Pressure

$$1\ \ bar = 10^5\ \ Pa$$
$$1\ \ atm = 101.325 \cdot 10^3 Pa$$
$$1\ \ Torr = 133.32\ \ Pa$$

Number of Molecules

$$N = nN_A,\ \ N_A = 6.022 \cdot 10^{23}$$

Gas Constant

$$\begin{aligned} R &= 8.315\ \ J\ \ K^{-1}\ \ mol^{-1} \\ &= 8.315 \cdot 10^{-2}\ \ L\ \ bar\ \ K^{-1}\ \ mol^{-1} \\ &= 8.206 \cdot 10^{-2}\ \ L\ \ atm\ \ K^{-1}\ \ mol^{-1} \\ &= 62.36\ \ L\ \ Torr\ \ K^{-1}\ \ mol^{-1} \end{aligned}$$

Boltzman Constant

$$k = 1.381 \cdot 10^{-23}\ \ J\ \ K^{-1}$$

Root Mean Square Speed

$$V_{rms} = c = \sqrt{\frac{3RT}{M}}$$

Average Speed

$$V_{avg} = \bar{c} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$

Most Probable Speed

$$c^* = \left(\frac{2RT}{M}\right)^{\frac{1}{2}}$$

Related Speed

$$\begin{aligned} \bar{c}_{rel} &= 2^{\frac{1}{2}} \bar{c} \\ &= \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}\ \ bases\ \ \mu = \frac{m_1 m_2}{m_1 + m_2} \end{aligned}$$

Collision Frequency

$$\begin{aligned} z &= \rho \bar{c}_{rel} \frac{N}{V},\ \ \rho = \pi d^2,\ \ d = collision\ \ diameter \\ &= \frac{\rho \bar{c}_{rel} P}{kT} \end{aligned}$$

Mean Free Path

$$\lambda = \frac{\bar{c}}{z}$$

Compression Factor

$$Z = \frac{PV_m}{RT}$$

$$\lim_{\frac{1}{V_m} \to \infty} \frac{dZ}{d\left(\frac{1}{V_m}\right)} = 0\ \ at\ \ T = T_B : Boyle\ \ temp$$

Van der Waals Equation

$$\begin{aligned} PV_m &= RT(1 + B'P + C'P^2 + \ldots) \\ &= RT(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots) \end{aligned}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$
$$V_m^3 - \left(b + \frac{RT}{P}\right) V_m^2 + \left(\frac{a}{P}\right) - \frac{ab}{P} = 0$$
$$b = N_A \frac{3}{4} \pi (2r_{mol})^3$$

Adiabatic Process

$$q = 0,\ \ \Delta U = w = nC_v \Delta T$$
$$P_i V_i^{\gamma} = P_f V_f^{\gamma},\ \ \gamma = \frac{C_p}{C_V},\ \ C_p - C_v = nR$$

Isothermal Process

$$q = -w,\ \ \Delta U = 0$$

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ &= C_V dT + \Pi_T dV \end{aligned}$$

$$\Pi_T\ \ is\ \ internal\ \ pressure,\ \ \Pi_T = \left(\frac{\partial U}{\partial P}\right)_H$$

Perfect Gas

$$\Pi_T = 0,\ \ \Leftrightarrow dU = C_V \Delta T$$

Isothermal Reversible Expansion

$$q = -w = -\int -P_{ex} dV = nRT \ln\left(\frac{V_f}{V_i}\right)$$
$$dH = C_p dT = 0 \Rightarrow \Delta H = 0$$

Joule-Thomson Coefficient

$$\mu = \left(\frac{\partial H}{\partial P}\right)_T$$
$$\mu > 0 \Rightarrow cooling,\ \ \mu > 0 \Rightarrow heating,$$
$$\mu = 0 \Rightarrow \text{ideal gas}$$

Entropy

- definition

$$dS = \frac{dQ}{T}$$

- at constant pressure

$$\Delta S_{sys} = nC_{P.m.} \ln\left(\frac{T_f}{T_i}\right) \quad at \quad p \quad const$$

- at constant temperture

$$q = -w = -\int -P_{ex}dV = nRT\ln\left(\frac{V_f}{V_i}\right)$$
$$= nRT\ln\left(\frac{P_i}{P_f}\right)$$

$$dS = \frac{dQ}{T}$$
$$\Delta S = \int \frac{dQ}{T} = \int \frac{dq}{T} = \int nRT\ln\left(\frac{P_i}{P_f}\right)dT$$
$$= nR\ln\left(\frac{P_i}{P_f}\right)$$

Carnot Engine

$$\varepsilon = \frac{gain}{pay} = 1 - \frac{T_c}{T_h} < 1 \quad \text{(2nd Law)}$$
$$\mathrm{d}S \geq \frac{\mathrm{d}q}{T} \quad \text{(Clausius Inequality)}$$
$$\mathrm{d}S \geq 0 \quad \text{(2nd Law)}$$

1st, 2nd 3rd Law of Thermodynamics

| | |
|---|---|
| 1st Law | $U = Q + W$ |
| 2nd Law | $\mathrm{d}S \geq 0$ |
| 3rd Law | $T \to 0, \quad \Delta S \to 0$ |

Math

$$\left(\frac{\partial z}{\partial y}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

$$\int x^n e^{-ax}dx = \frac{n!}{a^{n+1}}$$

Various Coefficient

Basics

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \text{Volume Heat Capacity}$$
$$\left(\frac{\partial U}{\partial V}\right)_T = \Pi_T \quad \text{internal pressure}$$
$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha \quad \text{expansion coefficient}$$
$$\left(\frac{\partial V}{\partial P}\right)_T = \mu_T \quad \text{isothermal Joule-Thomson Coefficient}$$
$$\left(\frac{\partial T}{\partial P}\right)_H = \mu \quad \text{Joul-Thomson Coefficient}$$

Arranged

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu C_p$$
$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$
$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$
$$\left(\frac{\partial H}{\partial H}\right)_T = C_P$$

$\Pi_T Question$

probe $\Pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{T\mathrm{d}S - P\mathrm{d}V}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}_T\right) - P\left(\frac{\partial V}{\partial V}\right)$$
$$= T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$\Pi_T$ of real gas

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$
$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{nR}{V - nb}\right)_V$$

$$\Pi_T = \left(\frac{\partial P}{\partial T}\right)_T = \left(\frac{\partial T\mathrm{d}S - P\mathrm{d}V}{\partial T}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$
$$= T\left(\frac{nR}{V - nb}\right)_V - P = \left(P + a\frac{n^2}{V^2}\right) - P$$
$$= \frac{a}{V_m^2}$$

Maxwell Relation

Basics

$$df = \overbrace{g\,\mathrm{d}x}^{\rightarrow} - \underbrace{h\,\mathrm{d}y}_{\leftarrow}$$
$$\Rightarrow \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$
$$\left(\frac{\partial g}{\partial y}\right)_x = \frac{\mathrm{d}^2 f}{\mathrm{d}y\mathrm{d}x}$$
$$\left(\frac{\partial h}{\partial x}\right)_y = \frac{\mathrm{d}^2 f}{\mathrm{d}x\mathrm{d}y}$$

Internal Energy

$$dU = TdS - PdV$$
$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Enthalpy

$$\begin{aligned} dH &= dU + d(PV) \\ &= TdS - PdV + PdV + VdP \\ &= TdS + VdP \\ &\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \end{aligned}$$

Gibbs Energy

$$\begin{aligned} dG &= dH - d(TS) \\ &= Tds + VdP - TdS - SdT \\ &= VdP - SdT \\ &\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \end{aligned}$$

Helmholtz Energy

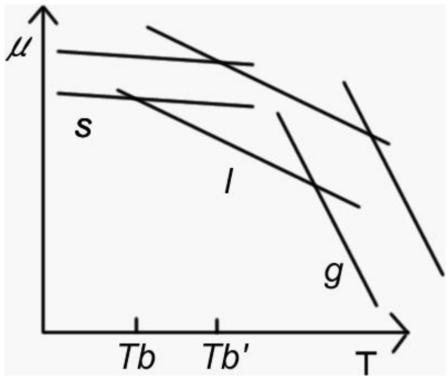
$$\begin{aligned} dA &= dU - d(TS) \\ &= dU - SdT - TdS \\ &= -PdV - SdT \\ &\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \end{aligned}$$

Gibbs-Helmholtz Equation

$$\begin{aligned} \left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_P &= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + G\left(-\frac{1}{T^2}\right) \\ &= \frac{1}{T}\left(\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right) \\ &= \frac{H}{T^2} \end{aligned}$$

$$\Rightarrow \left(\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right)_P = \frac{\Delta H}{T^2}$$
$$\Rightarrow \frac{\Delta G_f}{T_f} - \frac{\Delta G_i}{T_i} = \Delta H\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

$$\begin{aligned} \text{slope} &= \frac{dG}{dT} \\ &= S \leq 0 \end{aligned}$$

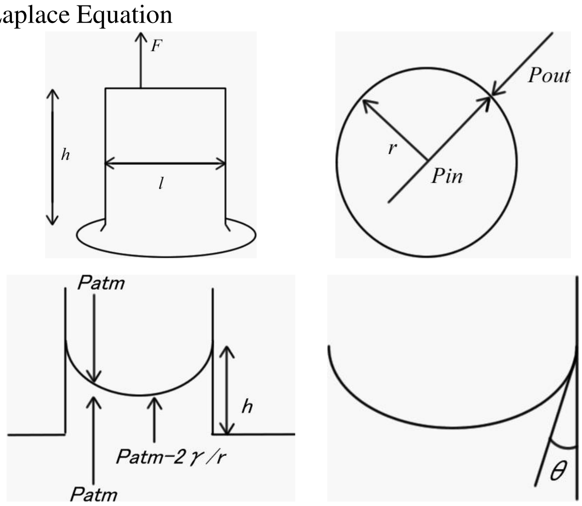



$$d\mu = V_m P - S_m dT$$
$$\uparrow P = \downarrow T$$
$\Rightarrow$ easy to melt

Surface Tensio0n

$$dw = \gamma d\sigma \quad (\sigma \text{ is area})// \quad = \gamma(ldh) = Fdh \quad (\because F = \gamma l)$$

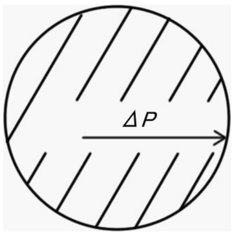
Laplace Equation



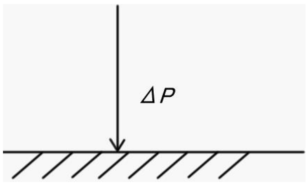

$$P_{in} - P_{out} = \frac{2\gamma}{r}$$
$$h = \frac{2\gamma}{r\rho g} \qquad h = \frac{2\gamma\cos\theta}{r\rho g}$$

Kelvin Equation for Vapor Pressure above Curved Surface

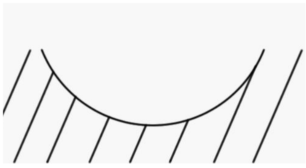
$P = P^* e^{\frac{\Delta P V_m}{RT}}$ for




$P = P^* e^{\frac{2\gamma V_m}{RT}}$ for




$P = P^* e^{\frac{-2\gamma V_m}{RT}}$ for



Binary Mixture

$$\begin{aligned}
\mathrm{d}V &= \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} \mathrm{d}n_A + \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_B} \mathrm{d}n_B \\
&= V_A \mathrm{d}n_A + V_B \mathrm{d}n_B \\
V &= n_A V_A + n_B V_B \\
\mathrm{G} &= V\mathrm{d}P - S\,\mathrm{d}T + \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B \\
\mu_j &= \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_i}
\end{aligned}$$

Eular Theorem

$$\begin{cases} V = \sum V_i n_i \\ G = \sum \mu_i n_i \\ m = \sum M_i n_i \end{cases} \qquad V_m = \frac{M}{\rho}$$

s-l

$$P \approx P^* + \frac{T - T^* \Delta_{fus} H}{T^* \Delta_{fus} V}$$

l-g

$$P \approx P^* e^{\frac{\Delta_{vap} H \left(\frac{1}{T} - \frac{1}{T^*}\right)}{R}}$$