in order to maintain constant pressure, some of the gas was allowed to escape. What mass of gas was released from the container?

Example: The Gas Law and Stoichiometry

$$2\ H_2O_2(liq) \rightarrow 2\ H_2O(g)\ +\ O_2(g)$$

1.1 g of H_2O_2 are decomposed in a flask with a volume of 2.50 L. What is the pressure of O2 at 25°C? What is the P of H_2O vapour?



Your Turn…

In the previous example,

$$2\ H_2O_2(liq) \rightarrow 2\ H_2O(g) + O_2(g)$$

What is the pressure of H_2O in the flask?

A. 0.16 atm

B. 0.32 atm

C. 0.48 atm

D. 0.80 atm

E. I'm not sure

Mixtures of Gases and Dalton's Law of Partial Pressures

$$2\ H_2O_2(liq) \rightarrow 2\ H_2O(g) + O_2(g)$$

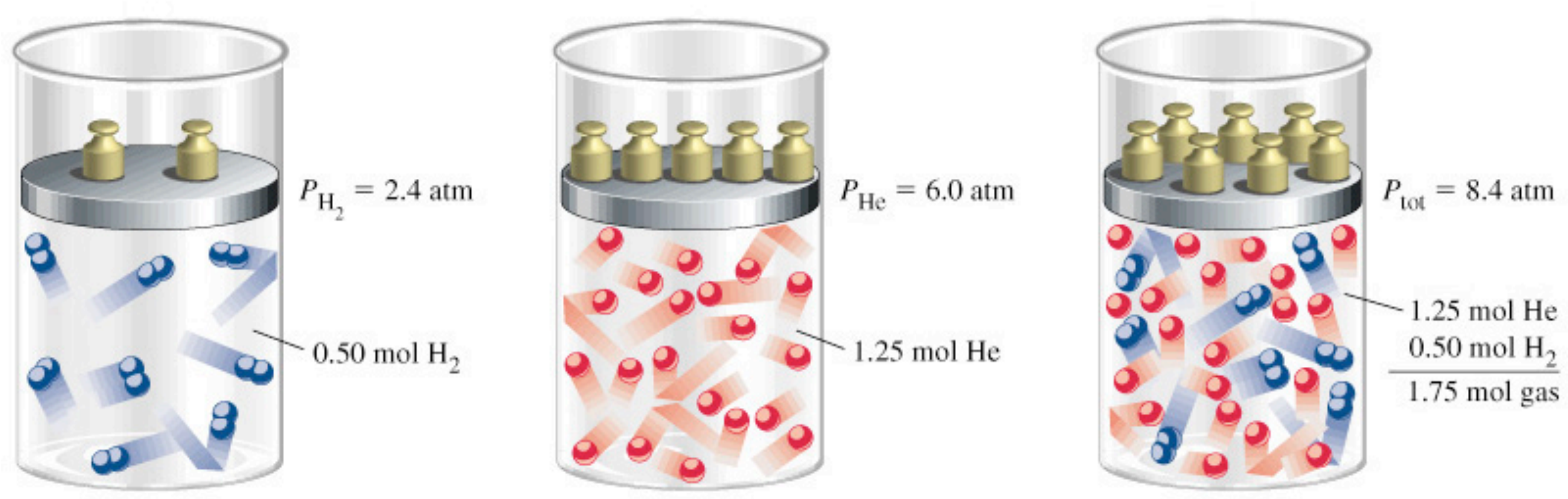
What is the total pressure in the flask?

$$P_{total} \text{ in gas mixture} = P_A + P_B + \ldots$$

Therefore, P_{total} =

Dalton's Law: total P is sum of PARTIAL pressures.

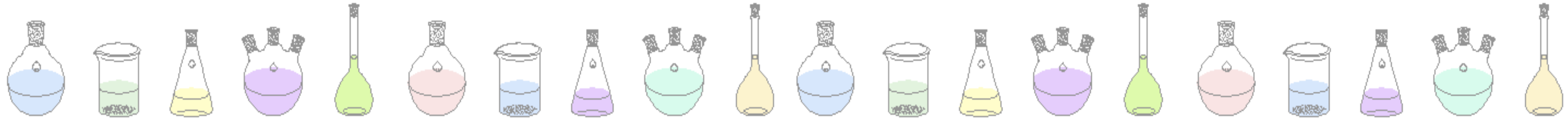
Daltons Law of Partial Pressure



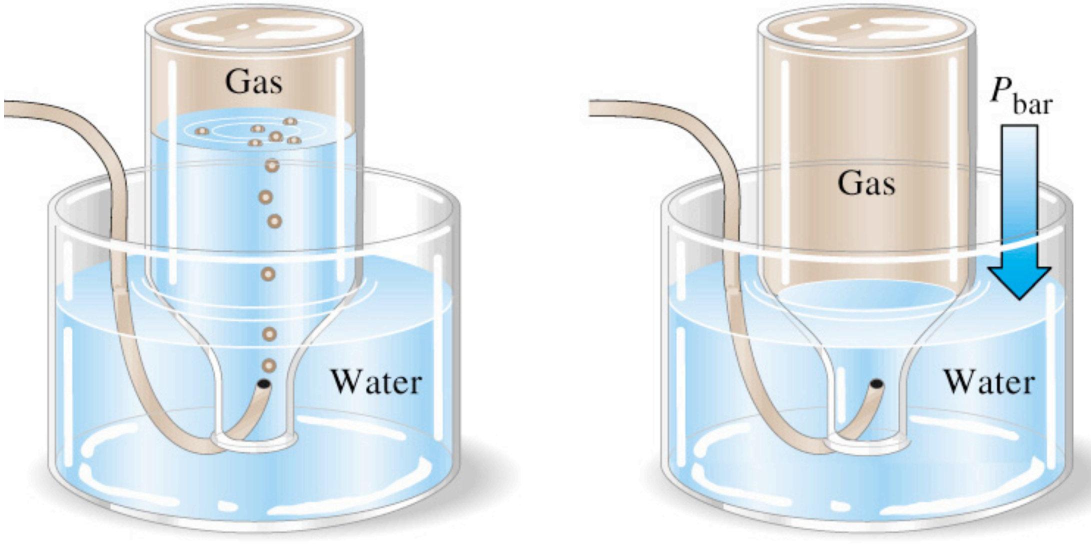
(a) 5.0 L at 20 °C **(b)** 5.0 L at 20 °C **(c)** 5.0 L at 20 °C

- the partial pressure of of each gas in the mixture (c) are:
- the total pressure, P_T, of this mixture is:

$$P_{He} = \frac{n_{He}RT}{V} \qquad P_{H_2} = \frac{n_{H_2}RT}{V} \qquad P_T$$



Partial Pressure Pneumatic Trough



$$P_{tot} = P_{bar} = P_{gas} + P_{H_2O}$$

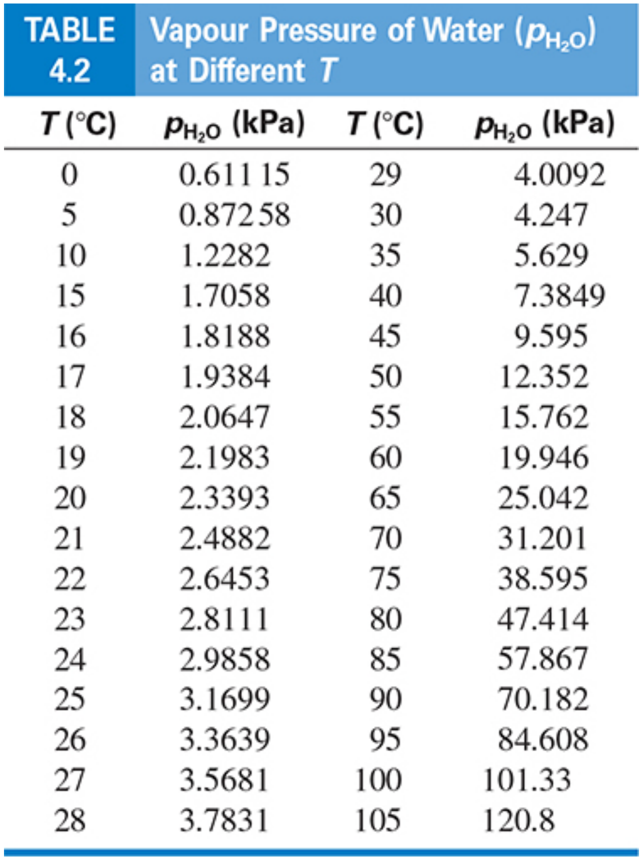


TABLE 4.2 Vapour Pressure of Water (p_{H_2O}) at Different T

T (°C)	p_{H_2O} (kPa)	T (°C)	p_{H_2O} (kPa)
0	0.611 15	29	4.0092
5	0.872 58	30	4.247
10	1.2282	35	5.629
15	1.7058	40	7.3849
16	1.8188	45	9.595
17	1.9384	50	12.352
18	2.0647	55	15.762
19	2.1983	60	19.946
20	2.3393	65	25.042
21	2.4882	70	31.201
22	2.6453	75	38.595
23	2.8111	80	47.414
24	2.9858	85	57.867
25	3.1699	90	70.182
26	3.3639	95	84.608
27	3.5681	100	101.33
28	3.7831	105	120.8

Dalton’s Law of Partial Pressures

- the partial pressure of a gas A, P_A, in a gaseous mixture is:

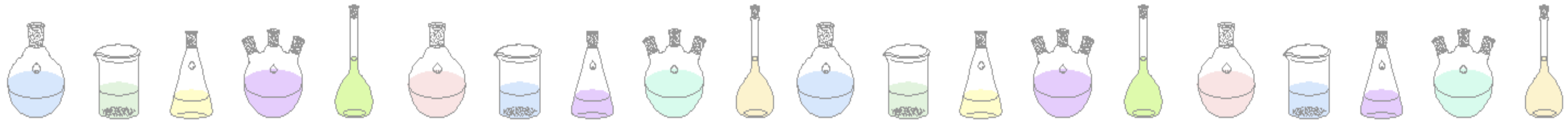
$$P_A = \frac{n_A RT}{V}$$

- the law of partial pressures says that the total pressure of the mixture, P_T, is given by:

$$P_T = P_A + P_B + P_C + \ldots$$

$$P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V} + \ldots$$

$$P_T = (n_A + n_B + n_C + \ldots)\frac{RT}{V} = n_T \frac{RT}{V}$$



Molar Fractions

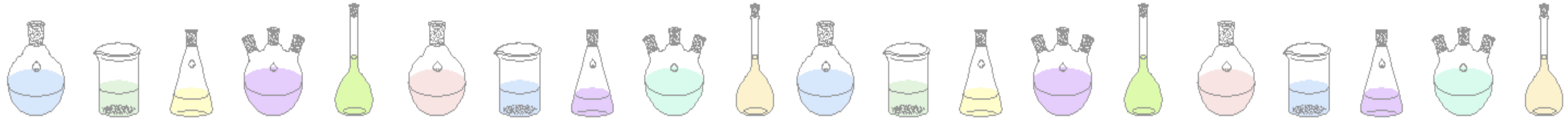
- the molar fraction of gas A in a mixture, X_A, is:

$$X_A = \frac{n_A}{n_T} = \frac{n_A}{n_A + n_B + n_C + \ldots}$$

- therefore, according to the law of partial pressures:

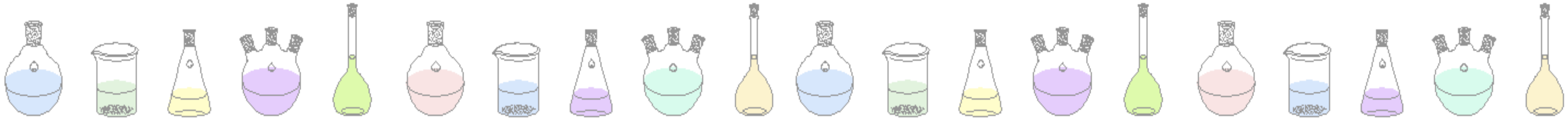
$$\frac{P_A}{P_T} = \left. \frac{n_A RT}{V} \middle/ \frac{n_T RT}{V} \right. = \frac{n_A}{n_T} = X_A$$

$$\boxed{P_A = X_A P_T}$$



Example: PP of a gas in a mixture

A sample of natural gas contains 8.24 mol of CH_4, 0.421 mol of C_2H_6 and 0.116 mol of C_3H_8. If the total pressure is 1.37 atm, what is the partial pressure of each gas?

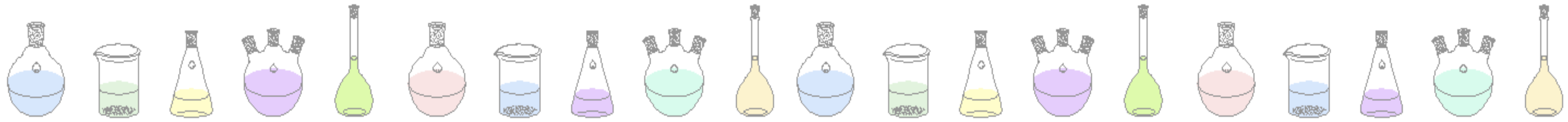


KINETIC MOLECULAR THEORY (KMT)

- the ideal gas law was derived empirically – it was not understood ***why*** PV = nRT
- Maxwell and Boltzmann tried to explain the physical properties of gases using the movement of individual gas molecules
- in an ideal gas, there are no attractions or repulsions between the gas molecules, therefore the energy of the gas must entirely come from the kinetic energy of the individual gas molecules
- the kinetic energy of a molecule depends only its **mass** and its **velocity**

The Assumptions of the Model:

1. the volume occupied by the molecules is negligible
2. gaseous molecules are in constant, random, straight-line motion in all directions; they collide fleetingly and frequently with each other and the walls of the container
3. there are no attractive or repulsive forces between molecules; all collisions are perfectly elastic; thus the average kinetic energy is constant

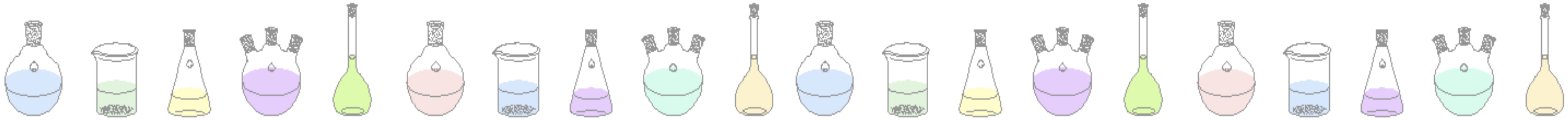


Kinetic Energy of Gas Molecules

- the *average kinetic energy* of the molecules of a gas is given by

$$E_K = \frac{1}{2} m \overline{u^2}$$

- where $\overline{u^2}$ is the mean-square speed: $\overline{u^2} = \dfrac{u_1^2 + u_2^2 + \ldots + u_N^2}{N}$



More Equations…

Using Boyle’s Law, we can derive the following expression:

$$PV = \frac{1}{3}N_A m\overline{u^2} = \frac{2}{3}N_A\left(\frac{1}{2}m\overline{u^2}\right)$$

BUT! PV=RT so: $$RT = \frac{2}{3}N_A \cdot \overline{E_K}$$

Solve for $\overline{E_K}$: $$\overline{E_K} = \frac{3}{2}\cdot\left(\frac{R}{N_A}\right)\cdot T$$

So, here’s the point:

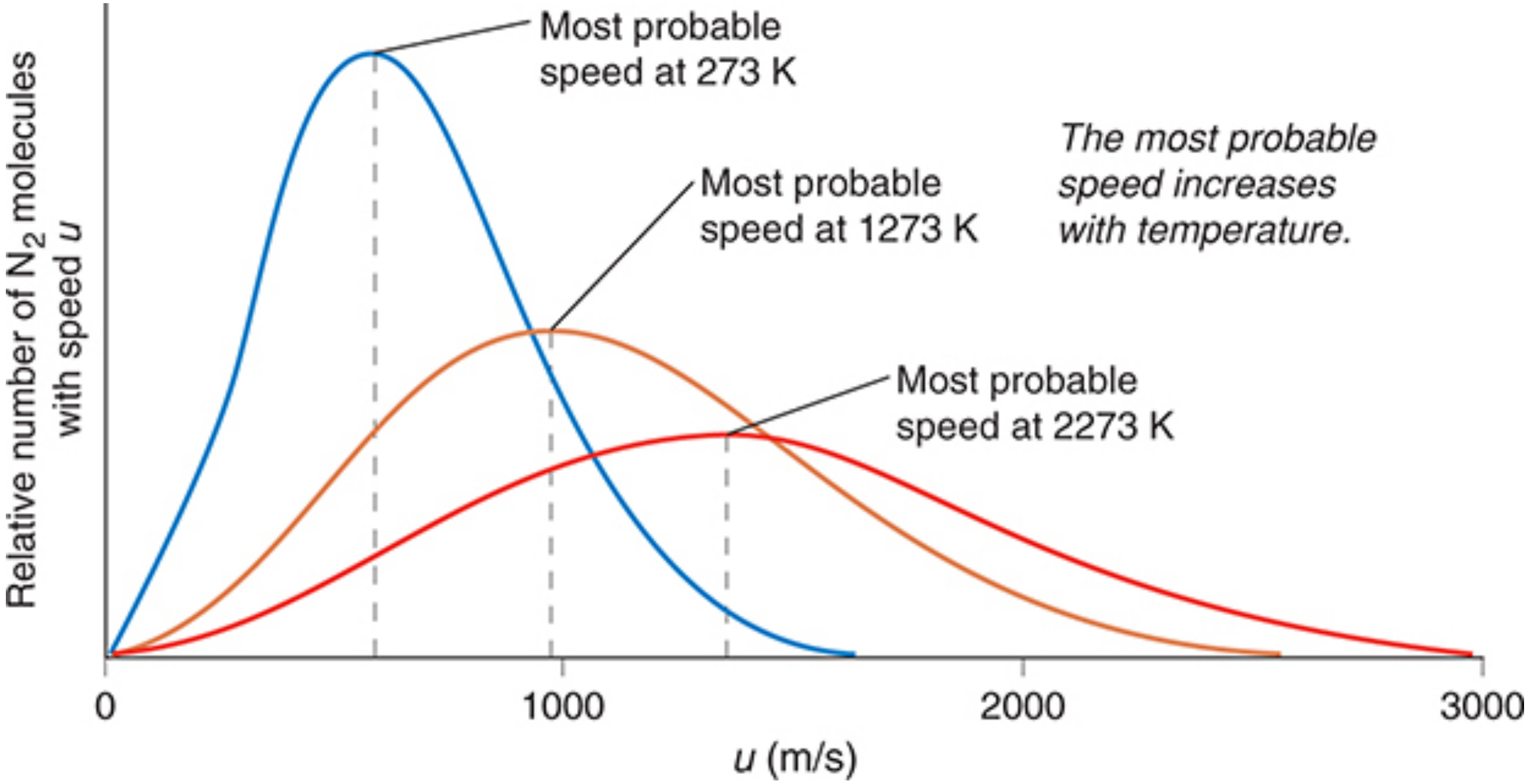
$$\overline{E_K} = \frac{3}{2}\cdot\left(\frac{R}{N_A}\right)\cdot T$$

$$\overline{E_K} = \frac{1}{2}m\overline{u^2}$$

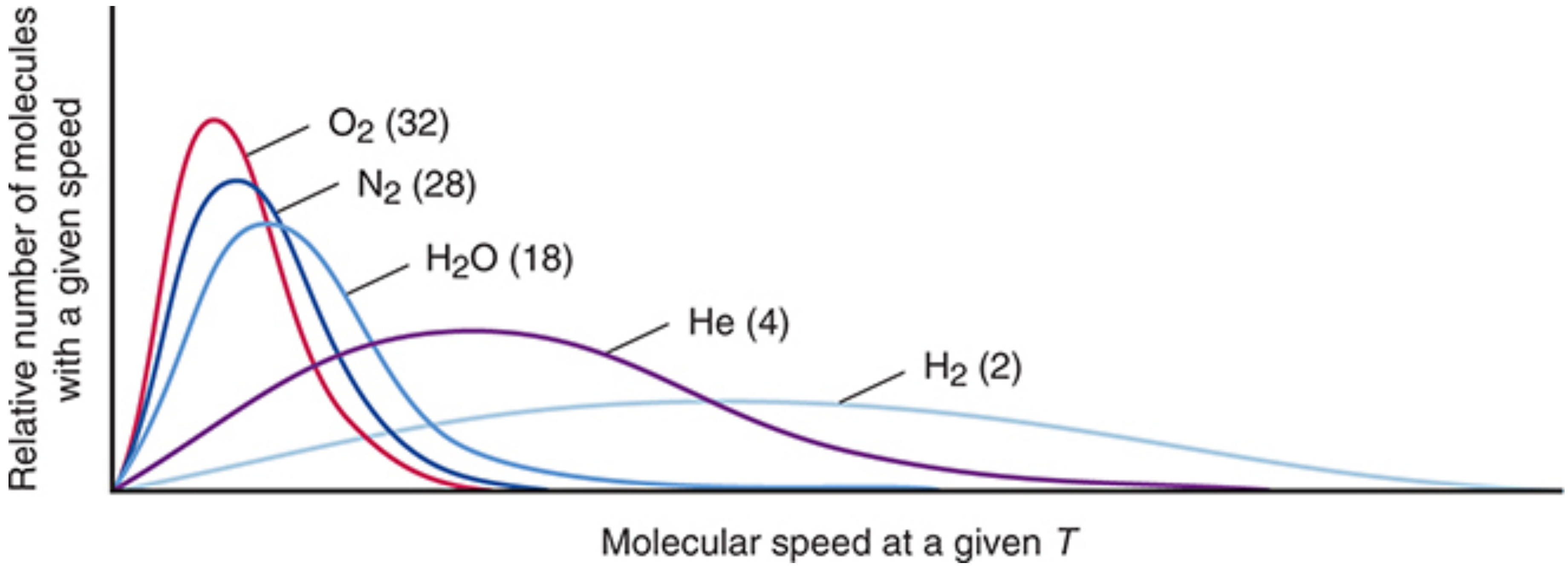
At constant m:

At constant T:

Effect of Temperature



Effect of Mass



Root-mean-square speed, u_{rms}

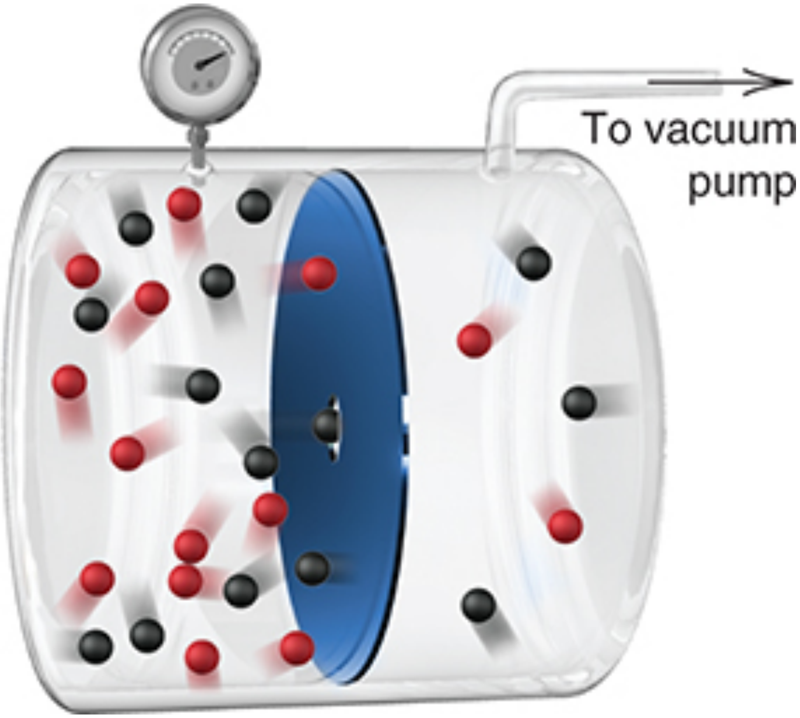
$$u_{rms} = \sqrt{\frac{3RT}{MM}}$$

- the ***root-mean-square speed, u_{rms},*** increases when T increase or MM decreases
- usually, u_{rms} is in m/s (i.e., SI), so MM must be in kg/mol (SI) and R is 8.3145 Pa m³/mol • K (SI)

GAS DIFFUSION AND EFFUSION

An application of KMT:

- *diffusion* is the gradual mixing of molecules of different gases.
- *effusion* is the movement of molecules through a small hole into an empty container.



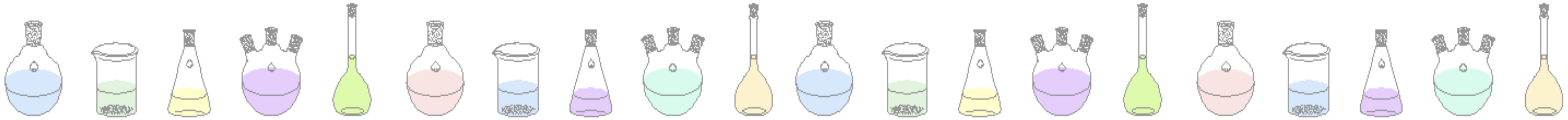
GAS EFFUSION

Thomas Graham, 1805-1869

Graham's Law governs effusion of gas molecules:

$$\frac{\text{effusion of A}}{\text{effusion of B}} = \frac{(u_{rms})_A}{(u_{rms})_B} = \frac{\sqrt{\dfrac{3RT}{MM_A}}}{\sqrt{\dfrac{3RT}{MM_B}}} = \sqrt{\frac{MM_B}{MM_A}}$$

Rate of effusion is inversely proportional to species molar mass.



Your Turn…

The normal economical cruising speed of a Boeing 767 is 854 km h^{-1} (237 m s^{-1}). Xe (131.29 g mol^{-1}) has about the same root mean square speed at 298 K. Which of the following would beat the Boeing 767 in a race?

A. Cl_2

B. Kr

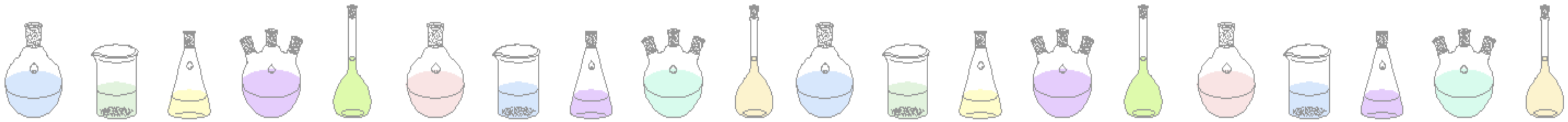
C. Br_2

D. Cl_2 and Kr

E. All of them

F. I'm not sure

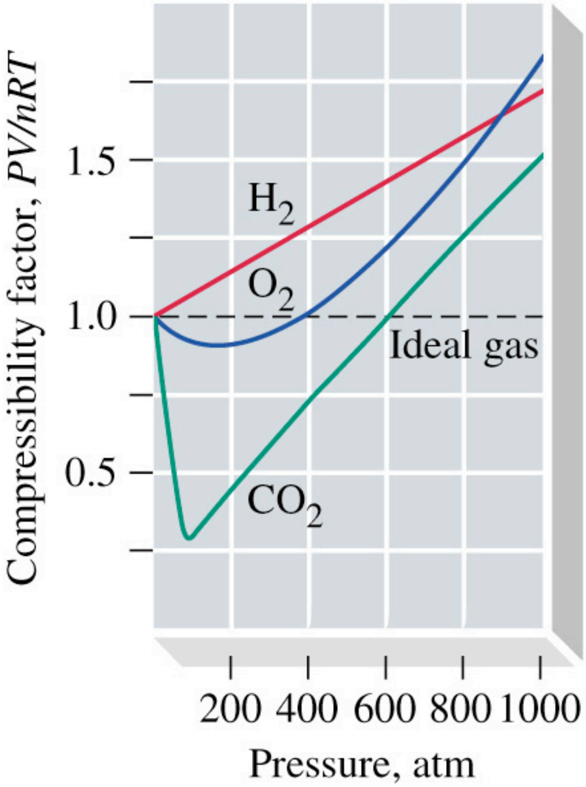
17	35	36
Cl	**Br**	**Kr**
35.4527	79.904	83.80



Deviations from the Ideal Gas Law

- real gases don't always obey the Gas Law
  - the volume of the molecules is not zero!
  - there are intermolecular forces between the gas molecules!

- the Ideal Gas Law begins to give erroneous results when P > 5-10 atm or when T approaches the condensation temperature of the gas



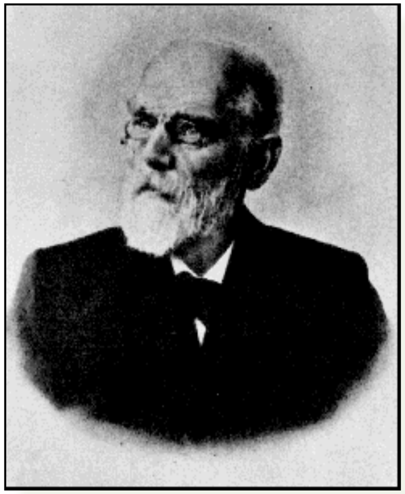
Deviations from Ideal Gas Law

We account for volume of molecules and intermolecular forces with VAN DER WAAL'S EQUATION:

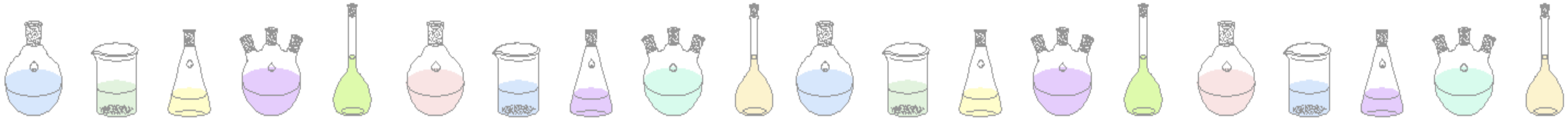
$$\left(P + \frac{n^2a}{V}\right)(V - nb) = RT$$

correction for intermolecular forces

correction for volume

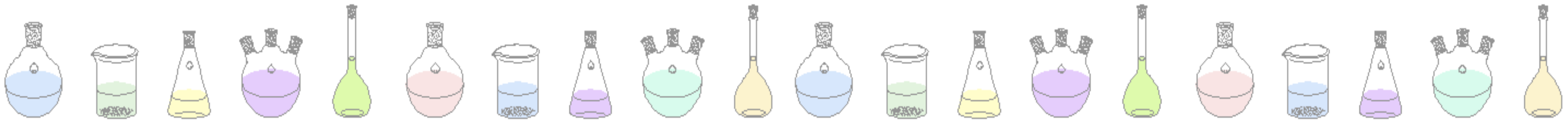


J. van der Waals, 1837-1923



Chapter 4: Key Concepts

1. gas pressure: units and measurement
2. the Gas Laws (Boyle, Charles, and Avogadro)
3. the Ideal Gas Law
4. Dalton's Law of Partial Pressures
5. Kinetic Theory of Gases
6. Graham's Law
7. van der Waal's Equation



Chapter 4: Suggested Problems

4.5, 4.8, 4.10, 4.12, 4.19, 4.22,
4.30, 4.33, 4.41, 4.45, 4.49, 4.51,
4.55, 4.57, 4.58, 4.65, 4.68, 4.69,
4.71, 4.73, 4.78, 4.80, 4.83, 4.90,
4.98, 4.104, 4.106, 4.114, 4.121,
4.124, 4.132, 4.139, 4.150