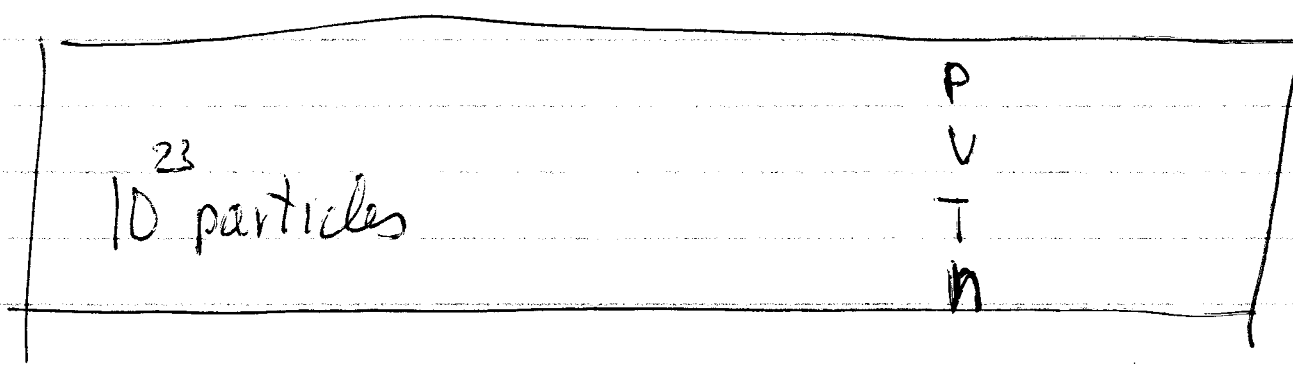
ZEROth LAW

IF A is IN THERMAL EQUILIBRIUM WITH C,
AND B IS IN THERMAL EQUILIBRIUM WITH C

THEN A AND B ARE IN THERMAL EQUILIB

GIVE A SYSTEM (MACRO)



We cannot solve 10^{23} NEWTON EQUATIONS!

P, V, T AND n ARE MACRO AVERAGED PROPERTIES.

THERMOMETER

Physical property $\propto$ T (linear)

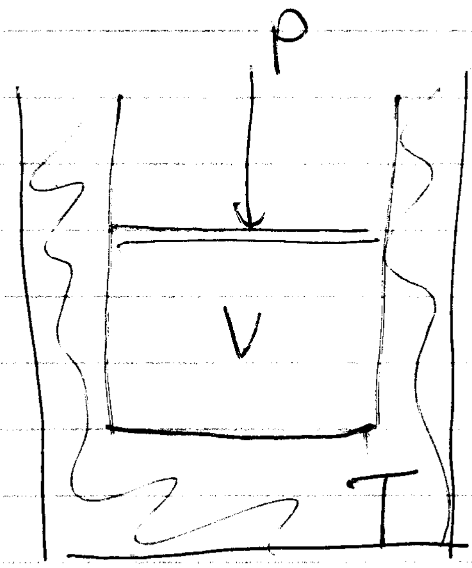
Mercury $\rightarrow$ $l \propto T$

Arbitrary scale

Centigrade	0°C EQUI ICE/WATER (FREEZING POINT)	100 °C EQUI BOILING
CELSIUS	0.01 °C TRIPLE POINT ICE/WATER/VAPOR	1 atm boiling 99.975 °C
°F	0°F EQUI ICE/WATER/SALT	96 °F BODY TEMP ⇓ 212 °F BOILING WATER

Physical properties are nonlinear.

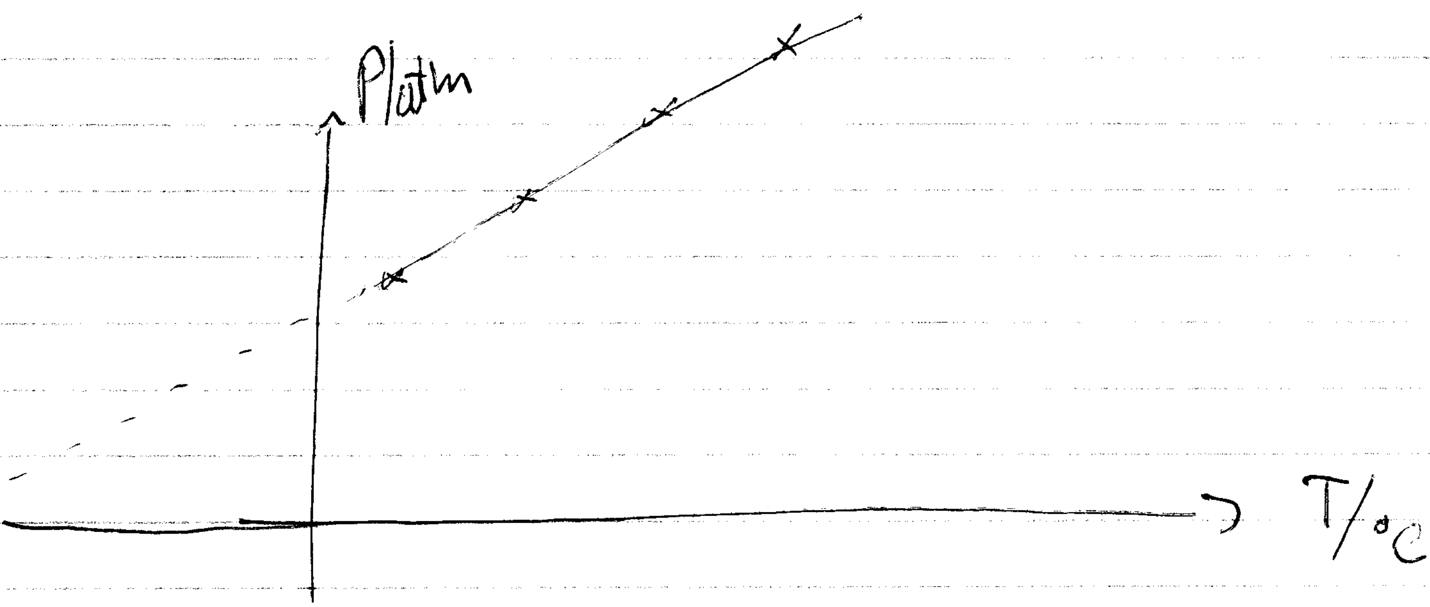
GAS THERMOMETER (LOW PRESSURE GAS)



$P \propto T$ (FIXED V, n)

$V \propto T$ (FIXED P, n)

$V \propto \frac{1}{P}$ (FIXED T, n)



$$\frac{P}{\text{atm}} = P_0 + \frac{P_0}{273^\circ C} T_C$$

$T_c = -273\,°C \Rightarrow P = 0!$

DEF $T_K \equiv T_c + 273\,K$

$$\frac{P}{atm} = \frac{P^o}{273K} T_K \quad \text{(FIXED V and n.)}$$

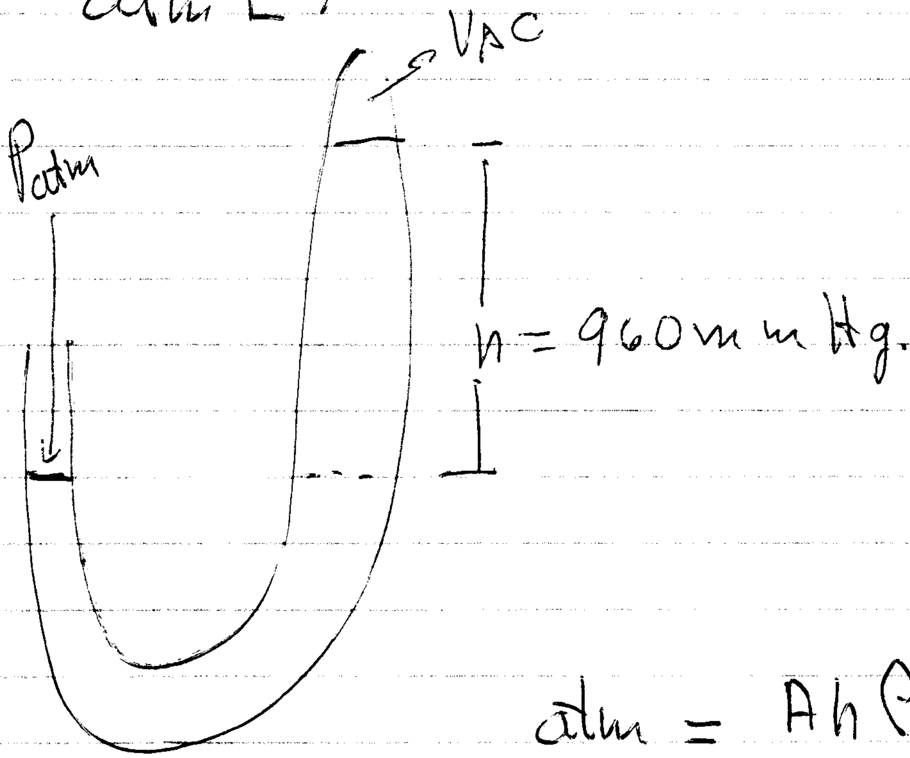
DILUTE GASES (IDEAL OR PERFECT GAS)

$$PV = nRT \quad \text{T IN KELVIN}$$

$$\frac{PV}{nT} = R$$

$$\frac{1\,atm\ 24.2\,L}{1\,mol\ 298\,K} \simeq R = 8.206 \times 10^{-2} \frac{L\,atm}{K\,mol}$$

atm L ?



$$atm = \frac{A h \rho_{Hg} g}{A} = h g \rho_{Hg}$$

$$\rho_{Hg} = 1.35 \frac{g}{cc} = 13534 \frac{Kg}{M^3}$$

$$atm\,L \simeq 0.960\,M\,\rho_{Hg}\,9.8\,\frac{M}{S^2}\,10^{-3} M^3$$

$$\simeq 1 M\,10 \frac{M}{S^2}\,M \frac{Kg}{M^3}\,1{,}3534\,10^{-3} M^3$$

$$R = 8.314 \frac{J}{K\,mol}$$

THE RELATION BETWEEN OBSERVABLES (P, T, V, n) IS AN EXAMPLE OF AN EQUATION OF STATE

$$PV = NRT$$

$$P = \frac{NRT}{V - b} - \left(\frac{a}{V}\right)^2$$

AT LOW PRESSURE ALL GASES FOLLOW

THE IDEAL OR PERFECT GAS EQ.

$$PV = nRT.$$

R = UNIVERSAL GAS CONSTANT $= N_0 k_B$

$= 8.3144 \ J\,K^{-1}\,mol^{-1}$

$= 0.08315 \ bar\,dm^3\,K^{-1}\,mol^{-1}$

$= 0.08206 \ atm\,dm^3\,K^{-1}\,mol^{-1}$

<u>PRESSURE</u>

PASCAL $Pa \equiv 1\,N\,m^{-2}$ (SI UNITS)

$bar = 10^5\,Pa$

$1 atm \equiv 101\,325\,Pa = 1.01325 \times 10^5\,Pa$

$bar \equiv 10^5\,Pa$

$1\,atm \simeq bar$

$1\,atm \cdot L = 101.325\,J$

MOLAR VOLUME $\frac{V}{n} \equiv \overline{V} = V_m$

$$\boxed{P\overline{V} = RT}$$

IDEAL GAS MIXTURE

$$PV = nRT$$

$$= \sum_i n_i RT$$

$$= \sum_i n_i \frac{RT}{V} \equiv \sum_i P_i$$

$$P = \sum_i P_i$$

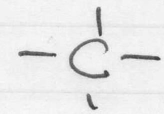
$$1 = \sum_i \frac{P_i}{P} = \sum_i \frac{n_i}{n} = \sum_i X_i$$

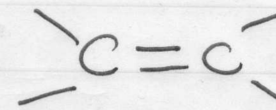
X_i mole fraction

IF YOU KNOW n_i YOU KNOW THE PARTIAL PRESSURE

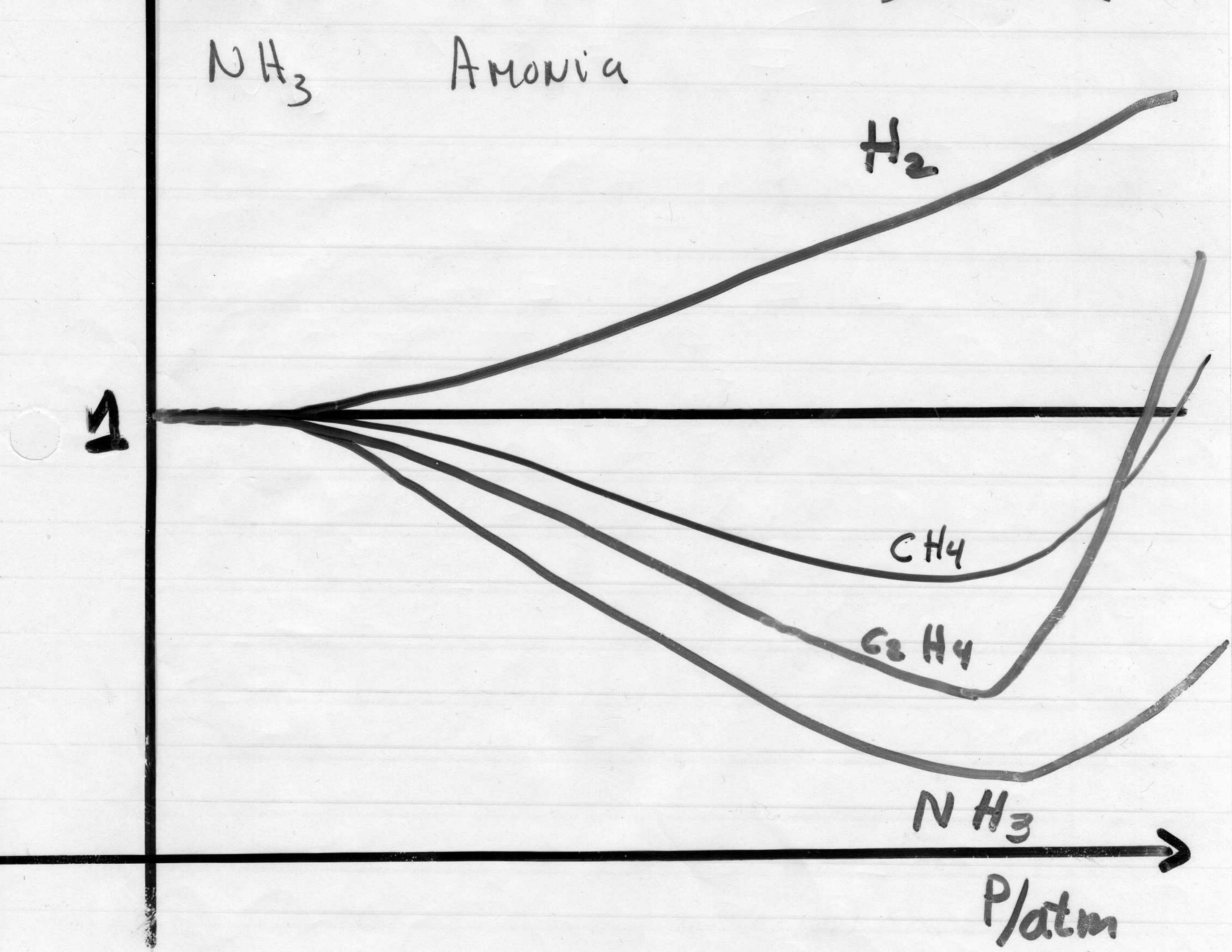
$$\frac{P_i}{P} = X_i = \frac{n_i}{n}$$

$$P_i = \frac{n_i}{n} P$$

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