The Gaseous State of Matter

Preparation for College Chemistry
Columbia University
Department of Chemistry

Chapter Outline

- ***KMT***
- ***Gas Laws***
- ***Ideal Gas Equation***
- ***Gas Stoichiometry***
- ***Air Pollution***

Preliminary Observations

Molar mass of water: 18g /mole

6.02×10^{23} molecules weigh 18g

Density of water: 1g/cc

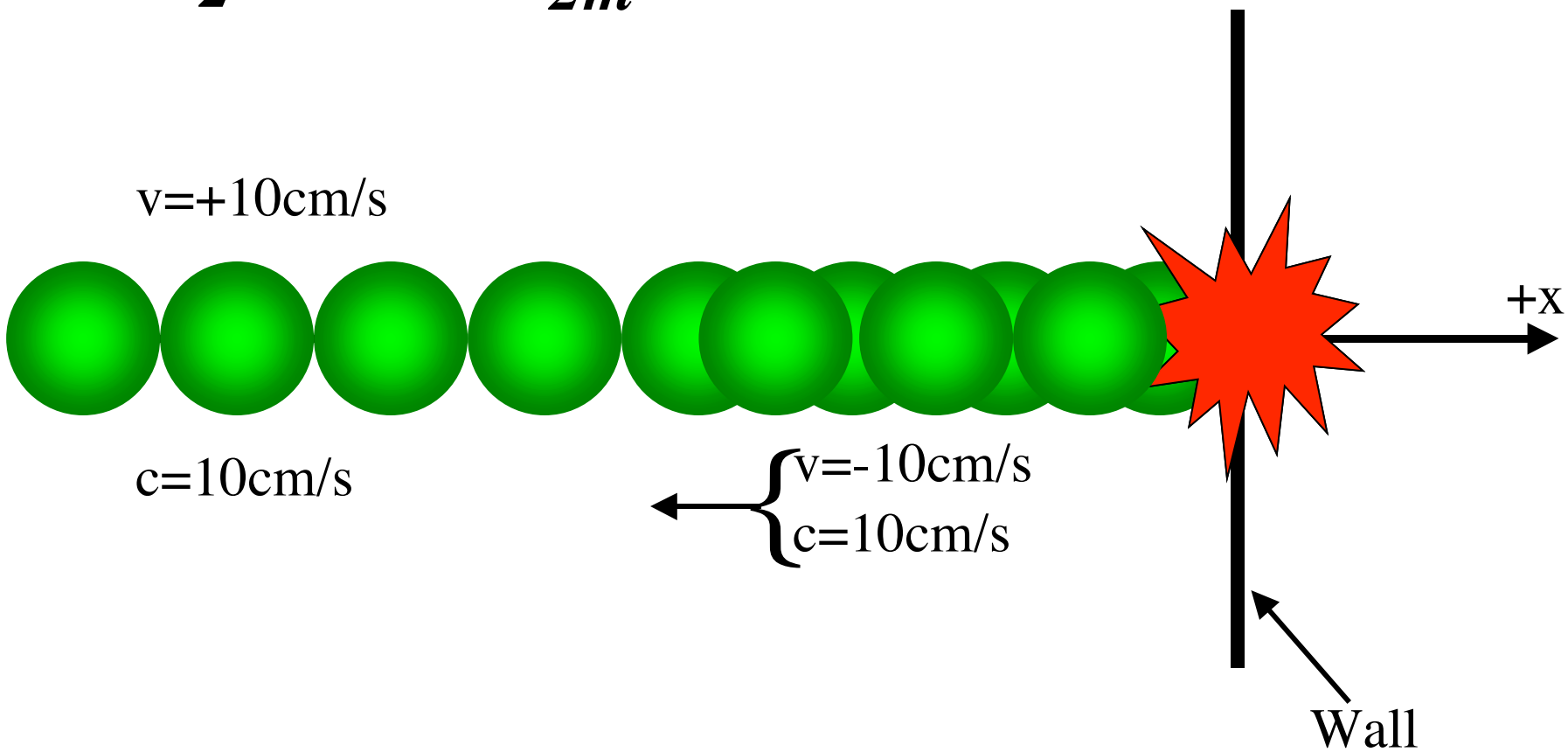
18 g liquid water occupies 18mL

18 g gaseous water occupies 22,400mL

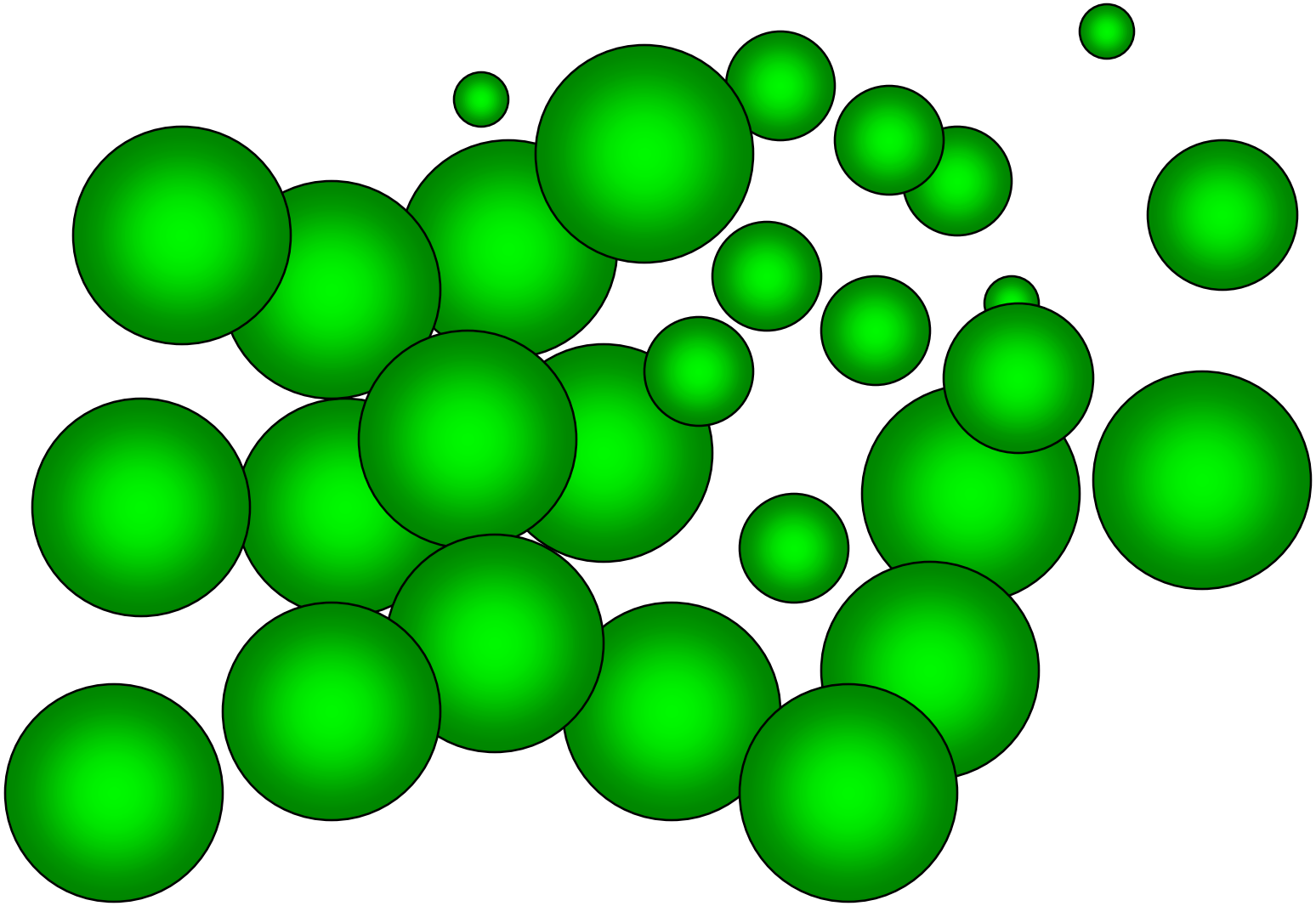
Kinetic Molecular Theory of Gases

$$KE = \frac{1}{2} m c^2 = \frac{p^2}{2m} \qquad p = m c$$

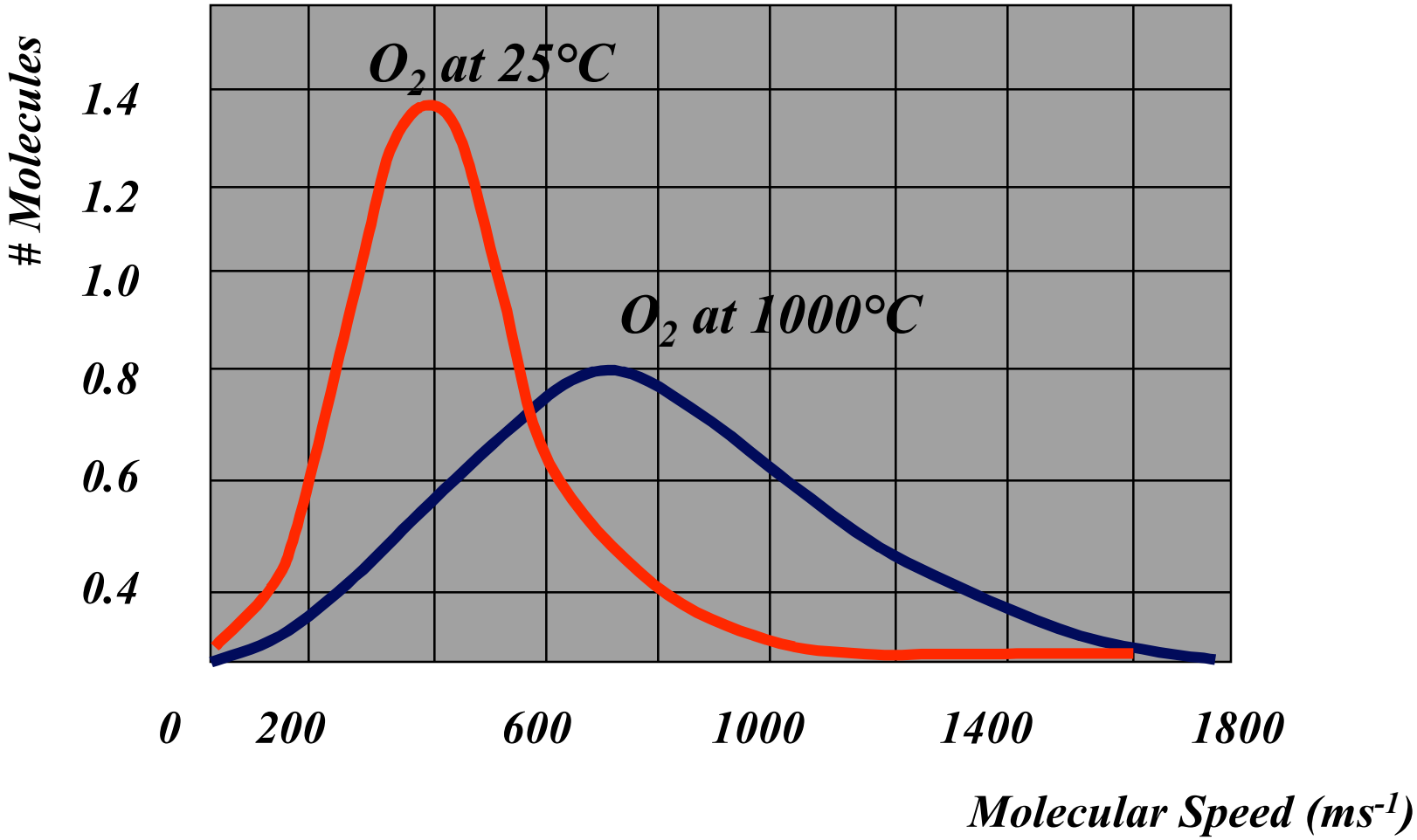
$$\frac{1}{2} mc^2 = \frac{3}{2} kT$$



Kinetic Molecular Theory of Gases



Distribution of Molecular Speeds
Maxwell-Boltzmann Distribution



Graham's Law of Effusion

At the same T and P, the rates of Effusion of two gases are inversely proportional to their densities or molar masses.

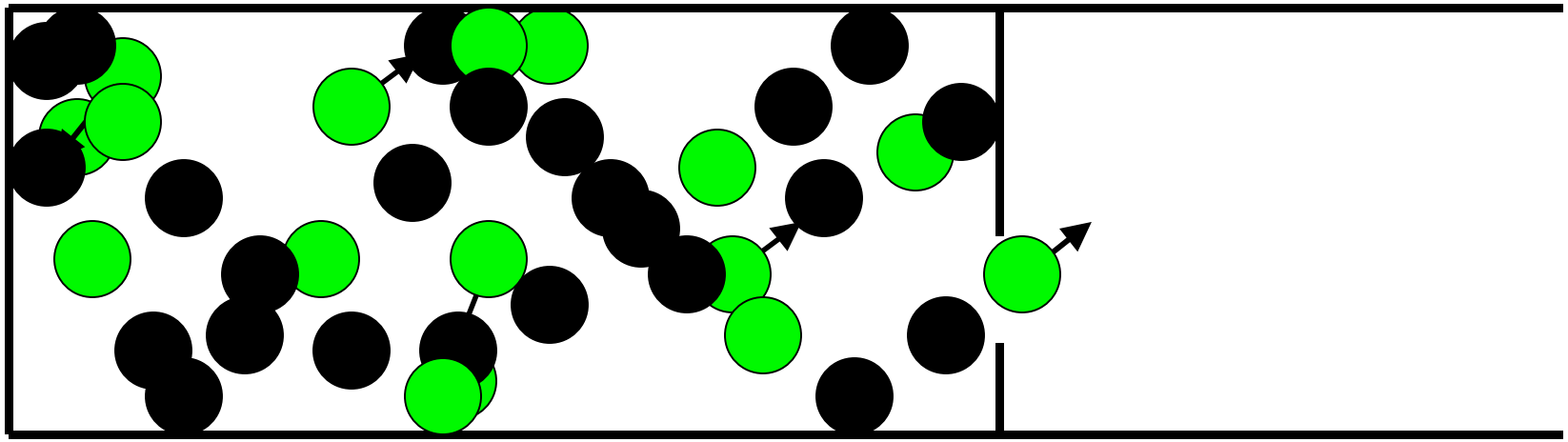
$$\frac{\mathbf{R}ate_{gasA}}{\mathbf{R}ate_{gasB}} = \sqrt{\frac{d_B}{d_A}} = \sqrt{\frac{M_B}{M_A}}$$

Naturally occurring Uranium : U-235 / U238 = 1 / 140

1st step: U + 6 F $\longrightarrow$ $\left({}^{235}UF_6 \diagdown {}^{238}UF_6 \right)_{(g)}$

$$\frac{R_{235\,UF_6}}{R_{238\,UF_6}} = \sqrt{\frac{m_{238\,UF_6}}{m_{235\,UF_6}}} = \sqrt{\frac{352}{349}} = 1.0043$$

2nd step: Diffusion through thousands of membranes (cascades)



Gas **Vacuum**

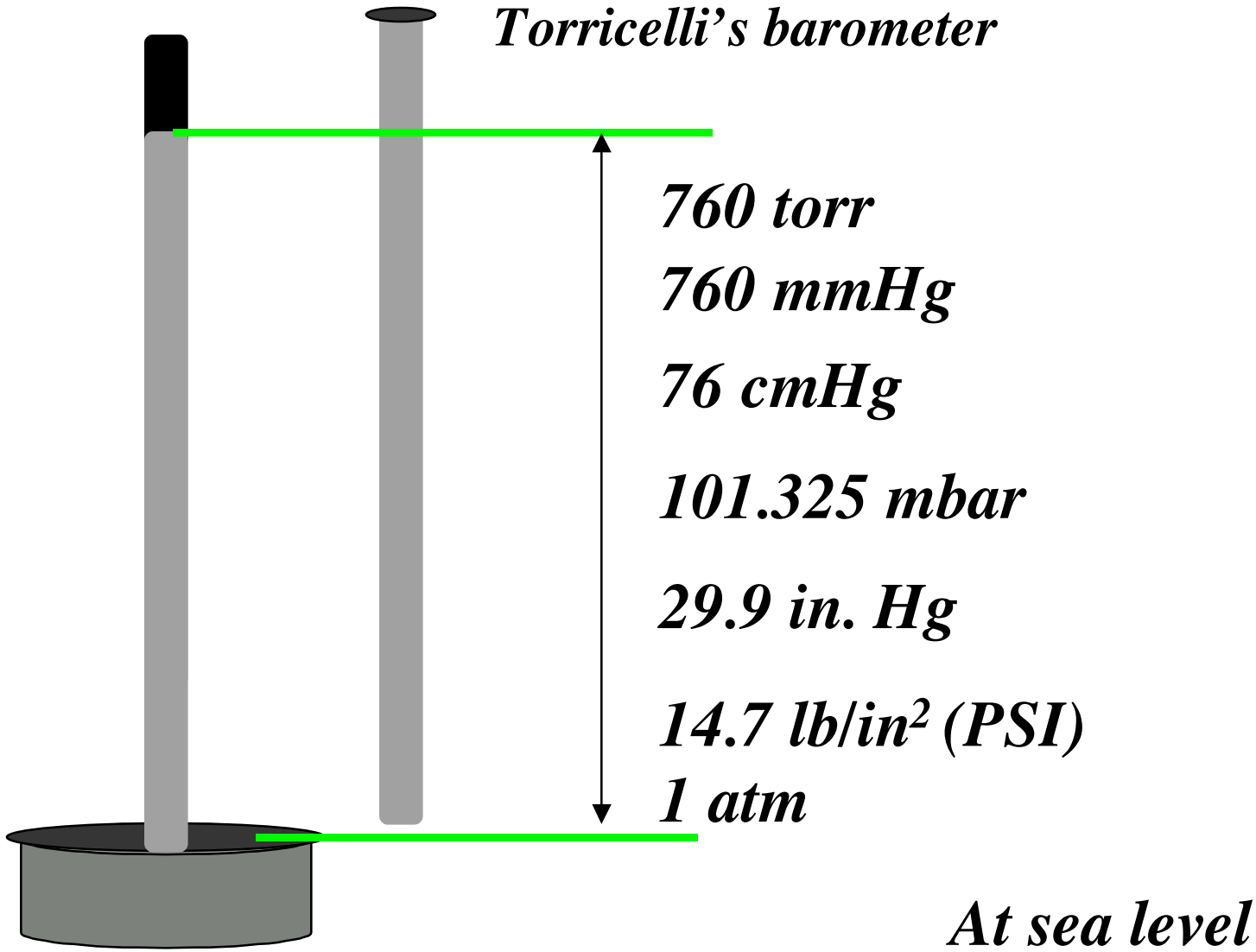
3rd step: ${}^{235}UF_6 \longrightarrow {}^{235}U$ Fully enriched weapons-grade Uranium

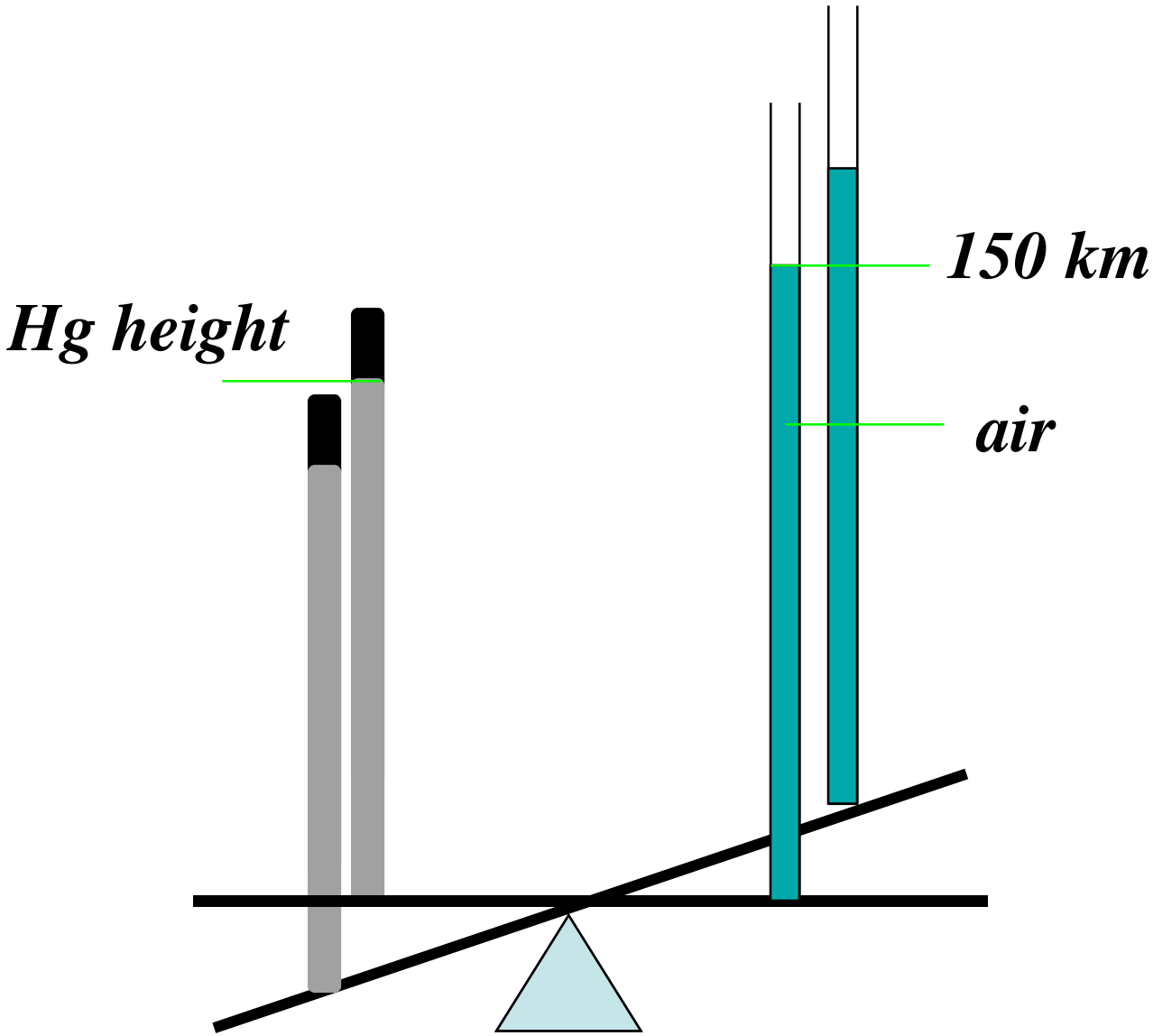
State Variables

V = volume (liters, cm^3, m^3)

T = temperature (in K)

P = pressure (atmospheres, mmHg, kPa)

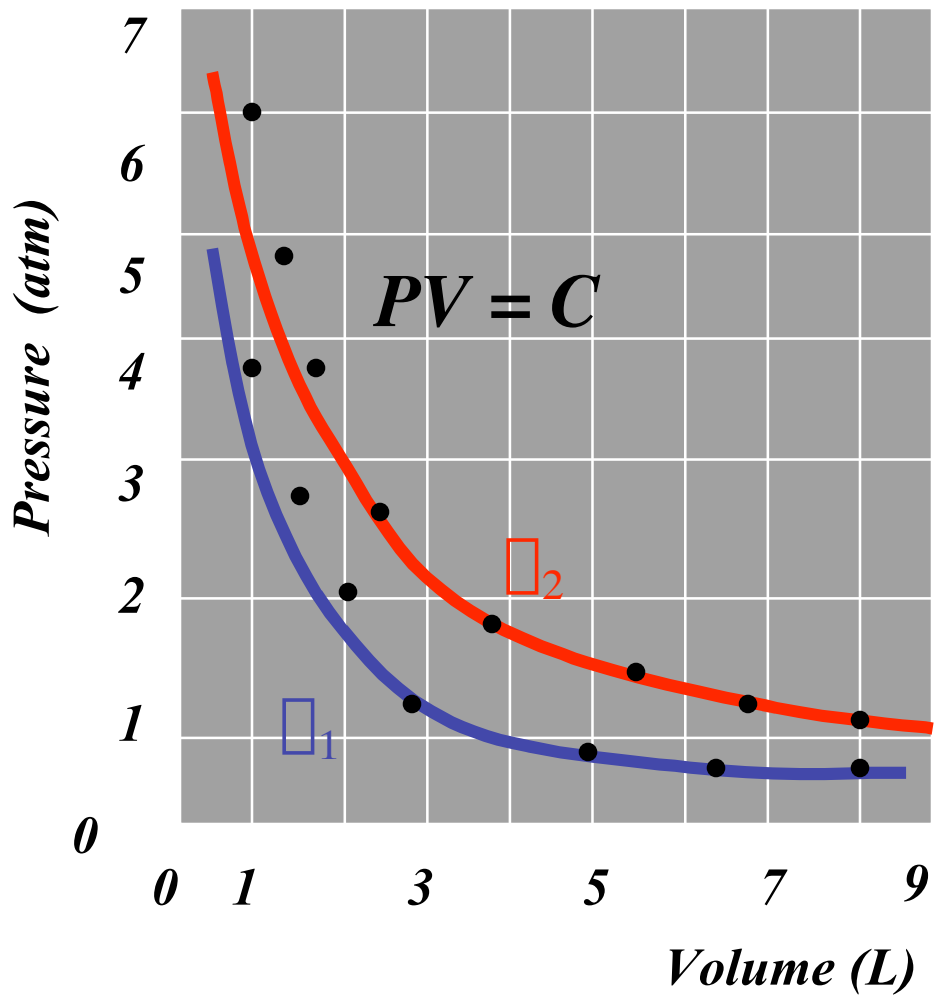

Torricelli's barometer
760 torr
760 mmHg
76 cmHg
101.325 mbar
29.9 in. Hg
14.7 lb/in2 (PSI)
1 atm
At sea level



Atmospheric Pressure

Boyle's Law

At Constant T
For an Ideal Gas



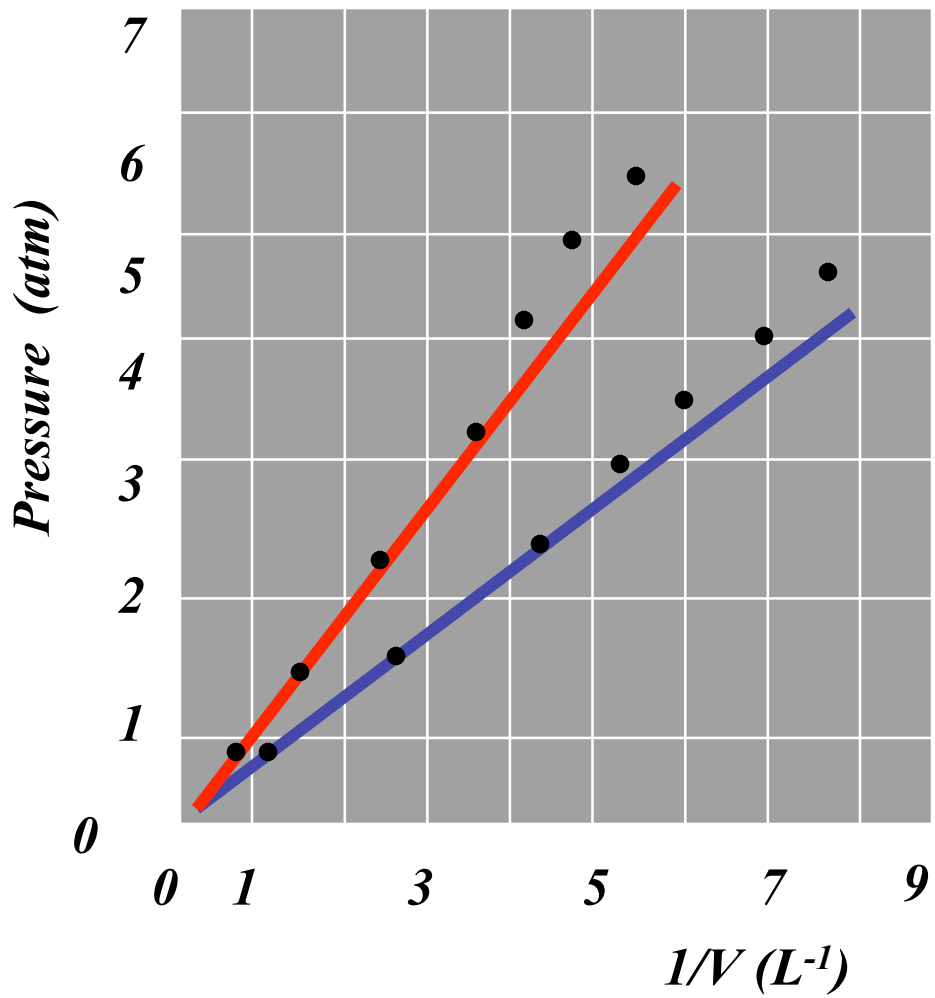
$$P_1 V_1 = P_2 V_2$$

$$\frac{P_1}{V_2} = \frac{P_2}{V_1}$$

$T_2 > T_1$

Boyle's Law

At Constant T
For an Ideal Gas

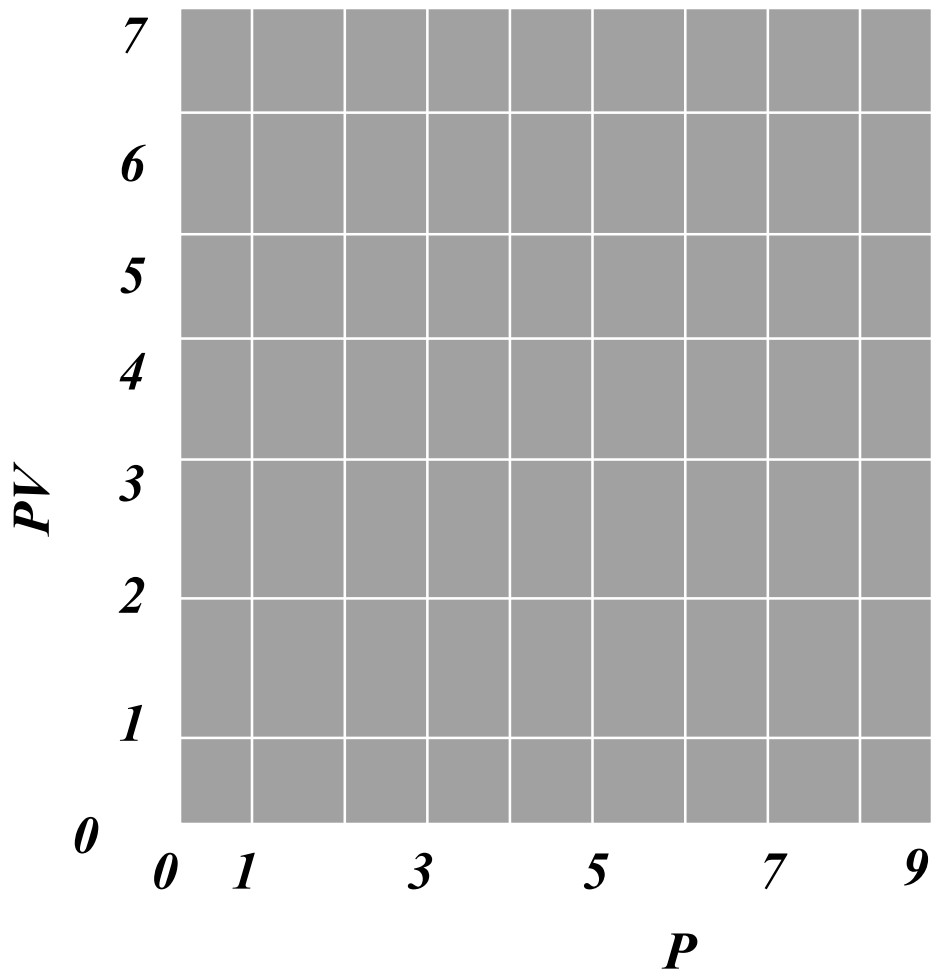


$$P = C\left(\frac{1}{V}\right)$$

$T_2 > T_1$

Boyle's Law

At Constant T
For an Ideal Gas

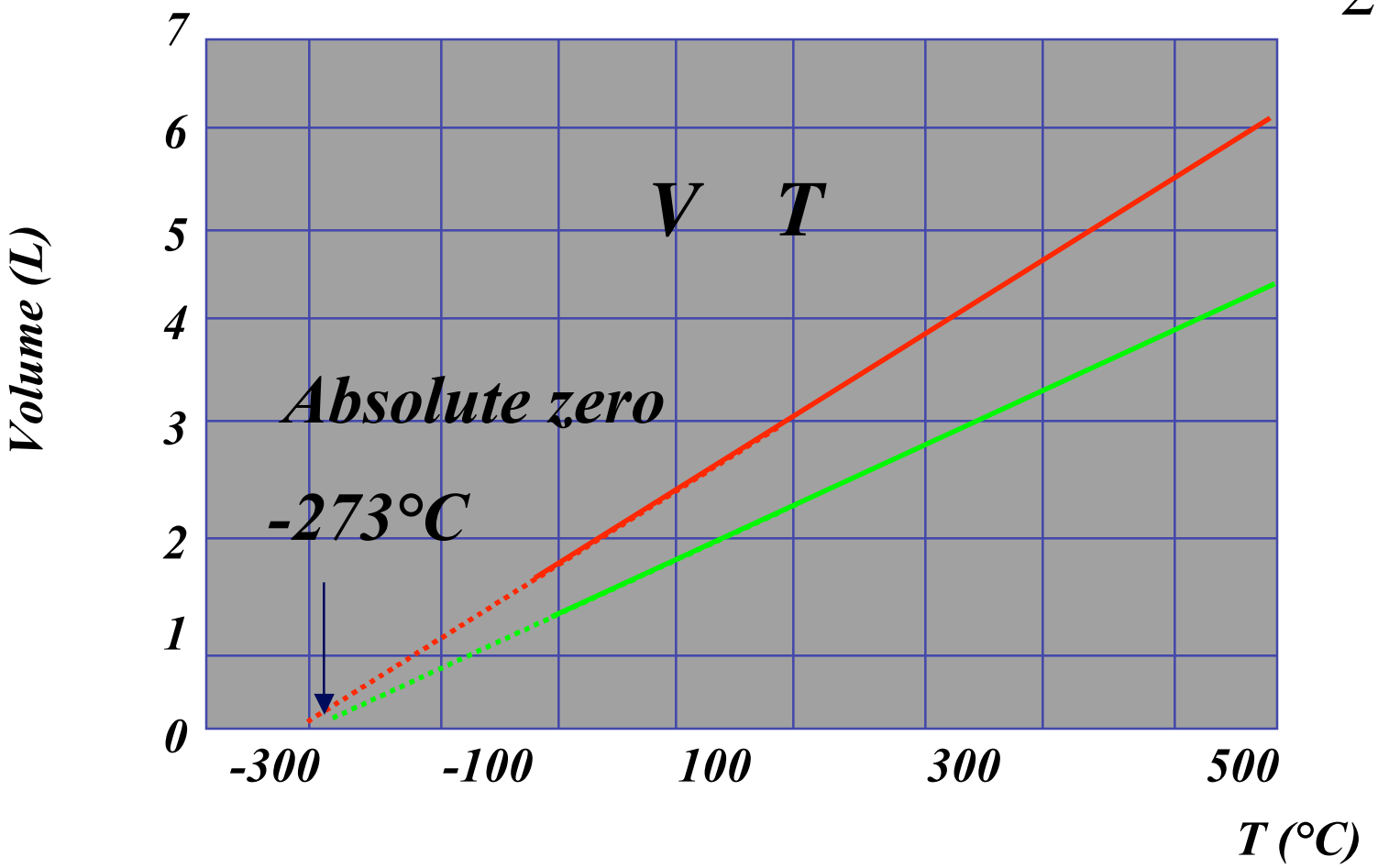


$T_2 > T_1$

Charles' Law

At Constant P for an Ideal Gas

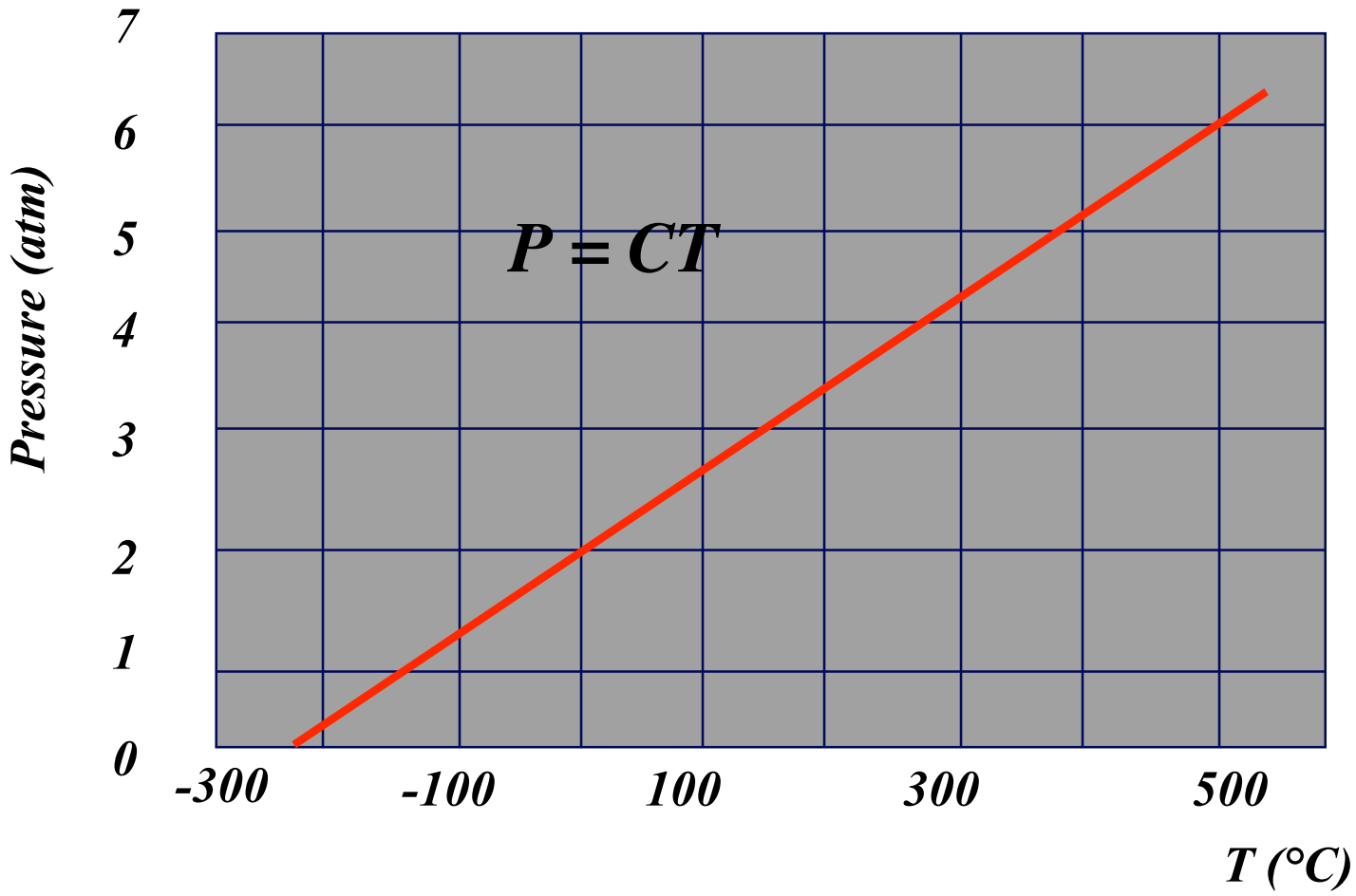
$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$



Gay-Lussac's Law

At Constant V for an Ideal Gas $P \quad T$

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



Combined Gas Laws

Charles'

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

Boyle's

$$P_1 \ V_1 = P_2 \ V_2$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{V_1 \ P_1 T_2}{P_2 T_1}$$

STP Conditions

Reference Points for T and P for comparison

Standard Temperature: 273.15 K= 0°C

Standard Pressure: 1 atm

Dalton's Law of Partial Pressures

$$P_{tot} = P_1 + P_2 + P_3 + \ldots$$

where P_1 is the partial pressure of gas 1, etc...

$$P_n = X_n P_{total}$$

$$X_n = \frac{n_n}{n_1 + n_2 + n_3 + \ldots}$$ ***Molar fraction of gas_n***

$$P_{gas} = P_{total} - P_{H_2O}$$ ***(table 11.3 p. 387)***

where P_{H_2O} is the vapor pressure of water at the specified temperature. Most often used in collection of insoluble gases over water. In open systems, $P_{total} = P_{atm}$

1809

Gay-Lussac's Law of combining volumes

"When measured at the same T and P, the ratios of the V of reacting gases are small whole numbers"

1811

Avogadro's Law

"Equal volumes of different gases at the same T and P contain the same number of molecules"

Consequences of Avogadro's Law

1. ***Explanation of Gay-Lussac's combining volumes law. Diatomic nature of elemental gases.***

2. ***Method for determining molar masses of gases. The molar Volume.***

3. ***Firm foundation of KMT: gases consists of microscopic particles***

Density of Gases

$$d = \frac{m}{V} \qquad \text{But } V = f(P, T) \quad \Rightarrow \quad d_{gas}^{T,P}$$

Gas	M(g/mol)	STP d(g/L)	Gas	M(g/mol)	STP d(g/L)
H_2	2.016	0.900	H_2S	34.09	1.52
CH_4	16.04	0.716	HCl	36.46	1.63
NH_3	17.03	0.760	F_2	38.00	1.70
C_2H_2	26.04	1.16	CO_2	44.01	1.96
HCN	27.03	1.21	C_3H_8	44.09	1.97
CO	28.01	1.25	O_3	48.00	2.14
N_2	28.02	1.25	SO_2	64.07	2.86
air	28.9	1.29	Cl_2	70.90	3.17
O_2	32.00	1.43			

Ideal Gas Equation *Equation of State*

$$V \quad \frac{1}{P} \qquad V = R\frac{nT}{P} \qquad PV = nRT$$

$$V \quad n$$

$$V \quad T$$

$$PV = \frac{m}{M} RT \qquad M = \frac{mRT}{PV} \qquad d = \frac{PM}{RT}$$

For one mole of a gas at STP, R constant:

$$R = \frac{(1\ atm)(22.4L)}{273K} = 0.082\ \frac{L\text{-}atm}{mol\text{-}K}$$

Ideal Gas Equation

The ideal gas constant has energy/mol degrees dimensions

$$[R] = \frac{[pressure][Volume]}{[temperature][mol]} = \frac{[force][volume]}{[area][temperature][mol]}$$

$$[R] = \frac{[force][length]}{[temperature][mol]} = \frac{[energy]}{[temperature][mol]}$$

$$R = 8.134\ J\ mol^{-1}\ K^{-1} \sim 2\ Cal\ mol^{-1}\ K^{-1}$$

Gas Stoichiometry

Concentrated nitric acid acts on copper and produces nitrogen dioxide and dissolved copper. 6.80 g Cu is consumed and NO_2 is collected at a pressure of .970atm and a temperature of 45°C (318 K) . Calculate the volume of NO_2 produced.

$$\mathbf{Cu(s) + 4H^+ + 2NO_3^-(aq) \longrightarrow Cu^{+2}(aq) + 2NO_2(aq) + 2H_2O}$$

$$6.80 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol } NO_2}{1 \text{ mol Cu}} = 0.214 \text{ mol } NO_2$$

$$V = \frac{nRT}{P} = 5.76 \text{ L } \underline{NO_2}$$

Real Gases

Follow the ideal gas law at sufficiently low densities

- ***Gas molecules attract one another***
- ***Gas molecules occupy a finite volume***

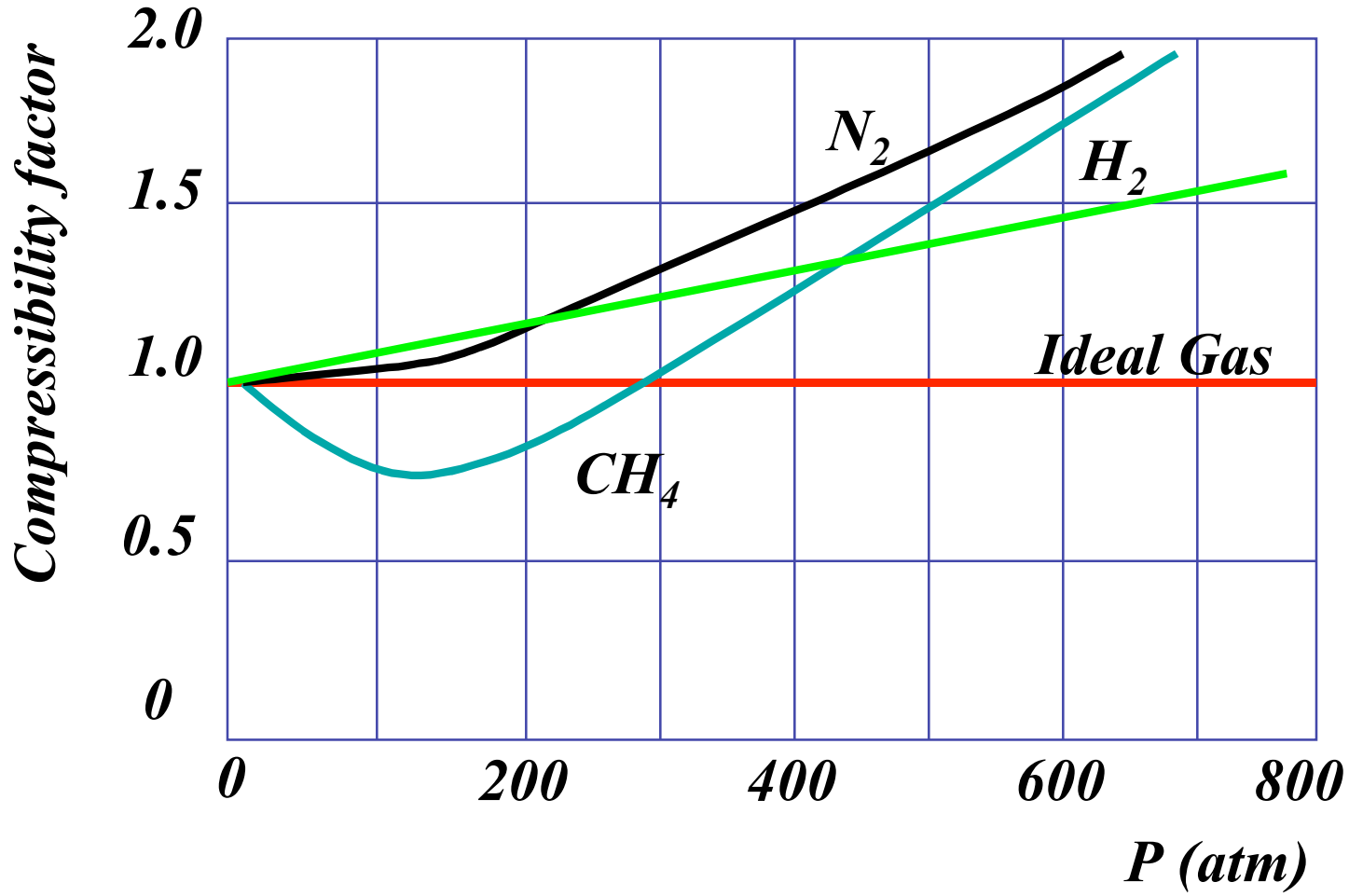
Both factors increase in importance when the molecules are close together (high P. low T).

Deviations from ideality are quantified by the Compressibility factor z

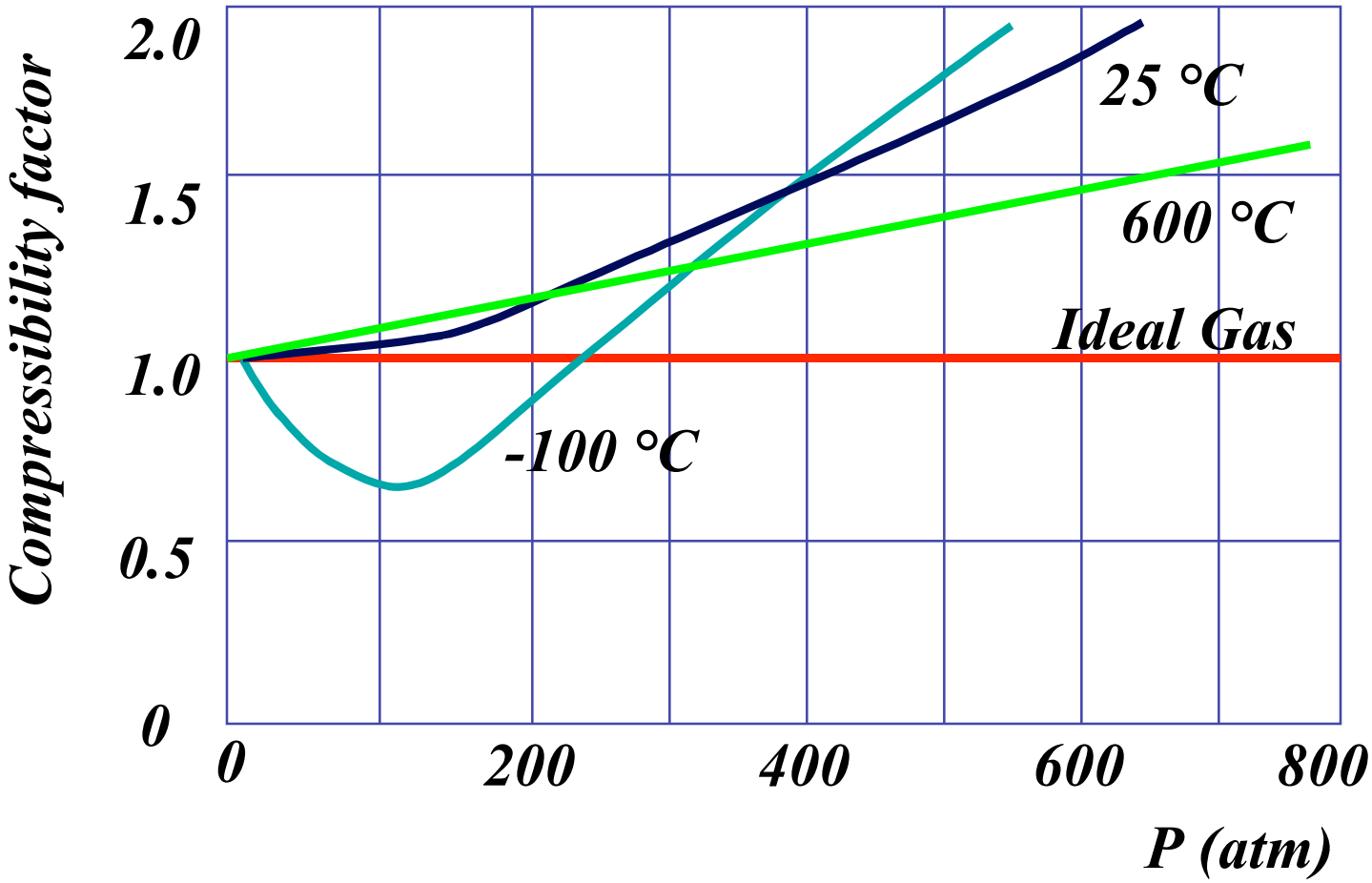
$$z = \frac{P\,V}{n\,R\,T}$$

Real Gases

Intermolecular Forces



Nitrogen at several T



Van der Waals Equation (1873)

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

***b* = constant representing volume excluded per mole of molecules**

***a* = depends on the strength of attractive forces**

$\frac{n^2}{V^2}$ ***Proportional to reduction of wall collisions due to cluster formation.***

Air Pollution

Upper and Lower Atmosphere Ozone

Sulfur Dioxide

Nitrogen Oxides

Green House Effect

Upper atmosphere Ozone

$$O_2 \xrightarrow{h\square} 2O$$

$$O_2 + O \longrightarrow O_3$$ *Allotropic Transformation*

$$O_3 \xrightarrow{h\square} O_2 + O + \text{heat}$$ *Ozone shield*

$$CCl_3F \xrightarrow{h\square} CCl_2F^{\cdot} + Cl^{\cdot}$$ *Ozone Layer Destruction*

$$Cl^{\cdot} + O_3 \longrightarrow ClO^{\cdot} + O_2$$ *Chain propagation*

$$ClO^{\cdot} + O \longrightarrow O_2 + Cl^{\cdot}$$

Tropospheric Chemistry

$$NO_2 \xrightarrow{h\nu} NO + O$$

Photochemical Smog

$$O_2 + O + M \longrightarrow O_3$$

< 3 ppm Ozone alert,
M= N_2 or O_2

$$SO_2 + OH \longrightarrow SO_2OH$$

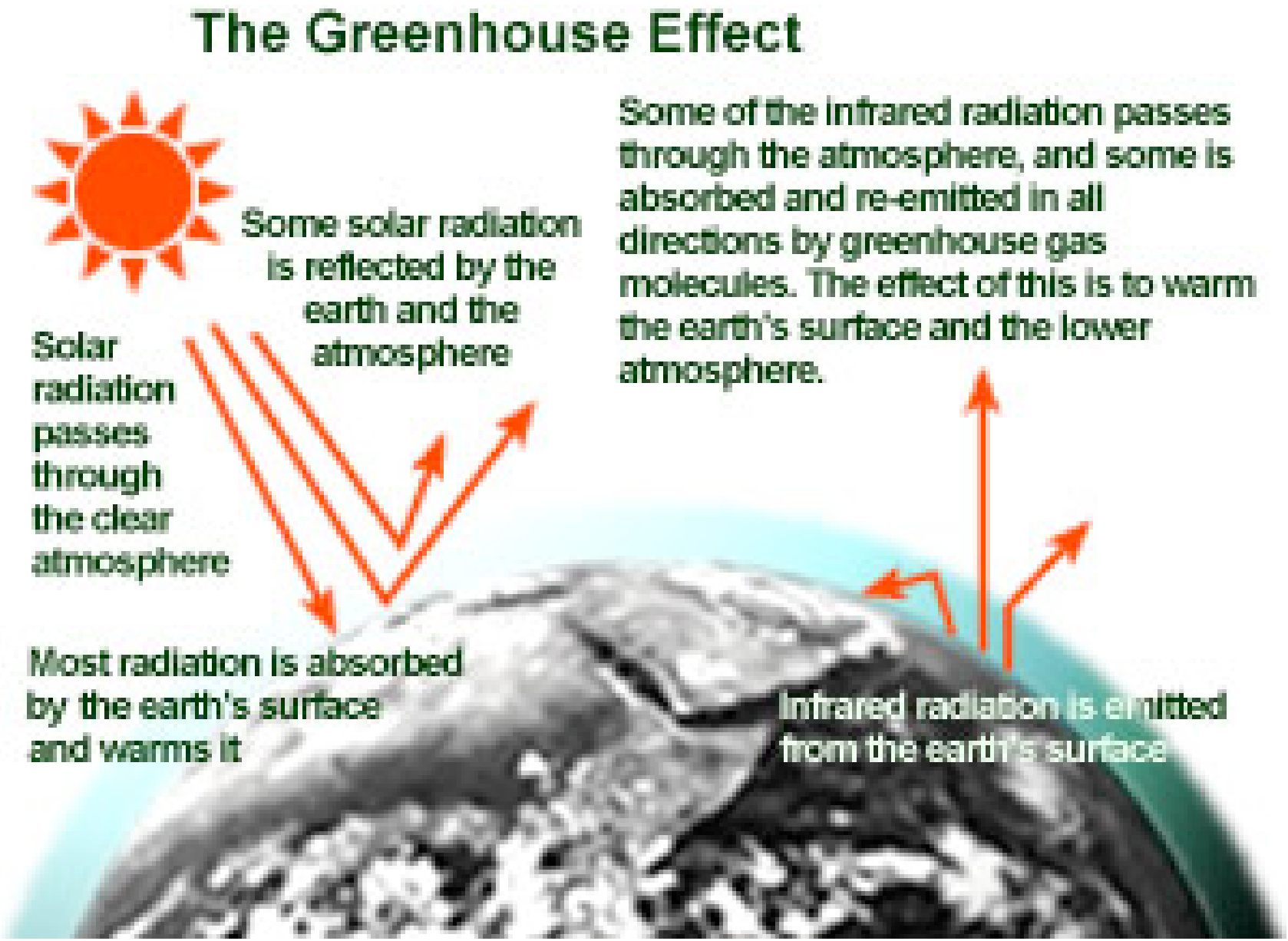
Radical Oxidation

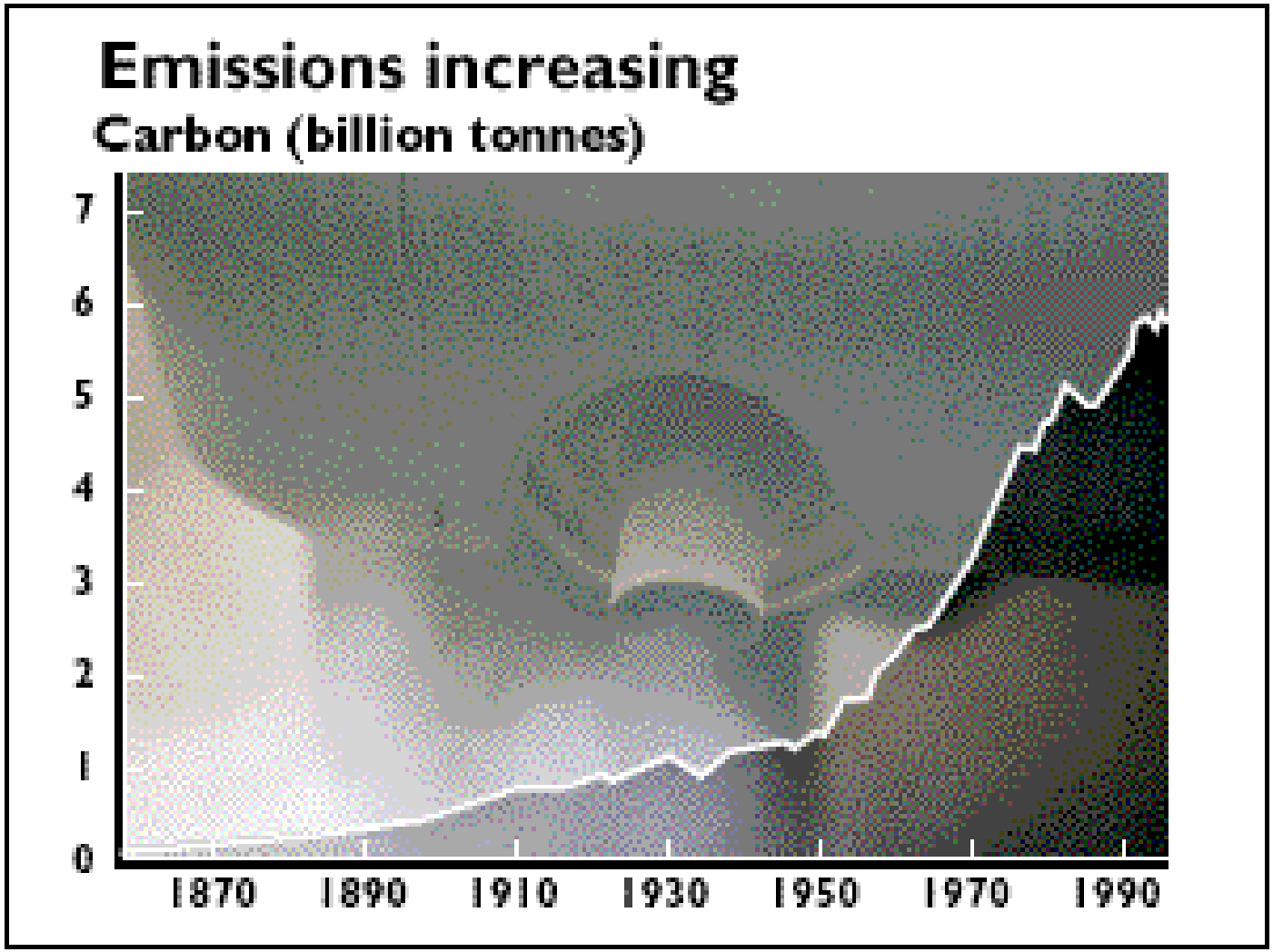
$$SO_2OH + O_2 \longrightarrow SO_3 + OOH$$

Acid Rain Precursor

$$OOH \longrightarrow O + OH$$

http://www.epa.gov/globalwarming/emissions/index.html





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