PRESSURE

$$P = \frac{F}{A} = \frac{\Delta p}{\Delta t}\frac{1}{A} = \frac{m\Delta v}{\Delta t}\frac{1}{A}$$

$$\Delta P_{x\,mol} = -2mv_x$$

$$\Delta P_{x\,Box} = 2mv_x$$

AFTER THE COLLISION IT WILL TAKE $\frac{2L}{v_x}$ SECONDS
IN THIS TIME ALL THE MOL IN THE BOX
COLLIDE ONCE WITH THE WALL
FOR THE NEXT COLLISION WITH THE SAME
WALL

MOMENTUM TRANSFERRED ~~PER~~ TO THE WALL SECOND

$$\frac{\Delta P_{wall}}{\Delta t} = \frac{2mv_x}{\frac{2L}{v}} = \frac{mv_x^2}{L} \equiv F$$

For N mol

$$F = \frac{m}{L}v_{x1}^2 + \frac{m}{L}v_{x2}^2 + \cdots + \frac{m}{L}v_{xN}^2$$

$$F = \frac{m}{L} N \frac{\sum_{j=1}^{N} v_{xj}^2}{N} = N \frac{m}{L} \overline{v_x^2}$$

AVERAGE OF THE SQUARE OF THE x COMPONENT

$$P = \frac{F}{A} = \frac{N m \overline{v_x^2}}{V}$$

$$PV = N m \overline{v_x^2}$$

NO PREFERRED DIRECTION (SYMMETRY)

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

OR

$$\overline{u^2} = 3 \overline{v_x^2}$$

$$\boxed{PV = \frac{1}{3} N m \overline{u^2}}$$

$$n RT = \frac{1}{3} N m \overline{u^2}$$

$$\frac{\cancel{N}}{N_0} RT = \frac{1}{3} \cancel{N} m \overline{u^2}$$

$$\frac{3RT}{N_0 m} = \overline{u^2}$$

ROOT-MEAN-SQUARE SPEED u_{rms}

$$\boxed{u_{rms} = \sqrt{\frac{3RT}{M}}}$$

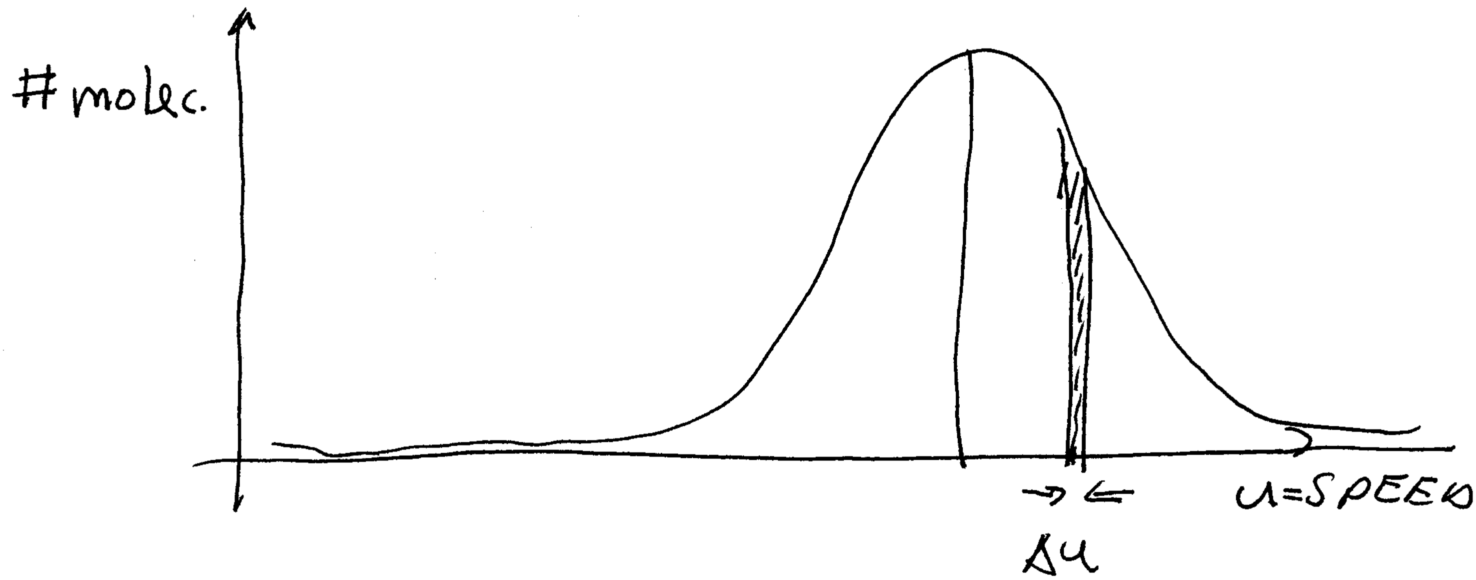
$M = N_0 m =$ MOLAR MASS

AT 298 K

$$u_{rms}(He) = 1360 \ \frac{m}{s}$$

$$u_{rms}(Xe) = 238 \ \frac{m}{s}$$

DISTRIBUTION OF MOLECULAR SPEEDS



$$\frac{\Delta N}{N} = f(u)\,\Delta u$$

FRACTION OF MOLECULES $\Delta N/N$ THAT HAVE SPEED BETWEEN

$u + \Delta u$

MAXWELL-BOLTZMANN SPEED DISTRIBUTION

$$f(u) = 4\pi\left[\frac{m}{2\pi k_B T}\right]^{3/2} u^2\, e^{-\frac{mu^2}{k_B T}}$$

k_B = Boltzman const.

$$k_B = R / N_0$$

$f(u)$ IS A PROBABILITY DISTRIBUTION

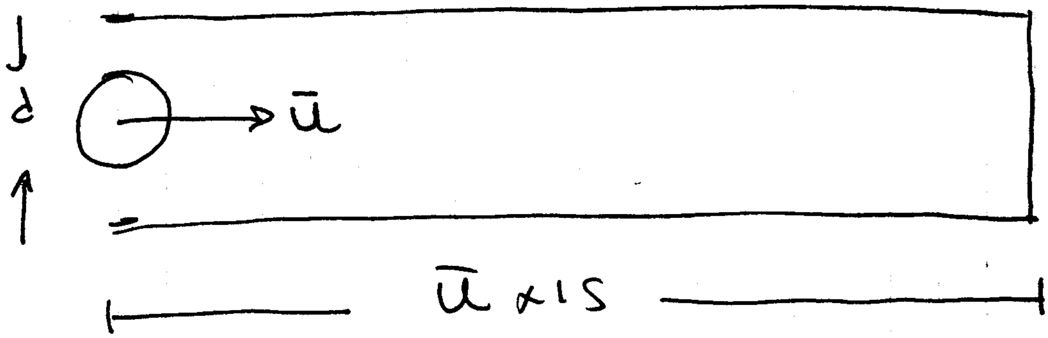
MORE PROBABLE SPEED $\longleftrightarrow$ MAX OF $f(u)$

$$u_{mp} = \sqrt{\frac{2RT}{M}}$$

<u>AVERAGE SPEED</u>

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}$$

FREQUENCY OF MOLECULAR COLLISIONS



$A = \pi d^2$

$$Z_1 \propto \pi d^2 \bar{u} \frac{N}{V}$$

$$\boxed{Z_1 = 4 \frac{N}{V} d^2 \sqrt{\frac{\pi R T}{M}}}$$

MAX

rate constants

collisions per second

Mean free path ~ Distance between coll.

TIME BETWEEN COLLISIONS

$$\tau = \frac{1}{Z_1}$$

$$\lambda = \bar{u} \tau = \frac{1}{\sqrt{2}\, \pi d^2 (N/V)}$$

DIFFUSION COEFFICIENT

$$\overline{(\Delta r)^2} = 6 D t$$

FROM KTG

$$D = \frac{3\pi}{16} \bar{u} \lambda = \frac{3}{8} \sqrt{\frac{RT}{\pi M}} \frac{1}{d^2 (N/V)}$$

H_2 IN INTERSTELLAR SPACE

$$\lambda = 4.1 \times 10^8 \, m$$

$$D = 1.4 \times 10^{11} \, \frac{m}{s^2}$$

OTHER RESULTS

Wall Collisions

$$Z_A \propto A \frac{N}{V} \bar{u}$$

EXACT CALCULATION USING $f(u)$

$$Z_A = \frac{1}{4} \frac{N}{V} \sqrt{\frac{8RT}{\pi M}}\, A$$

Graham's Law of Effusion

A is A HOLE !

$$\frac{\text{rate of effusion of } A}{\text{rate of effusion of } B} = \frac{N_A}{N_B} \sqrt{\frac{M_B}{M_A}}$$

ENRICHMENT FACTOR $\sqrt{\frac{M_B}{M_A}}$ FOR THE LIGHTER SPECIES A

REAL GASES

$$PV = nRT$$ FOR LOW PRESSURE

ACTUALLY V CANNOT REACH A ZERO VALUE

$$\Rightarrow \quad V \rightarrow V - nb$$

FOR HIGHER PRESSURES, MOLECULES SHOULD "FEEL" THE PRESENCE OF OTHER MOLECULES. THUS AN ATTRACTION OR REPULSION HAS TO OCCUR. IF WE CONSIDER AN ATTRACTIVE INTER MOLECULAR FORCE, THERE IS A TENDENCY TO LOWER THE PRESSURE, AND, TO LOWEST APPROXIMATION, THE FORCE DEPENDS ON THE PAIRING OF MOLECULES. AND THE PAIRING DEPENDS ON THE NUMBER CONCENTRATION N/V SQUARE. ($N \sim n$)

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

1873 J. van der Waals

$$\frac{PV}{nRT} = \frac{V}{V-nb} - \frac{a}{RT}\frac{n^2}{V}$$

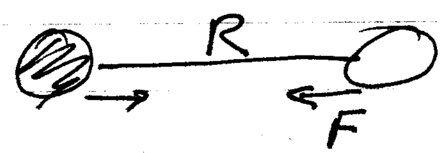
$a > 0$ ATTRACTIVE FORCE

$a < 0$ REPULSIVE FORCE

$$Z \equiv \text{Compressibility Factor} \equiv \frac{PV}{nRT}$$

INTERMOLECULAR POTENTIAL ENERGY CURVE

$V(R)$



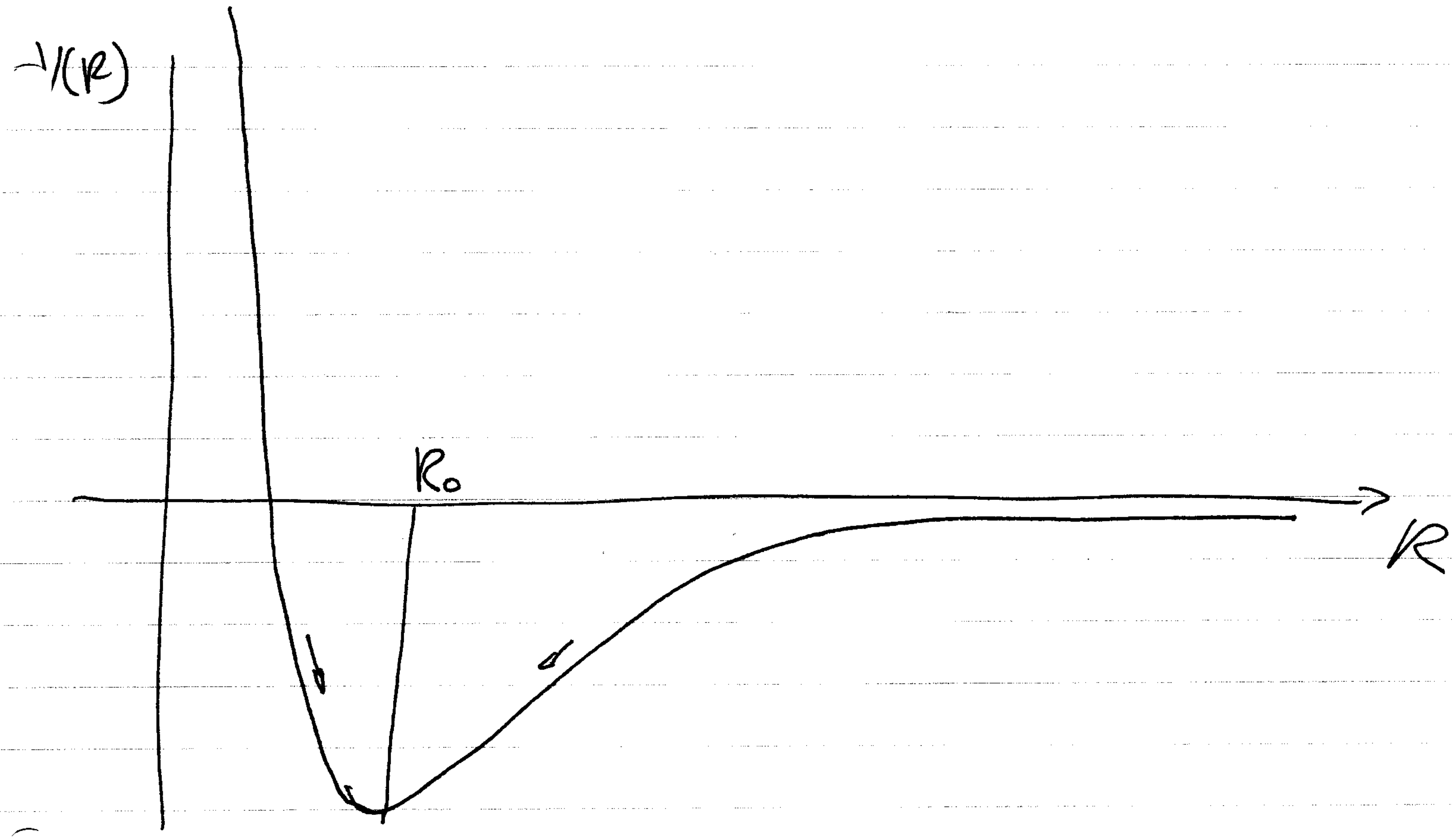
FROM PHYSICS WE KNOW THAT

$$\boxed{F = -\frac{dV}{dR}}$$

FORCE IS A VECTOR WHILE V IS A SCALAR FUNCTION

SHORT DISTANCE $\rightarrow$ REPULSION

LONG DISTANCE $\rightarrow$ ATTRACTION



R_0 "EQUILIBRIUM" DISTANCE

$$\left.\frac{dV}{dR}\right|_{R_0} = 0$$

LENNARD-JONES POT.

$$V_{LJ}(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

CHARACTERIZATION OF GASES, LIQUIDS, AND SOLIDS.

MOLAR VOLUME

COMPRESSIBILITY

Thermal EXPANSION

Fluidity and Rigidity

Diffusion

Surface Tansion

Covalent Bond $Cl - Cl$
(Sharing of e^-)

It takes 239 KJ to break a mole of $Cl-Cl$ covalent bonds

Intermolecular forces

1.- Weaker than covalent bonds
2.- Less directional than covalent bonds.
3.- Longer range than covalent bonds

a) Ion-Ion → Na^+ Cl^- (Coulomb Forces)

Strong as covalent bonds

$$V(R) \sim \frac{1}{R}$$

b) Dipole-dipole $\overset{\delta+}{H}\overset{\delta-}{Cl}$

$$V(R) \sim \frac{1}{R^3}$$

ION - DIPOLE $Na^+ Cl^-$ IN H_2O

INDUCED DIPOLE FORCES

ION CAN INDUCE POLARITY TO A NONPOLAR

INDUCED DIPOLE - INDUCED DIPOLE

WEAKER $V(R) \sim \frac{1}{R^6}$

BETWEEN NON POLAR DUE TO FLUCTUATIONS OF THE ELECTRONIC CHARGE = DISPERSION FORCES

REPULSIVE FORCES

Short range $V(R) \sim \frac{1}{R^n}$

$n \gtrsim 12$

OTHER RESULTS

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WALL COLLISIONS

$$Z_A = \frac{1}{4} \frac{N}{V} \sqrt{\frac{8RT}{\pi M}} A$$

Graham's Law of Effusion