1 Internal Energy and Introduction

Internal Energy: $\boxed{\begin{array}{l} \Delta U = Q + W \\ dU = \delta Q + \delta W \end{array}}$

(1st Law)

$$\boxed{dU = T\ dS - P\ dV + \sum \mu_i\ dN_i + \dots}$$

Maxwell Identity: $\quad \dfrac{\partial}{\partial V}\left(\dfrac{\partial U}{\partial S}\right) = \dfrac{\partial}{\partial S}\left(\dfrac{\partial U}{\partial V}\right)$

$$\to \boxed{\left(\dfrac{\partial T}{\partial V}\right)_{N,S} = -\left(\dfrac{\partial P}{\partial S}\right)_{N,V}} \quad \text{(other iden. with } \mu, N)$$

1.1 Initial Assumptions

Equipartition Theorem (ET):

$$\boxed{U_{\text{therm}} = f\left(\tfrac{1}{2}Nk_bT\right)} \qquad f=x^2 \text{ DOF}$$

-Solid: 3 [vib.] = 3 trans. + 3 pot.
-Mono Gas: 3 trans.
-Dia Gas: 3 trans. + 2 rot. + 1 vib.

(1 K)   (1000 K)

(Some DOF "freeze" at low temp)

Ideal Gas Law (IG): $\quad \boxed{PV = Nk_bT}$

Quasistatic Approx. (QS): slow enough that conditions are equal throughout

$$\bullet\ \boxed{W_{\text{cpr}} = -\int P\ dV} \qquad \text{QS Work (QW)}$$

1.2 Reversible (RV)

Infinitesmal small changes can be reversed back

to the original state

- $\delta W = P\ dV = \delta W_{\text{cpr}} + \cancel{\delta W_{\text{other}}}$

- $\delta Q = T\ dS$

1.3 Isothermal (iT): $\boxed{\frac{dT}{dt} = 0}$

$\to\ $ ET : $\Delta U \sim \Delta T = 0$

$$\boxed{dU \sim dT = 0}$$

(Energy as heat moves to and from environment)

- IG : $\boxed{P = \dfrac{Nk_bT}{V}}$ (Isotherm $1/V$ level-curves)

$$\Rightarrow \boxed{W = Nk_bT\ln\left(\dfrac{V_i}{V_f}\right) = -Q}$$

$$\bullet\ \boxed{\Delta S = \int \dfrac{PdV}{T} = Nk_b\ln\left(\tfrac{V_f}{V_i}\right) = \int \dfrac{\delta Q}{T}}$$

1.4 Free Expansion

$$\boxed{\Delta U = Q = W = 0}$$

- IG: $\boxed{0 = \Delta T}$, $\boxed{\Delta S = \frac{\int PdV}{T} = Nk_b\ln(V_f/V_i)}$

- Else: See Throttling

1.5 Adiabatic (aB): $\boxed{Q = 0}$

$\to\ \Delta U = W \qquad$ (Compressed fast enough so no heat escapes)

$$\boxed{dU = \delta W}$$

- ET & IG : $WRONG$

$$\Rightarrow\ V_f\ T_f^{f/2} = \left(V_i\ T_i^{f/2} = \text{constant}\right)$$

$$\Rightarrow\quad TV^{\frac{2}{f}} = \left(\dfrac{PV}{Nk_b}\right)V^{\frac{2}{f}}$$

$$PV^{\left(1+\frac{2}{f}\right)} = \boxed{PV^\gamma = \text{constant}} = V_i^{\frac{2}{f}}Nk_bT_i$$

(connects isotherm level-curves)

- QS : $\boxed{\Delta S = 0 = \int \dfrac{\delta Q}{T}}$ (See Isentropic)

2 Enthalpy and Heat Capacity

Enthalpy: $\boxed{H \equiv U + PV}$

$$\boxed{\begin{aligned} dH &= dU + P\,dV + V\,dP \\ &= T\,dS + V\,dP + \sum \mu_i\,dN_i + \dots \end{aligned}}$$

Maxwell Identity: $\dfrac{\partial}{\partial P}\left(\dfrac{\partial H}{\partial S}\right) = \dfrac{\partial}{\partial S}\left(\dfrac{\partial H}{\partial P}\right)$

$$\rightarrow \boxed{\left(\frac{\partial T}{\partial P}\right)_{N,S} = \left(\frac{\partial V}{\partial S}\right)_{N,P}} \quad \text{(other iden. with } \mu, N\text{)}$$

Heat Capacity: $\boxed{C = \dfrac{Q}{\Delta T} = \dfrac{\Delta U - W}{\Delta T}}$

Specific Heat Capacity : $c \equiv C/m$

3rd Law : $\boxed{\lim_{T \to 0} S(T) \to 0 = C(T) \ \Rightarrow\ T \not< 0}$

2.1 Isochoric (iV): $\boxed{\frac{dV}{dt} = 0}$ & "Isomolic" (iN): $\boxed{\frac{dN}{dt} = 0}$

$\rightarrow \ \Delta U = Q + W_{\text{other}} + \cancel{W_{\text{cpr}}} \quad$ (QW)

$\boxed{dU = \delta Q + \delta W_{\text{other}}}$

- IG Energy Capacity :

$C_V = \frac{Q}{\Delta T} = \frac{\Delta U}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_{N,V}$

$\qquad = \partial_t \left(\frac{f}{2} nRT\right) \quad$ (normal temp. ET)

$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{f}{2} nR}$

- $\boxed{\Delta U = Q = \frac{f}{2} nRT}$

- $\boxed{\begin{aligned} \Delta S &= \int \frac{\delta Q}{T} = \int \frac{C_V\,dT}{T} \\ &= \frac{f}{2} nR \ln\left(\frac{T_f}{T_i}\right) \end{aligned}}$ (3rd Law)

$\lim_{T \to 0} S(T) = 0$

(ignoring residual)

2.2 iN & Isobaric (iP): $\boxed{\frac{dP}{dt} = 0}$

$\rightarrow \ \Delta H = \Delta U + P\Delta V$

$\qquad = Q + W_{\text{other}} + \cancel{W_{\text{cpr}}} + \cancel{P\Delta V} \quad$ (QW)

$\boxed{dH = \delta Q + \delta W_{\text{other}}}$

- IG Enthalpy Capacity :

$C_P = \frac{Q}{\Delta T} = \frac{\Delta U + P\Delta V}{\Delta T} = \left(\frac{\partial H}{\partial T}\right)_{N,P}$

$\qquad = \left(\frac{\partial U}{\partial T}\right)_{N,P} + P\left(\frac{\partial V}{\partial T}\right)_{N,P}$

$\qquad = C_V + P\,\partial_t \left(\frac{nRT}{P}\right) \quad$ (normal temp. ET)

$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_{N,P} = \frac{f}{2} nR + nR \ = \ C_V + nR}$

- $\boxed{\Delta H = Q = (C_V + nR)T}$

- $\boxed{\begin{aligned} \Delta S &= \int \frac{\delta Q}{T} = \int \frac{C_P\,dT}{T} \\ &= (C_V + nR) \ln\left(\frac{T_f}{T_i}\right) \end{aligned}}$ (3rd Law)

$\lim_{T \to 0} S(T) = 0$

(ignoring residual)

- Latent Heat of Transformation : $L \equiv Q/m$

(phase change at constant 1 atm)

3   Entropy and Engine Efficiency

<u>Entropy :</u> $\boxed{S \equiv k_b \ln \Omega}$

<u>2nd Law :</u> $\boxed{\text{System Action s.t. } \Omega \uparrow \ \& \ S \uparrow}$

$$\boxed{dS = \frac{1}{T} \ dU + \frac{P}{T} \ dV - \sum \frac{\mu_i}{T} \ dN_i + \dots}$$

- $\boxed{\left(\dfrac{\partial S}{\partial U}\right)_{V,N} \equiv \dfrac{1}{T}}$

  $$0 < \left(\frac{1}{T_1} = \frac{\Delta S_1}{\Delta U_1}\right) < \left(\frac{1}{T_2} = \frac{\Delta S_2}{\Delta U_2}\right)$$

  $\Rightarrow \ (\Delta U_1 < 0 < \Delta U_2)$

  $\Rightarrow \ (U_1 > U_2) \ \Leftrightarrow \ \boxed{\text{``}U_1 \to U_2\text{''}}$

  $\Rightarrow \ (T_1 > T_2) \ \Leftrightarrow \ \boxed{\text{``}T_1 \to T_2\text{''}}$

  <div align="center">(Ener. flows from high temp. to low temp.)</div>

- $\boxed{T\left(\dfrac{\partial S}{\partial V}\right)_{U,N} = P}$

  $$0 < \left(P_1 \sim \frac{\Delta S_1}{\Delta V_1}\right) < \left(P_2 \sim \frac{\Delta S_2}{\Delta V_2}\right)$$

  $\Rightarrow \ (\Delta V_1 < 0 < \Delta V_2)$

  $\Rightarrow \ (V_1 > V_2) \ \Leftrightarrow \ \boxed{\text{``}V_1 \to V_2\text{''}}$

  $\Rightarrow \ (P_1 < P_2) \ \Leftrightarrow \ \boxed{\text{``}P_1 \to P_2\text{''}}$

  <div align="center">(Vol. flows from low pres. to high pres.)</div>

- <u>Chemical Potential:</u> $\boxed{\mu \equiv -T\left(\dfrac{\Delta S}{\Delta N}\right)_{U,V} = \left(\dfrac{\Delta U}{\Delta N}\right)_{S,V}}$

  (usually negative, but particle may include kinetic energy that converts to potential, for it to be added into the system)

$$\mu_2 < \mu_1 < 0 < \left(\|\mu_1\| \sim \frac{\Delta S_1}{\Delta N_1}\right) < \left(\frac{\Delta S_2}{\Delta N_2} \sim \|\mu_2\|\right)$$

$\Rightarrow \ (\Delta N_1 < 0 < \Delta N_2)$

$\Rightarrow \ (N_1 > N_2) \ \Leftrightarrow \ \boxed{\text{''}N_1 \to N_2\text{''}}$

$\Rightarrow \ (\mu_1 > \mu_2) \ \Leftrightarrow \ \boxed{\text{''}\mu_1 \to \mu_2\text{''}}$ (Part. flows from high μ to low μ)

3.1   QW

$\to \ T \ dS = dU + P \ dV - \mu \ dN + \dots$

$$\boxed{dS = \frac{\delta Q}{T} + \frac{\delta W_{\text{other}}}{T} - \frac{\mu \ dN}{T} + \dots}$$

- (iN) $\Rightarrow \ \boxed{\delta Q = T \ dS}$

  <div align="center">(if no other work)</div>

  <div align="center">(means RV)</div>

3.2   Isentropic (iS): $\boxed{\Delta S = 0}$

- (QS, aB, iN) $\Rightarrow \ \boxed{\delta Q = T \ dS = 0 = \Delta S}$

  <div align="center">(if no other work)</div>

  <div align="center">(means RV)</div>

3.3   Engines and Efficiency

Engine Efficiency, e:

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \quad \rightarrow$$

$$\boxed{e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}}$$

$$\boxed{e \leq 1 - \frac{T_c}{T_h} = \frac{T_h - T_c}{T_h}}$$

Carnot Engine Cycle:

1. iT Expansion at $\sim_< T_h$ to Absorb Q_h

2. aB Expansion to Reduce Temp to $\sim_> T_c$ and Expel W

3. iT Compression to Expel Q_c

4. aB Compression to Increase Temp to $\sim_< T_h$

- $\boxed{\int P \, dV = W = Q = \Delta T \cdot \Delta S}$

Carnot Fridge Cycle:

1. iT Compression at $\sim_> T_h$ to Expel Q_h

2. aB Expansion Absorbing W to Reduce Temp to $\sim_< T_c$

3. iT Expansion to Absorb Q_c

4. aB Compression to Increase Temp to $\sim_< T_h$

Refrigerator Coefficient of Performance (COP):

$$\frac{Q_h}{T_h} \geq \frac{Q_c}{T_c} \quad \rightarrow$$

$$\boxed{\text{COP} = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{Q_h/Q_c - 1}}$$

$$\boxed{\text{COP} \leq \frac{1}{T_h/T_c - 1} = \frac{T_c}{T_h - T_c}}$$

$$\left(W + Q_c = W + [\text{COP}] \cdot W \right)$$

Real Fridge:

1. Reduce High Pressure Liquid to Low Pressure and Temp Liquid/Gas By Throttling (see below)

2. Absorb Q_c In Evaporator to Complete Phase Change (Maybe Increase Temp A Little)

3. Adiabatically Compress Low Pressure Gas To High Pressure and Temp in Compressor

4. Cool Down Gas To Liquid in Condenser (Pipes to Outside Heat Reservoir)

— Joule-Thompson Effect (Throttling) —

- H is conserved

- "The force between any two molecules is weakly attractive at long distances and strongly repulsive at short distances. Under most (though not all) conditions the attraction dominates; then $U_{\text{potential}}$ is negative, but becomes less negative as the pressure drops and the distance between molecules increases. To compensate for the increase in potential energy, the kinetic energy generally drops, and the fluid cools as desired." - Schroeder, P.140

"...Starting from room temperature, the Hampson-Linde cycle can be used to liquefy any gas except hydrogen or helium. These gases, when throttled starting at room temperature and any pressure, actually become hotter. This happens because the attractive interactions between the molecules are very weak; at high temperatures the molecules are moving too fast to notice much attraction, but they still suffer hard collisions during which there is a large positive potential energy. When the gas expands the collisions occur less frequently, so the average potential energy decreases and the average kinetic energy increases. To liquefy hydrogen or helium, it is therefore necessary to first cool the gas well below room temperature, slowing down the molecules until attraction becomes more important than repulsion."

3.4   Shannon Entropy: $\boxed{S = -k_b \sum_s P(s) \ln P(s)}$

$$S = -k \sum_s P(s) \ln P(s) = -k \sum_s \frac{e^{-\beta E(s)}}{Z} \left(\ln e^{-\beta E(s)} - \ln Z \right) \qquad \text{(see Canonical Ensemble)}$$

$$= k\beta \sum_s E(s) \frac{e^{-\beta E(s)}}{Z} + k \ln Z \sum_s \frac{e^{-\beta E(s)}}{Z}$$

$$= \frac{\overline{E}}{T} + k \ln Z = \frac{U - F}{T} \quad \checkmark \qquad \text{(see Helmholtz Free Energy)}$$

Form Motivation

- Extensive : $S_{AB} = S_A + S_B$
- Probability : $P_{A_B} = P_A P_B$

$\Leftarrow S \propto \sum_s \ln P(s)$

- Positive : $S \sim -\sum_s \ln P(s)$

- Bounded : $S \sim -\sum_s P(s) \ln P(s)$

$S_{AB} \propto -\sum P_{AB} \ln P_{AB}$

$= -\sum P_A \ln P_A - \sum P_B \ln P_B$

$= S_A + S_B$

4 Microcanonical Ensemble (NVE*)   *(E means U here)

Generalized Partition Function:

1.) Ω (multiplicity)

Characteristic State Function, TS:

1.) $[S = k \ln \Omega] \leftrightarrow [\beta TS = \ln \Omega] \leftrightarrow \left[\Omega = e^{\beta TS}\right]$

2.) $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$

3.) $\Delta S = \int \frac{\delta Q}{T}$

Total [Relevant] Energy:

1.) $\left[\frac{\partial S}{\partial U} = \frac{1}{T}\right] \rightarrow \left[\frac{\partial U}{\partial q_i} = T\frac{\partial S}{\partial q_i}\right]$

2.) $\beta \frac{\partial U}{\partial \beta} = \frac{\partial(\beta TS)}{\partial \beta} = \frac{\partial \ln \Omega}{\partial \beta} = \frac{1}{\Omega}\frac{\partial \Omega}{\partial \beta}$

Stirling's Approximation:

1.) $N! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$

2.) $\ln N! \approx N \ln N - N$

4.1 Monoatomic Ideal Gas

- $\Omega = f(N)V^N U^{3N/2}$

- Sackur-Tetrode

$$S/k = N\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

$$= N\ln V + N\ln U^{3/2} + f(N)$$

- $1/T = \left(\frac{\partial S}{\partial U}\right)_{N,V} \rightarrow \boxed{U = \frac{3}{2}Nk_bT}$

- $P/T = \left(\frac{\partial S}{\partial V}\right)_{U,N} \rightarrow \boxed{PV = Nk_bT}$

Free Expansion, Isothermic Expansion

$$\Delta S = \int \frac{PdV}{T} = Nk_b \ln \frac{V_f}{V_i}$$

Isothermic Mixing Two Different Gases

$$\Delta S = 2\int \frac{PdV}{T} = 2Nk_b \ln \frac{2V_i}{V_i} = 2Nk_b \ln 2$$

Adiabatic & QS

$$\Delta S = \int \frac{0}{T} = 0$$

4.2 Einstein Solid/Oscillator/Vibration   • $\boxed{\left(\frac{\partial U}{\partial q} = \hbar\omega\right)}$

- $\left[\Omega(N,q) = \frac{(q+N-1)!}{q!(N-1)!}\right] \approx \left(\frac{q+N}{q}\right)^q\left(\frac{q+N}{N}\right)^N \approx \left[\left(\frac{eq}{N}\right)^N e^{N^2/q} \approx \left(\frac{eq}{N}\right)^N\right]$ $q \gg N$

- $S/k \approx q\ln\left(\frac{q+N}{q}\right) + N\ln\left(\frac{q+N}{N}\right) \approx N + N\ln\left(\frac{q}{N}\right)$ $q \gg N$

- $\left(T\frac{\partial S}{\partial q} = \frac{\partial U}{\partial q}\right)_{N,V} \rightarrow \boxed{U = \frac{N\hbar\omega}{e^{\hbar\omega/kT} - 1}} \rightarrow \boxed{C_V = Nk_b}$ $q \gg N, \; kT \gg \hbar\omega$

4.3 Two-State Paramagnet

- $\Omega(N, N_\uparrow) = \frac{N!}{N_\uparrow! N_\downarrow!}$

- $S/k \approx N\ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow)\ln(N - N_\uparrow)$

- $\boxed{(U = -MB)} = -\mu B N_\uparrow + \mu B N_\downarrow = \mu B(N - 2N_\uparrow)$

- $\left(T\frac{\partial S}{\partial N_\uparrow} = \frac{\partial U}{\partial N_\uparrow}\right)_{N,V,B}$

$$\boxed{M = N\mu \tanh \frac{\mu B}{kT}} \quad (\tanh x \approx x \approx 0)$$

5 Gibbs Free Energy

(see Helmholtz initally for easier comparison first)

Gibbs Free Energy :

$$G \equiv H - TS$$
$$= U + PV - TS$$

Maxwell Identity: $\dfrac{\partial}{\partial V}\left(\dfrac{\partial H}{\partial T}\right) = \dfrac{\partial}{\partial T}\left(\dfrac{\partial H}{\partial V}\right)$

$$dG = dH - T\ dS - S\ dT$$
$$= -S\ dT + V\ dP + \sum \mu_i\ dN_i + \dots$$

$\rightarrow$ $\boxed{-\left(\dfrac{\partial S}{\partial P}\right)_{N,T} = \left(\dfrac{\partial V}{\partial T}\right)_{N,P}}$ (other iden. with μ,N)

- $\boxed{\mu_i = \left(\dfrac{\partial G}{\partial N_i}\right)_{T,P}}$ $\Rightarrow$ $\boxed{G = \sum \mu_i N_i}$ ($\underline{T}$ and P are intensive, so $\mu \neq \mu(N)$)

IG : $\dfrac{\partial \mu}{\partial P} = \dfrac{1}{N}\dfrac{\partial G}{\partial P} = \dfrac{V}{N} = \dfrac{k_b T}{P}$ $\Rightarrow$ $\boxed{\mu(T,P) = \mu^\circ(T) + k_b T \ln\left(\frac{P}{P^\circ}\right)}$

5.1 iPT

$\boxed{\Delta G = \Delta H + T\Delta S}$

$$= \Delta U + P\Delta V - T\Delta S$$
$$= Q + \cancel{W_{\text{cpr}}} + W_{\text{other}} + \cancel{P\Delta V} - T\Delta S$$
$$= W_{\text{other}} - \left(W_{\text{other}} - \sum \mu_i \Delta N_i + \dots\right)$$
$$= \sum \mu_i \Delta N_i - \dots$$

$\rightarrow$

$$
\begin{array}{rcl}
dG & \leq & \delta W_{\text{other}} \\
& \text{(and)} & \\
dG & \leq & \sum \mu_i\ dN_i
\end{array}
$$

5.2 iNPT

$$dS_{\text{total}} = dS + dS_R = dS + \frac{dU_R}{T_R}$$

$$= dS - \frac{dU}{T} - \frac{P\ dV}{T} = -\frac{1}{T}(dU + P\ dV - T\ dS)$$

$\boxed{dS_{\text{total}} \uparrow = -\dfrac{dG \downarrow}{T}}$ $\qquad$ $G \downarrow = \boxed{U \downarrow} + \boxed{PV \downarrow} - TS \uparrow$

5.3   Example: Electrolysis Chemical Reaction

	H_2O $\longrightarrow$ H_2 $+$ $\frac{1}{2}O_2$	
S	$(70 \text{ J/K}) \longrightarrow (131 \text{ J/K}) + \frac{1}{2}(205 \text{ J/K})$	$\Delta S = 163 \text{ J/K}$
$\Delta_f H$	$(\text{-286 J}) \longrightarrow (0 \text{ J}) + \frac{1}{2}(0 \text{ J})$	$\Delta H = 286 \text{ J}$

$$\Delta G \quad + \quad T\Delta S \quad = \quad \Delta U \quad + P\Delta V$$
$$(237 \text{ kJ}) + (298 \text{ K})(163 \text{ J/K}) = (282 \text{ kJ}) + (4 \text{ kJ})$$

5.4   Clausius-Clapeyron Relation (Phase Boundaries)

$$\left.\begin{array}{l} \text{At Phase Boundary:} \quad G_g = G_l \\ \text{Remain on Boundary:} \quad dG_g = dG_l \end{array}\right\} \quad \Rightarrow \quad -S_l \, dT + V_l \, dP = -S_g \, dT + V_g \, dP$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \left(\frac{\Delta S}{\Delta V}\right)_{gl} = \left(\frac{L}{T\Delta V}\right)_{gl}}$$

5.5   van der Waals Model (Liquid-Gas)

$$P = P_{\text{no attraction}} + P_{\text{vdW}}$$

$$= \frac{NkT}{V - Nb} - \frac{\partial}{\partial V}\left(U_{\text{pot. e. attraction}}\right)$$

$$= \frac{NkT}{V - Nb} - \frac{\partial}{\partial V}\left(-a\left[\tfrac{N}{V}\right] \cdot N\right)$$
$$(\uparrow \text{ dens.} = \uparrow \text{ attract.})$$

$$= \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

$$\Rightarrow \boxed{\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_b T}$$

$$\left(\frac{\partial G}{\partial P}\right)_{N,T} = V \;\Rightarrow\; \boxed{\left(\frac{\partial G}{\partial V} = V \frac{\partial P}{\partial V}\right)_{N,T}}$$

An isotherm (V, P) is either a monotonic decrease like an exponential curve for $T \geq T_c$ (one-to-one), or like a mexican-hat curve for smaller $T < T_c$ (not one-to-one). The mexican-hat curve could be misinterpreted since it looks like decreasing volume will start decreasing pressure at the hill/peak of the curve. Graphing (G, P) parametrically with decreasing V, one sees that the line does a triangular loop and intersects itself at the point of vapor pressure. Since the thermodynamic stable state is at the lowest G, the system will skip the loop (representing unstable states). On the PV diagram, this corresponds to a flat, straight line at the vapor pressure between the curve's two critical points (in the differential sense) - the peak and trough - connecting a higher volume to a lower volume (the mexican-hat is not one-to-one). This sharp decrease in volume at the same pressure describes a phase change from higher volume gas to lower volume liquid at vapor pressure. The curve between these two volumes represents the thermodynamic state if the fluid were homogenous. But these "are unstable, since there is always another state (gas or liquid) at the same pressure with a lower Gibbs free energy."

Maxwell Construction: To find the vapor pressure without graphing (G, P) and finding the intersection, note that

$$0 = \int_{\text{loop}} dG = \int_{\text{loop}} \left(\frac{\partial G}{\partial P}\right)_{N,T} dP = \int_{\text{loop}} V dP.$$

On the (P, V) graph, this corresponds to the summing the area between the mexican-hat curve and the flat vapor pressure line. The area is divided in two: one beneath the curve's hill/peak (positive area) and above the line, and the other beneath the line and above the curve's valley/trough (negative area). The line should be chosen so that the sum of the two is zero.

Such a line can't be made when the isotherm is in a monotonic decrease (or increase at a decreasing volume) when the temperature exceeds the critical point, $T \geq T_c$. Here, decreasing volume consistently means an increasing pressure, and there is no loop in the (G, P) parametric graph. Above T_c, there is no phase change between liquid and gas, and there is little distinction between them.

The model is good qualitatively, but not quantitatively in practice.

6   Helmholtz Free Energy

Helmholtz Free Energy : $\boxed{F \equiv U - TS}$ Maxwell Identity: $\dfrac{\partial}{\partial V}\left(\dfrac{\partial F}{\partial T}\right) = \dfrac{\partial}{\partial T}\left(\dfrac{\partial F}{\partial V}\right)$

$$\boxed{\begin{aligned} dF &= dU - T\,dS - S\,dT \\ &= -S\,dT - P\,dV + \sum \mu_i\,dN_i + \dots \end{aligned}}$$

$\rightarrow \boxed{\left(\dfrac{\partial S}{\partial V}\right)_{N,T} = \left(\dfrac{\partial P}{\partial T}\right)_{N,V}}$ (other iden. with μ,N)

6.1   iT

$$\begin{aligned} \Delta F &= \Delta U - T\Delta S \\ &= W + Q - T\Delta S \\ &= W_{\text{cpr}} + W_{\text{other}} - \left(W_{\text{other}} - \sum \mu_i \Delta N_i + \dots\right) \\ &= W_{\text{cpr}} + \sum \mu_i \Delta N_i - \dots \end{aligned}$$

$\rightarrow$

$$\boxed{\begin{aligned} dF &\leq \delta W \\ &\text{(and)} \\ dF &\leq \delta W_{\text{cpr}} + \sum \mu_i\,dN_i \end{aligned}}$$

6.2   iVT

$$\Delta F = \sum \mu_i \Delta N_i - \dots \qquad \rightarrow \qquad \boxed{dF \;\leq\; \sum \mu_i\,dN_i}$$

6.3   iNVT

$$dS_{\text{total}} = dS + dS_R = dS + \frac{dU_R}{T_R} + \cancel{\frac{P\,dV - \sum \mu_i N_i}{T}}_{R}$$

$$= dS - \frac{dU}{T} = -\frac{1}{T}(dU - T\,dS)$$

$$\boxed{dS_{\text{total}} \uparrow = -\frac{dF \downarrow}{T}} \qquad F \downarrow = \boxed{U \downarrow} - TS \uparrow$$

6.4   iNV (see Canonical Ensemble)

1.) $\tilde{F} \equiv -kT \ln Z$:

$$\begin{aligned} \left(\frac{\partial \tilde{F}}{\partial T}\right)_{V,N} &= -k \ln Z - kT\,\frac{\partial \beta}{\partial T}\frac{\partial \ln Z}{\partial \beta} \\ &= \frac{\tilde{F}}{T} - kT\left(\frac{-1}{kT^2}\right)\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\ &= \frac{\tilde{F}}{T} - \frac{\overline{E}}{T} \equiv \frac{\tilde{F}}{T} - \frac{U}{T} \quad \text{\small (U is now $\overline{E}$?)} \end{aligned}$$

2.) $\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$

$$= \frac{F - U}{T}$$

3.) $T = 0$

$$\begin{aligned} \tilde{F}(0) &= -kT \ln Z(0) \\ &= -kT \ln e^{-U_0/kT} \\ &= U_0 = F(0) \end{aligned}$$

4.) $\Rightarrow \boxed{F = -k_b T \ln Z \;\Leftrightarrow\; Z(T) = e^{-\beta F}}$

7   Canonical Ensemble (NVT)

Single Particle:

- Particle Energy, E
- Ext. Heat Reservoir Energy, U_R

- $U_{R(s_1)} + E_{(s_1)} = U_{R(s_2)} + E_{(s_2)}$

$$\frac{P_{(s_2)}}{P_{(s_1)}} = \frac{\Omega_{(s_2)}}{\Omega_{(s_1)}} = \frac{d_{(s_2)}\ e^{S_R(s_2)/k}}{d_{(s_1)}\ e^{S_R(s_1)/k}}$$

$$\Rightarrow \frac{P_{(s_2)}}{P_{(s_1)}} = \frac{d_{(s_2)}\ e^{\beta U_R(s_2)}}{d_{(s_1)}\ e^{\beta U_R(s_1)}} = \frac{d_{(s_2)}\ e^{-\beta E(s_2)}}{d_{(s_1)}\ e^{-\beta E(s_1)}} \ , \quad \boxed{\beta \equiv \frac{1}{k_b T}}$$

$$\Rightarrow \underline{\text{Boltzmann Factor}} : \ \boxed{e^{-\beta E_i}} \sim \Omega_i(U) = e^{S(U)/k_b}$$

Partition Function:

1.) Single Particle/DOF :

$$\boxed{Z(T) \equiv \sum_{s_i} d_i\ e^{-E_i/k_b T}}$$

(DOF like x, y, z directions, rot., vib., etc.)

2.) Energy State Probability :

$$\boxed{P_{(s_i)} = \frac{d_i\ e^{-E_i/k_b T}}{Z}}$$

3.) Nonint., Mult. Dist. Particles/DOF :

$$\boxed{Z^{(N)} = Z_1 Z_2 \ldots Z_N = \prod_i^N Z_i}$$

4.) Nonint., Mult. Indist. Particles :

$$\boxed{Z^{(N)} \approx \frac{1}{N!} Z_1^N} \quad \begin{array}{l}\text{(same-state particles are overcounted,} \\ \text{but are less likely in non-dense systems)}\end{array}$$

$$\mu = -kT \frac{\partial}{\partial N} \ln Z^{(N)} \ \approx \ -kT \frac{\partial}{\partial N}(N \ln Z_1 - N \ln N + N)$$

$$\boxed{\mu = -k_b T \ln \frac{Z_1}{N}}$$

Average Energy :

1.) $\boxed{\overline{E} \equiv \sum_s E_{(s)} P_{(s)} \equiv U_1}$

2.) $\boxed{\overline{E}, U^{(N)} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial(\beta F)}{\partial \beta}}$

Characteristic State Function, F (see F) :

1.) $\boxed{[F = -k_b T \ln Z] \leftrightarrow \big[-\beta F = \ln Z \big]}$

$$\boxed{\leftrightarrow \big[Z = e^{-\beta F} \big]}$$

2.) $\boxed{dF = -SdT - PdV + \mu dN}$

3.) $\boxed{S = \frac{\partial(kT \ln Z)}{\partial T}}$

7.1 Equipartition Theorem Proof

$d_q = 1 \ , \quad E_q = cq^2$

1.) $Z = \displaystyle\sum_q e^{-\beta c q^2} \approx \frac{1}{\Delta q} \int_0^\infty e^{-\beta c q^2} \, dq$

$\qquad\qquad = \frac{1}{\Delta q \sqrt{\beta c}} \displaystyle\int_0^\infty e^{-q^2} \, dq$

$\qquad\qquad = \frac{\sqrt{\pi}/2}{\Delta q \sqrt{c}} \, \beta^{-1/2}$

2.) $\overline{E} = -\dfrac{1}{Z}\dfrac{\partial Z}{\partial \beta} = \tfrac{1}{2} k_b T$ ☑

$\qquad (kT \gg \Delta q)$

not good for quantum systems
or low temp.

7.2 Diatomic Gas/Rotation

$d_j = 2j+1 \ , \qquad E_j = j(j+1)\epsilon \qquad (\epsilon \sim 1/2I)$

Dist. Atoms (Like CO, $\epsilon = 2.4\text{E-4 eV}$)

1.) $Z_{\text{rot}} = \displaystyle\sum d_j \, e^{-\beta E_j}$

$\qquad \approx \displaystyle\int d_j \, e^{-\beta E_j} \, dj = \frac{\beta}{\epsilon}{}_{(\beta \gg \epsilon)}$

2.) $\overline{E}_{\text{rot}} = -\dfrac{1}{Z_{\text{rot}}}\dfrac{\partial Z_{\text{rot}}}{\partial \beta} = k_b T \qquad \text{(ET)}$ ☑

3.) $\displaystyle\lim_{T \to 0} Z_{\text{rot}} = 1 + 3e^{-2\epsilon/kT} + \ldots$

$\qquad \Rightarrow \displaystyle\lim_{T \to 0} C_{\text{rot}}(T) = \lim_{T \to 0} \frac{\partial \overline{E}}{\partial T} = 0$ ☑

Indist. Atoms (H2 Example, $\epsilon = 7.6\text{E-3 eV}$)

1.) $Z_{\text{rot}} \approx \dfrac{\beta}{2\epsilon}{}_{(\beta \gg \epsilon)}$

2.) $\overline{E}_{\text{rot}} = -\dfrac{1}{Z_{\text{rot}}}\dfrac{\partial Z_{\text{rot}}}{\partial \beta} = k_b T \qquad \text{(ET)}$ ☑

3.) $\displaystyle\lim_{T \to 0} Z_{\text{rot}} = \sum d_j \, e^{-\beta E_j}$
$\begin{cases} j=2n & \text{para-H}_2 \\ \text{(sym.)} & \text{(sing. nuclei)} \\ \\ j=2n+1 & \text{ortho-H}_2 \\ \text{(anti-sym.)} & \text{(trip. nuclei)} \end{cases}$

$\qquad \Rightarrow$ Graph $\dfrac{C_{\text{rot}(kT/\epsilon)}}{k}$ with a few terms

7.3 Einstein Solid/Oscillator/Vibration

1.) $E_n = \hbar\omega(\tfrac{1}{2} + n)$ $\qquad\qquad\qquad \Delta E_n = n\hbar\omega \qquad$ (only care about exchangable energy)

2.) $Z_1 = \displaystyle\sum_n e^{-\beta(n+1/2)\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \qquad \rightarrow \qquad Z_1^\Delta = \sum_n e^{-\beta\Delta E} = \frac{1}{1 - e^{-\beta\hbar\omega}}$

3.) $U^\Delta = N\overline{E} = -\dfrac{N}{Z_1^\Delta}\dfrac{\partial Z_1^\Delta}{\partial \beta} = \dfrac{N\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \dfrac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \rightarrow \quad C_V = N k_b T$ ☑

$\qquad\qquad U = -\dfrac{N}{Z_1}\dfrac{\partial Z_1}{\partial \beta} = \dfrac{N\hbar\omega}{e^{\beta\hbar\omega} - 1} + \dfrac{N\hbar\omega}{2}e^{-\beta\hbar\omega/2}$

7.4 Two-State Paramagnet

$$\left(-MB \equiv U\right) = N\sum_s E(s)P(s)$$

$$= N\left[(-\mu B)P_\uparrow + (\mu B)P_\downarrow\right] \quad = \quad \mu B N (1 - 2P_\uparrow) \qquad \text{(compare to Microcanonical)}$$

$$= -\mu B N \left(\frac{e^{\mu B/kT} - e^{-\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}}\right) = -\mu B N \tanh \frac{\mu B}{kT} \quad \boxed{\checkmark}$$

7.5 Ideal Gas

1.) $Z_{\text{kin}} = \left(\sum_n e^{-\beta E_{\text{inf. sq. well}}}\right)^3 \approx \left(\int_0^\infty e^{-\beta \frac{\hbar^2 k_n^2}{2m}}\, dn\right)^3 = \left(\frac{1}{2}\int_{-\infty}^\infty e^{-\beta \frac{\hbar^2 (\pi/L)^2}{2m} n^2}\, dn\right)^3$

$$= \left(\frac{\sqrt{\pi}}{2\sqrt{\beta \frac{\hbar^2 (\pi/L)^2}{2m}}}\right)^3 = \left(\frac{1}{\sqrt{\pi}}\frac{L}{2\pi/\sqrt{2mkT/\hbar^2}}\right)^3$$

$$= \left(\frac{1}{\sqrt{\pi}}\frac{L}{h/\sqrt{2mkT}}\right)^3 = \left(\frac{1}{\sqrt{\pi}}\frac{L}{\lambda_\beta}\right)^3 \equiv \left(\frac{L}{l_Q}\right)^3 = \frac{V}{v_Q} \qquad \begin{array}{l}(l_Q,\ \text{quantum length})\\ (v_Q,\ \text{quantum volume})\end{array}$$

2.) $Z^{(N)} = \dfrac{(Z_{\text{kin}}Z_{\text{int}})^N}{N!} = \dfrac{1}{N!}\left(\dfrac{V Z_{\text{int}}}{v_Q}\right)^N \quad \Rightarrow \quad \ln Z^{(N)} \approx N\left(\ln V + \ln Z_{\text{int}} - \ln v_Q - \ln N + 1\right)$

3.) $U^{(N)} = -\dfrac{\partial \ln Z^{(N)}}{\partial \beta} = \frac{3}{2}NkT + NU_{\text{int}}^{(1)} \qquad \boxed{\checkmark} \qquad \text{(rot. and vib. each add an } Nk \text{ to the } C_V\text{)}$

4.) $F^{(N)} = -kT\ln Z^{(N)} = -NkT\left(\ln V + \ln Z_{\text{int}} - \ln v_Q - \ln N + 1\right)$

$$= -NkT\left(\ln V - \ln v_Q - \ln N + 1\right) + NF_{\text{int}}^{(1)}$$

5.) $P = -\left(\frac{\partial F^{(N)}}{\partial V}\right)_{T,N} = \frac{Nk_b T}{V} \qquad \boxed{\checkmark}$

6.) $\left(\frac{\partial F}{\partial N}\right)_{T,V} = \boxed{\mu = -k_b T\ln\left(\frac{V Z_{\text{int}}}{N v_Q}\right) = -kT\ln\left(\frac{Z_1}{N}\right)}$

8 Grand Canonical Ensemble (μVT)

Gibb's Factor : $\boxed{e^{-\beta[E(s)-\mu N(s)]} \quad \rightarrow \quad e^{-\beta n_s(\epsilon_s - \mu_s)} = e^{-nx}}$ $\qquad$ $\begin{array}{l} n \equiv \text{part. per state, } s \\ x \equiv \beta(\epsilon - \mu) \end{array}$

Grand Partition Function : $\boxed{\mathcal{Z} = \sum_s e^{-\beta[E(s) - \sum_i \mu_i N_i(s)]} \quad \rightarrow \quad \sum_s e^{-\beta n_s(\epsilon_s - \mu_s)} = \sum_s e^{-nx}}$

Grand Potential : $\boxed{\Phi \equiv U - TS - \mu N = -kT \ln \mathcal{Z}}$

Average Particles Per State : $\quad \sum_n n P_n = \sum_n n \dfrac{e^{-nx}}{\mathcal{Z}} = -\dfrac{1}{\mathcal{Z}} \sum_n \dfrac{\partial}{\partial x} e^{-nx} = \boxed{\overline{n} = -\dfrac{1}{\mathcal{Z}} \dfrac{\partial \mathcal{Z}}{\partial x}}$

Average Total Particles : $\boxed{\overline{N} = \sum_i d_{(\epsilon_i)} \overline{n}_{(\epsilon_i)} \approx \int \rho_{(\epsilon)} \overline{n}_{(\epsilon)} \, d\epsilon}$ $\qquad$ $\begin{array}{l} (d_{(\epsilon_i)} \text{ degeneracies}) \\ (\rho_{(\epsilon)} \text{ state density}) \end{array}$

8.1 Example: O_2 and CO Bonding to Hemaglobin

1.) Variables :

$\epsilon_{O_2} \approx -0.7$ eV $\qquad\qquad\qquad\qquad$ $\epsilon_{CO} \approx -0.85$ eV

$\left. \begin{array}{l} T = 310 \text{ K} \\[2mm] P_{O_2} = .2 \text{ atm} \end{array} \right\} \rightarrow$ $\begin{array}{l} \mu_{O_2} = -k_b T \ln\left(\dfrac{V Z_{\text{int}}}{N v_Q}\right) \\[3mm] \approx -0.6 \text{ eV} \end{array}$ $\qquad$ $\begin{array}{l} P_{CO} = P_{O_2}/100 \rightarrow \mu_{CO} \approx \mu_{O_2} - kT \ln 100 \\[2mm] \approx -0.72 \text{ eV} \end{array}$

2.) O_2: $\qquad\qquad\qquad\qquad\qquad\qquad$ 3.) O_2 and CO:

$\quad$ (No Bonding) $\quad$ (O_2 Bonding) $\qquad\qquad\qquad$ (No Bonding) $\qquad$ (O_2 Bonding) $\qquad$ (CO Bonding)

$\mathcal{Z} = e^{-\beta(0)(\epsilon - \mu)} \; + \; e^{-\beta(\epsilon_{O_2} - \mu_{O_2})}$ $\qquad\qquad$ $\mathcal{Z} = e^{-\beta(0)(\epsilon - \mu)} \; + \; e^{-\beta(\epsilon_{O_2} - \mu_{O_2})} \; + \; e^{-\beta(\epsilon_{CO} - \mu_{CO})}$

$\qquad\quad 1 \qquad\qquad\qquad 40 \qquad\qquad\qquad\qquad\qquad\qquad 1 \qquad\qquad\qquad\qquad 40 \qquad\qquad\qquad\qquad 120$

$P\big(O_2 \text{ Bonding}\big) = \frac{40}{1+40} = 98\%$ $\qquad\qquad$ $P\big(O_2 \text{ Bonding}\big) = \frac{40}{1+40+120} = 25\%$

8.2   Fermi-Dirac Distribution (Fermions)

$$\overline{n} = \frac{(0)e^{-\beta(0)(\epsilon-\mu)} + (1)e^{-\beta(1)(\epsilon-\mu)}}{e^{-\beta(0)(\epsilon-\mu)} + e^{-\beta(1)(\epsilon-\mu)}}$$

$$= \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}}$$

$$\boxed{\overline{n}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}}$$

$$\begin{cases} \epsilon \ll \mu & \overline{n} \to 1 \\ \epsilon = \mu & \overline{n} = 1/2 \\ \epsilon \gg \mu & \overline{n} \to 0_+ \end{cases} \Rightarrow \begin{cases} \lim\limits_{T \to 0} \left.\dfrac{\partial \overline{n}}{\partial \epsilon}\right|_\mu = -\infty \\ \lim\limits_{T \to \infty} \left.\dfrac{\partial \overline{n}}{\partial \epsilon}\right|_\mu = 0 \end{cases}$$

$$\boxed{\overline{N} = \sum d_\epsilon \overline{n}\, d\epsilon = \int \rho_\epsilon \overline{n}\, d\epsilon} \quad \Rightarrow \quad \boxed{\lim_{T \to 0} \overline{N} = \int_0^\infty \rho_\epsilon \overline{n}\, d\epsilon = \int_0^\mu \rho_\epsilon\, d\epsilon}$$

8.3   Bose-Einstein Distribution (Bosons)

$$\mathcal{Z} = 1 + e^{-\beta(1)x} + e^{-\beta(2)x} + \dots$$

$$= \frac{1}{1 - e^{-\beta x}} \quad (\epsilon \ge \mu)$$

$$\downarrow$$

$$\boxed{\overline{n} = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}}$$

$$\begin{cases} \epsilon = \mu_+ & \overline{n} \to \infty \\ \epsilon \gg \mu & \overline{n} \to 0_+ \end{cases}$$

$$\boxed{\overline{N} = \sum d_\epsilon \overline{n}\, d\epsilon = \int \rho_\epsilon \overline{n}\, d\epsilon} \quad \Rightarrow \quad \boxed{\lim_{T \to 0} \overline{N} = ? \text{(split between ground state and higher states)}}$$

8.4   Maxwell-Boltzmann Distribution (Distinguishable)

$$\overline{n} = N P_1(\epsilon)$$

$$= \frac{N e^{-\beta\epsilon}}{Z_1} = \frac{N e^{-\beta\epsilon}}{N e^{-\beta\mu}}$$

$$\boxed{\overline{n} = e^{-\beta(\epsilon-\mu)}}$$

$$\begin{cases} \epsilon \ll \mu & \overline{n} \to \infty \\ \epsilon = \mu & \overline{n} = 1 \\ \epsilon \gg \mu & \overline{n} \to 0_+ \end{cases}$$

$$\boxed{\overline{N} = \sum d_\epsilon \overline{n}\, d\epsilon = \int \rho_\epsilon \overline{n}\, d\epsilon}$$

FDD, BED $\to$ MBD Condition:

- $\beta(\epsilon - \mu) \gg (1 > 0)$

$$\to \left[-kT + \epsilon \approx -kT\right] \gg \left[\mu = -kT \ln \frac{Z_1}{N}\right]$$

$$\to \boxed{Z_1 \gg Ne > N}$$