Equilibrium and State Quantities

The Laws of Thermodynamics

Phase Tranisitions and Chemical Reactions

$$K(p,T) = \exp\left\{\frac{1}{kT}\left(\sum_i a_i\mu_i(p,T) - \sum_j b_j\mu_j(p,T)\right)\right\} = \frac{X_{B_1}^{b_1}X_{B_2}^{b_2}\dots}{X_{A_1}^{a_1}X_{A_2}^{a_2}\dots}$$

Law of mass action, determines concetration of species in chemical reaction (GNS 3.33)

$$\frac{\Delta p}{p(T)} = X_{\text{sub}}$$ Raoult's law, pressure of a solvent with dissolved material (GNS 3.39)

$$X = X_0\frac{p}{p_0}$$ Henry-Dalton law, concentration of a gas in a solution (GNS pg. 78)

$$\mu(p,T) = kT\left(\frac{5}{2} - s_0\right) - kT\ln\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}$$ Chem. pot. of ideal gas (GNS 4.14)

$$F = U - TS = -pV = \mu N$$ Free energy [Helmholtz potential] (GNS 4.36)

$$-S = \left.\frac{\partial F}{\partial T}\right|_{V,N,\dots}, \quad -p = \left.\frac{\partial F}{\partial V}\right|_{T,N,\dots}, \quad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V,\dots}$$

State quanties from free energy (GNS 4.39)

$$dF = 0, \quad F = F_{min}$$ Property of irreversible processes (GNS 4.50)

$$F(T,V,N) = NkT\left\{\frac{3}{2} - s_0 - \ln\left[\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right]\right\}$$ F of ideal gas (GNS 4.53)

$$H = U + pV = TS + \mu N$$ Definition of enthalpy (GNS 4.59)

$$T = \left.\frac{\partial H}{\partial S}\right|_{p,N,\dots}, \quad V = \left.\frac{\partial H}{\partial p}\right|_{S.N,\dots}, \quad \mu = \left.\frac{\partial H}{\partial N}\right|_{S,p,\dots}$$

State quantities from enthalpy (GNS 4.61)

$$H(T,p,N) = \frac{5}{2}NkT$$ Enthalpy of an ideal gas (GNS 4.78)

$$C_p = \frac{5}{2}Nk$$ Specific heat, constant pressure, of an ideal gas (GNS 4.79)

$$C_v = \frac{3}{2}Nk$$ Specific heat, constant volume, of an ideal gas (GNS 4.80)

$$G = U - TS + pV$$ Free enthalpy [Gibbs' potential] (GNS 4.81)

$$-S = \left.\frac{\partial G}{\partial T}\right|_{p,N,\dots}, \quad V = \left.\frac{\partial G}{\partial p}\right|_{T}, N, \dots, \quad \mu = \left.\frac{\partial G}{\partial N}\right|_{T,p,\dots}$$

State quantities from Gibbs' potential (GNS 4.83)

$$G(T,p,N) = N\mu(T,p)$$ Free enthalpy of the ideal gas (GNS Ex. 4.10)

$$H = G - T\left.\frac{\partial G}{\partial T}\right|_{p,N} = -T^2\frac{\partial}{\partial T}\left.\left(\frac{G}{T}\right)\right|_{p,N}$$ Gibbs-Helmholtz equation (GNS 4.94)

$$\Phi = U - TS - \mu N = -pV$$ Defintion of the grand potential (GNS 4.111,4.115)

$$-S = \left.\frac{\partial \Phi}{\partial T}\right|_{V,\mu}, \quad -p = \left.\frac{\partial \Phi}{\partial V}\right|_{T,\mu}, \quad -N = \left.\frac{\partial \Phi}{\partial \mu}\right|_{T,V}$$

State quantities from grand potential (GNS 4.113)

$$\left.\frac{\partial T}{\partial V}\right|_{S,N} = -\left.\frac{\partial p}{\partial S}\right|_{V,N}, \quad \left.\frac{\partial T}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial S}\right|_{V,N}, \quad -\left.\frac{\partial p}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial V}\right|_{S,N}$$

Maxwell relations following from potential energy (GNS 4.127)

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial p}{\partial T}\right|_{V,N}, \quad -\left.\frac{\partial S}{\partial N}\right|_{T,V} = \left.\frac{\partial \mu}{\partial T}\right|_{V,N}, \quad -\left.\frac{\partial p}{\partial N}\right|_{T,V} = \left.\frac{\partial \mu}{\partial V}\right|_{T,N}$$

Maxwell relations following from the free energy (GNS 4.129)

$$\left.\frac{\partial T}{\partial p}\right|_{S,N} = \left.\frac{\partial V}{\partial S}\right|_{p,N}, \quad \left.\frac{\partial T}{\partial N}\right|_{S,p} = \left.\frac{\partial \mu}{\partial S}\right|_{p,N}, \quad \left.\frac{\partial V}{\partial N}\right|_{S,p} = \left.\frac{\partial \mu}{\partial p}\right|_{S,N}$$

Maxwell relations following from the enthalpy (GNS 4.131)

$$-\left.\frac{\partial S}{\partial p}\right|_{T,N} = \left.\frac{\partial V}{\partial T}\right|_{p,N}, \quad -\left.\frac{\partial S}{\partial N}\right|_{T,p} = \left.\frac{\partial \mu}{\partial T}\right|_{p,N}, \quad \left.\frac{\partial V}{\partial N}\right|_{T,p} = \left.\frac{\partial \mu}{\partial p}\right|_{T,N}$$

Maxwell relations following from the free enthalpy (GNS 4.133)

$$\left.\frac{\partial S}{\partial V}\right|_{T,\mu} = \left.\frac{\partial p}{\partial T}\right|_{V,\mu}, \quad \left.\frac{\partial S}{\partial \mu}\right|_{T,V} = \left.\frac{\partial N}{\partial T}\right|_{V,\mu}, \quad \left.\frac{\partial p}{\partial \mu}\right|_{T,V} = \left.\frac{\partial N}{\partial V}\right|_{T,\mu}$$

Maxwell relations following from the grand potential (GNS 4.135)

$$\left.\frac{\partial V}{\partial T}\right|_{p} = \alpha V$$ Definition of the isobaric expansion ceofficient α (GNS 4.141)

$$\left.\frac{\partial V}{\partial p}\right|_{T} = -V\kappa$$ Defintion of the isothermal compressibility κ (GNS 4.143)

$$C_p = C_V + TV\frac{\alpha^2}{\kappa}$$ Relationship between C_p and C_V (GNS Ex. 4.12)

Number of Microstates Ω and Entropy S

$$\sigma(E) = \int_{E=H(q,p)} d\sigma$$ Surface area of energy hypersurface (GNS 5.7)

$$\omega(E,V,N) = \int_{H(q_\nu,p_\nu)\leq E} d^{3N}q\, d^{3N}p$$ Total phase-space volume (GNS 5.9)

$$\Omega(E,V,N) = \frac{\sigma(E,V,N)}{\sigma_0} = \frac{1}{\sigma_0}\frac{\partial\omega}{\partial E}$$ Microstates of distiguishable particles (GNS 5.13)

$$S = k\ln\Omega(E,V,N)$$ Statistical defintion of entropy (GNS 5.23)

$$\Omega(E,V,N) = \frac{1}{N!}\frac{\sigma(E,V,N)}{\sigma_0}$$ Microstates of indistiguishable particles (GNS 5.43)

$$S(E,V,N) = Nk\left\{\frac{5}{2} + \ln\left[\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right]\right\}$$ Sackur-Tetrode Equation (GNS 5.63)

$$\Omega(E,V,N) = g(E,V,N)E$$ Number of microstates from density of states (GNS 5.65)

$$g(E) = \frac{\partial\Sigma(E)}{\partial E}$$ Definition of the density of states (GNS 5.65)

$$\Sigma(E) = \frac{1}{N!h^{3N}}\int_{H(q_\nu,p_\nu)\leq E} d^{3N}p\, d^{3N}q$$

Number of microstates in energy sphere (GNS 5.65)

$$\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$ Thermal wavelength (GNS pg. 140)

Ensemble Theory and Microcanonical Ensembles

$$\langle f\rangle = \frac{1}{h^{3N}}\int d^{3N}q\, d^{3N}p\, f(q_\nu,p_\nu)\rho(q_\nu,p_\nu)$$

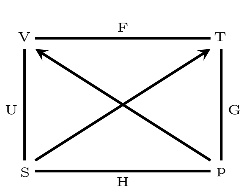
Definition of the ensemble average (GNS 6.8)

$$\rho_{\text{mc}} = \begin{cases}\frac{1}{\Omega} & E \leq H(q_v,p_v) \leq E + \Delta E\\ 0 & \text{otherwise}\end{cases}$$

Phase-space density of microcanonical ensemble (GNS 6.9)

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \{p,H\} = 0$$ Liouville's theorem (6.18)

$$S = \langle -k\ln\rho\rangle$$ Entropy as an ensemble average (GNS 6.37)



- The derivative of a potential (edge) with respect to a variable (corner) is given by the variable at the diagonally opposite corner. The arrows in the diagonals determine the sign.
- For the Maxwell relations, derivatives of variables along an edge of the quadrangle, at constant variable in the diagonally opposite corner, are just equal to the corresponding derivative on the other side.

The Canonical Ensemble

$$\rho_c(q_\nu, p_\nu) = \frac{\exp\{-\beta H(q_\nu, p_\nu)\}}{h^{-3N}\int d^{3N}q\, d^{3N}p\ \exp\{-\beta H(q_\nu, p_\nu)\}}$$

Canonical phase-space density (GNS 7.9)

$$Z = \sum_i \exp\{-\beta E_i\}$$ Canonical partition function (GNS 7.22)

$$Z = \frac{1}{h^{3N}}\int d^{3N}q\, d^{3N}p\ \exp\{-\beta H(q_\nu, p_\nu)\}$$ Continuous partition funciton (GNS 7.24)

$$F(T,V,N) = -kT \ln Z(T,V,N)$$ Free energy from the partition function (GNS 7.35)

$$Z(\beta) = \int_0^\infty dE\ g(E) e^{-\beta E}$$

Canonical partition function from microcanonical density of states (GNS 7.103)

$$g(E) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} d\beta\ e^{\beta E} Z(\beta)$$

Microcanonical density of states from partition function (GNS 7.107)

$$\langle T \rangle = -\frac{1}{2}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = \frac{3}{2} NkT$$ The virial theorem (GNS 7.149)

$$\langle H \rangle = \frac{1}{2} kT$$ Equipartition theorem (GNS 7.156)

Applications of Boltzmann Statistics

$$\chi = N\frac{g^2 \mu_B^2 j(j+1)}{3kT} = \frac{C}{T}$$ Magnetic susceptibility from the Curie law (GNS 8.52)

$$C = Nk\left(\frac{2\mu_B H}{kT}\right)^2 \exp\left\{\frac{2\mu_B H}{kT}\right\}\left(1 + \exp\left\{\frac{2\mu_B H}{kT}\right\}\right)^{-2}$$ Schottky heat cap. (GNS 8.60)

The Macrocanonical Ensemble

$$\rho_{gc}(N, q_\nu, p_\nu) = \frac{\exp\{-\beta(H(q_\nu, p_\nu) - \mu N)\}}{\sum_{N=0}^{\infty} h^{-3N}\int d^{3N}q \int d^{3N}p\ \exp\{-\beta(H(q_\nu, p_\nu) - \mu N)\}}$$

Grand canonical phase-space density (GNS 9.11)

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \int d^{3N}p\ \exp\{-\beta(H(q_\nu, p_\nu) - \mu N)\}$$

Grand canonical partition function (GNS 9.27)

$$\phi(T,V,\mu) = -kT \ln \mathcal{Z}(T,V,\mu)$$ Macrocanonical potential (GNS 9.38)

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty}\left(\exp\left\{\frac{\mu}{kT}\right\}\right)^N Z(T,V,N)$$

Relation between canonical and grand canonical partition functions (GNS 9.40)