THERMODYNAMICS

① DEFINITION OF THE SYSTEM (BOUNDARIES)

II SYSTEM + SURROUNDINGS = UNIVERSE

III SYSTEM → ISOLATED NO FLUXES
SYSTEM → CLOSE HEAT FLUX
SYSTEM → OPEN FLUXES

EQUI. SS

EQUI SS (T.)

NON EQUI SS

IV OBSERVABLES (ZEROTH LAW)
FOR GASES → V T P n

V RELATION BETWEEN OBSERVABLES
EQUATION OF STATE

VI NO LONG RANGE INTERACTIONS (LOW PRESSURE)

$$PV = nRT$$

$\bar{V} \equiv \frac{V}{n}$ molar volume

$$P\bar{V} = RT$$

$$Z \equiv \frac{P\bar{V}}{RT} = 1 \quad \text{IDEAL GAS}$$

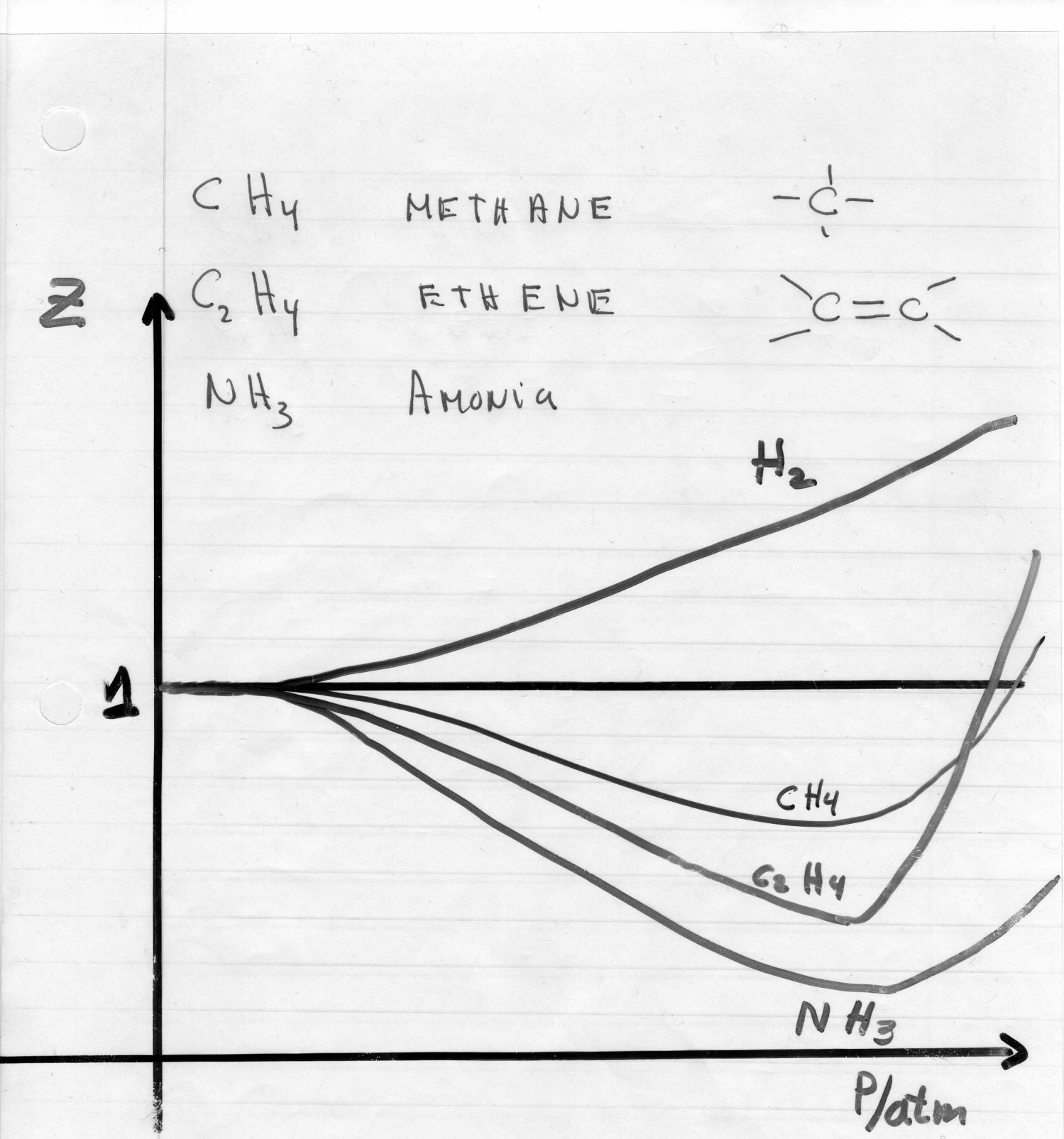
IDEAL GAS

1.- NO LONG RANGE INTERACTION
2.- POINT PARTICLES (NO VOLUME)

CH_4 METHANE

C_2H_4 ETHENE

NH_3 Amonia



$$Z = \frac{PV}{nRT}$$

Real Gases

Let us consider the compression factor

$$Z \equiv \frac{P\bar{V}}{RT}.$$

For an ideal gas i.e., $P\bar{V} = RT$.

$$Z = \frac{P\bar{V}}{RT} = 1.$$

When we plot Z for different substances as a function of pressure, we observe a universal agreement only at low pressures. But a great disagreement is observed at higher pressures

ANOTHER EXPERIMENTAL BEHAVIOR IS THE CONDENSATION OF GASES ONLY BELOW A CRITICAL TEMPERATURE. FOR EXAMPLE IT IS ~~IMPORTANT~~ IMPOSSIBLE TO PRODUCE LIQUID NITROGEN BY COMPRESSION ALONE IF THE TEMPERATURE IS GREATER THAN 126.2 K.

Van der Waals EQ.

A REAL GAS CANNOT BE COOLED OR COMPRESSED TO ZERO VOLUME. FIRST OF ALL, THE PARTICLES HAVE A VOLUME AND SECOND PARTICLES ARE AFFECTED BY ATTRACTIVE FORCES. REPULSIVE AT SHORT RANGE (A MOLECULAR DIAMETER) IMPEDING COMPRESSION AND ATTRACTIVE AT RELATIVE LONGE RANGE (SEVERAL MOLECULAR DIAMETERS).

ONE COULD TAKE IN CONSIDERATION THE MOLECULAR VOLUME BY A FACTOR $V - nb$ OR $\bar{V} - b$. THIS IMPLIES

$$P(\bar{V} - b) = RT.$$

THE ATTRACTIVE INTERACTIONS HOLD THE PARTICLES TOGETHER REDUCING THE FREQUENCY OF COLLISIONS WITH THE WALL AND THE

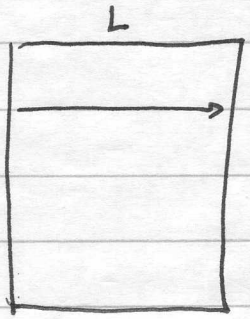
IMPULSE (CHANGE OF MOMENTUM) OF EACH COLLISION

$$\text{IMPULSE} \sim \frac{n}{V} \quad (\uparrow nT \quad \downarrow V\uparrow)$$

$$\text{FREQ} \sim \frac{n}{V}$$

$$\text{PRESSURE REDUCTION} \sim -\left(\frac{n}{V}\right)^2$$

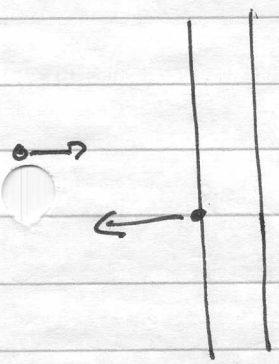
$$\boxed{P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}}$$ van der Waals EQ. (1879)



$\bar{v}$ $\frac{L}{\bar{v}}$ → TIME

$\frac{\bar{v}}{L}$ max # OF COLLISIONS $\sim \frac{1}{V}$

$\frac{n}{V}$ ~ # OF COLLISIONS AGAINST THE WALLS.



$V\uparrow$ EXTRA DIST. SLOWS DOW MORE THE PARTICLES. $\Delta P \downarrow$

$$P = \frac{RT}{\bar{V}} \frac{1}{1 - b/\bar{V}} - \frac{RT}{\bar{V}} \frac{a}{RT\bar{V}}$$

$$P = \frac{RT}{\bar{V}} \left\{ \frac{1}{1 - b/\bar{V}} - \frac{a}{RT\bar{V}} \right\}$$

ASSUME $\frac{b}{\bar{V}} << 1$

$$\frac{1}{1-X} = \sum_{n=0}^{\infty} X^n = 1 + X + X^2 + X^3 + \cdots + X^n + \cdots$$

IF $X < 1$.

$$P = \frac{RT}{\bar{V}} \left\{ 1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \cdots - \frac{a}{RT\bar{V}} \right\}$$

$$= \frac{RT}{\bar{V}} \left\{ 1 + \left(b - \frac{a}{RT} \right) \frac{1}{\bar{V}} + \cdots \right\}$$

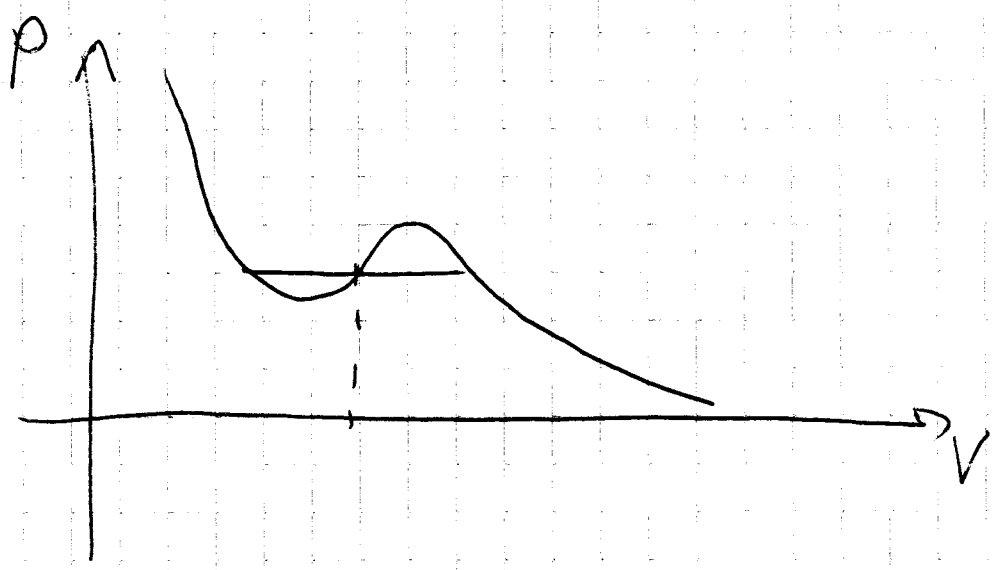
AT $T_B \equiv \frac{a}{b} \frac{1}{R}$ THE GAS BEHAVES IDEALLY. T_B IS CALLED THE BOYLE TEMP.

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

$$P(\bar{V}-b)\bar{V}^2 = RT\bar{V}^2 - a(\bar{V}-b)$$

$$P\bar{V}^3 - Pb\bar{V} - RT\bar{V}^2 + a\bar{V} - ab = 0$$

$$P\bar{V}^3 - (Pb+RT)\bar{V}^2 + a\bar{V} - ab = 0$$



$$\frac{\partial P}{\partial \bar{V}} = -\frac{RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3} = 0$$

$$\frac{\partial^2 P}{\partial \bar{V}^2} = \frac{2RT}{(\bar{V}-b)^3} - \frac{6a}{\bar{V}^4} = 0$$

$$\frac{2}{\bar{V}-b}\,\frac{2a}{\bar{V}^2} = \frac{6a}{\bar{V}^4}$$

$$4\bar{V} = 6(\bar{V}-b)$$

$$4\bar{V} = 6\bar{V} - 6b$$

$$6b = 2\bar{V}_c$$

$$\boxed{\bar{V}_c = 3b}$$

ENERGY — KINETIC ENERGY

POTENTIAL ENERGY

U ← INTERNAL ENERGY

U ⟷ vibrations, rotations, chemical bonds

FIRST LAW $\Delta U_{UNIVERSE} = 0$

$$\Delta U_{SYS} + \Delta U_{SUR} = 0$$

FOR SYSTEMS WITH NO CHEMICAL RXN
NO PHASE TRAN

$$\Delta U = q + w$$

q = heat

w = work

$q \equiv$ heat $\equiv$ flow of energy ACROSS A BOUNDARY DUE TO A TEMPERATURE DIFFERENCE