⇒ Solve sample midterms posted under "Modules" on Canvas

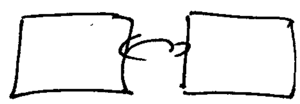
$S(E, V, N)$ $\qquad dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$

$S = k_B \ln \Omega$

All microstates are equally probable at equilibrium at const. (N, V, E)

Maximum Entropy Principle / 2^{nd} Law

S is max at Equil. at const N, E, V conditions



$\left.\begin{array}{l} T_1 = T_2 \\ P_1 = P_2 \\ \mu_1 = \mu_2 \end{array}\right\}$ if $\delta E, \delta V, \delta N$

S max @ N, V, E $\rightarrow$ E min @ S, V, N

$\left.\begin{array}{l} dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN \\ dE = T dS - P dV + \mu dN \end{array}\right\}$ Fundamental Equations

Euler's theorem $\qquad E = TS - PV + \mu N$

1^{st} Law $\qquad \Delta E = Q + W \qquad$ closed Systems

$dE = \delta Q + \delta W$

Quasistatic (internal equilibrium) + no ext. gradients:

<u>reversible</u> processes $\rightarrow (\delta Q)_{rev} = T dS$

$(\delta W) = -P dV$

$dE = T dS - P dV$ [<u>all</u> systems, const. N]

$$\Delta E = \int_{T_1}^{T_2} C_v\, dT + \underbrace{\Delta E_{kin}}_{\frac{1}{2}mu^2} + \underbrace{\Delta E_{pot}}_{mgh}$$

Reversible processes are "the best".
- lowest work input required
- highest work output produced

$E = C_v T$
$H = C_p T$
useful

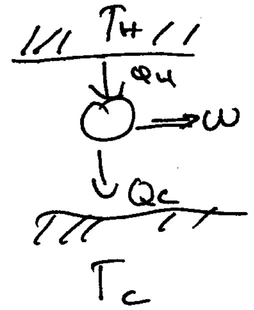
For ideal gases $dE = TdS - PdV = C_v\, dT \Rightarrow$

$$dS = C_v \frac{dT}{T} + R \frac{dV}{V} \Rightarrow \Delta S = C_v \ln\frac{T_2}{T_1} + R \ln\frac{V_2}{V_1} = C_p \ln\frac{T_2}{T_1} - R \ln\frac{P_2}{P_1}$$

Adiabatic (isentropic) expansion:

$$\Delta S = 0 \Rightarrow T_f = T_i \left(\frac{V_f}{V_i}\right)^{-R/C_v} \qquad T_f = T_i \left(\frac{P_f}{P_i}\right)^{R/C_p} \qquad P_f V_f^{\gamma} = P_i V_i^{\gamma}$$
$$\gamma = C_p / C_v$$

Heat Engines (Carnot) $\eta = \frac{T_H - T_C}{T_H}$ (for reversible)



$$\eta = -\frac{W}{Q_H}$$

Open Systems $dE = \delta Q + \delta W + \hat{h}_{in}\, dm_{in} - \hat{h}_{out}\, dm_{out}$

Steady state $0 = \dot{Q} + \dot{W} + \sum_{in} \hat{h}_{in} \dot{m}_{in} - \sum_{out} \hat{h}_{out} \dot{m}_{out}$

Entropy balance $\dot{S}_{world} = \sum_{out} \dot{m}_{out} \hat{S}_{out} - \sum_{in} \dot{m}_{in} \hat{S}_{in} - \frac{\dot{Q}}{T_{env}} \geq 0$
(steady-state only)

Fundamental Equations

$$dy^{(0)} = \xi_1 dx_1 + \xi_2 dx_2 + \cdots \xi_n dx_n$$
$$y^{(k)} = y^{(0)} - \xi_1 x_1 - \cdots - \xi_k x_k$$

$$dy^{(k)} = -x_1 d\xi_1 - x_2 d\xi_2 - \cdots - x_k d\xi_k + \xi_{k+1} dx_{k+1} + \cdots + \xi_n dx_n$$

$$y^{(0)} = E(S,V,N) \qquad dE = TdS - PdV + \mu dN$$

$$y^{(1)} = E - TS = A \qquad dA = -SdT - PdV + \mu dN$$

$$y^{(2)} = E - TS + PV = G \qquad dG = -SdT + VdP + \mu dN$$

$$y^{(3)} = E - TS + PV - \mu N = 0 \qquad \text{(Gibbs-Duhem)}$$

[The thermodynamic potential being minimized / maximized at equilibrium is the Legendre Transform with the proper variables (equil. constraints)]

E.g., @ const $P, S, N \rightarrow H$ is min @ equil

Manipulation of derivatives

Maxwell's $\quad \dfrac{\partial^2 f}{\partial x \partial y} = \dfrac{\partial^2 f}{\partial y \partial x} \qquad$ e.g. $\left.\dfrac{\partial V}{\partial T}\right)_{P,N} = -\left.\dfrac{\partial S}{\partial P}\right)$

Inversion $\quad \left.\dfrac{\partial x}{\partial y}\right)_z = \dfrac{1}{(\partial y/\partial x)_z} \qquad$ Chain $\quad \left.\dfrac{\partial x}{\partial y}\right)_z = \dfrac{(\partial x/\partial w)_z}{(\partial y/\partial w)_z}$

XYZ-1 $\quad \left.\dfrac{\partial x}{\partial y}\right)_z \left.\dfrac{\partial z}{\partial x}\right)_y \left.\dfrac{\partial y}{\partial z}\right)_x = -1$

Ideal Gases

monoatomic $\begin{cases} S = Nk_B\left[\ln\left[\left(\dfrac{E}{N}\right)^{3/2}\dfrac{V}{N}\right] + \dfrac{5}{2} + \dfrac{3}{2}\ln\dfrac{4\pi m}{3h^2}\right] \\ E = \dfrac{3}{2}k_B T N \qquad C_V = \dfrac{3}{2}k_B \end{cases}$

All : $\begin{cases} PV = k_B N T \\ \mu = k_B T \ln P + \mu^0(T) \end{cases}$

Non-ideal Gases

$$k_B T \ln f = \mu(T,P) - \mu^\circ(T,P^\circ)$$

$$f \to P \quad \text{as} \quad P \to 0$$

$$k_B T \left.\frac{\partial \ln f}{\partial P}\right)_T = v \quad \Rightarrow \quad \ln \frac{f}{P'} = \int_0^{P'} \left(\frac{v}{k_B T} - \frac{1}{P} \right) dP$$

Gas mixtures

$$P_i = y_i P = \frac{N_i P}{N}$$

$$PV = N k_B T \qquad \mu_i = \mu_i^{(0)}(T,P^\circ) + k_B T \ln P_i$$