Response function definitions:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Gases:

$$S(E,V,N) = k_B N \ln\left[(E/N)^{\frac{3}{2}}(V/N)\right] + \frac{3}{2}k_B N\left(\frac{5}{3} + \ln\left(\frac{4\pi m}{3h^2}\right)\right)$$

$$\mu(T,P) = \mu^0(T) + k_B T\ln(yP) \qquad \mu^0(T) \equiv -k_B T\ln\left(\frac{k_B T}{\Lambda(T)^3}\right) \qquad \Lambda(T) \equiv \left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{1}{2}}$$

$$\mu(T,P) = \mu^0(T) + k_B T\ln(yf) \qquad \ln\frac{f(T,P')}{P'} = \int_0^{P'}\left(\frac{v(T,P)}{k_B T} - \frac{1}{P}\right)dP = \int_0^{P'}\frac{Z(T,P)-1}{P}dP$$

Phase equilibrium:

$$\left(\frac{dP}{dT}\right)_{\text{phase boundary}} = \frac{\Delta h}{T\Delta v} \qquad \ln P^{\text{vap}}(T) = c_1 - \frac{c_2}{c_3 + T}$$

Stability criteria:

$$\frac{\partial^2 F}{\partial X^2} > 0 \qquad \frac{\partial^2 F}{\partial y^2} < 0$$

Solutions:

$$\mu_i(T,P,\{x\}) = \mu_i^*(T,P) + k_B T\ln(\gamma_i x_i)$$

$$y_i P = x_i P_i^{\text{vap}} \qquad T_b' \approx T_b\left(1 + \frac{k_B T_b}{\Delta h_{vap}}x_{solute}\right) \qquad \Pi = \frac{k_B T x_{\text{solute}}}{v} \approx \frac{k_B T c_{\text{solute}}}{\mathcal{M}_{\text{solute}}}$$

$$-SdT + VdP = \sum_i N_i d\mu_i$$

$$\bar{X}_i = \left(\frac{\partial X}{\partial N_i}\right)_{T,P,N_{j\neq i}} \qquad d\mu_i = -\bar{S}_i dT + \bar{V}_i dP + \sum_{k=1}^{C-1}\left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_{j\neq k}} dx_k$$

$$-[x_1\Delta S_1 + x_2\Delta S_2]dT + [x_1\Delta V_1 + x_2\Delta V_2]dP + \left[x_1 - x_2\frac{y_1}{y_2}\right]\left(\frac{\partial \mu_1^G}{\partial y_1}\right)_{T,P} dy_1 = 0$$

Solids:

$$\frac{c_V^{\text{E}}}{3k_B} = \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1\right)^2}, \quad \Theta_E \equiv \frac{h\nu}{k_B} \qquad c_V^{\text{D}}(T,V) = 9k_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\frac{x^4 e^x}{(e^x - 1)^2}dx, \Theta_D \equiv \frac{h\nu_m}{k_B}$$

Independent particles in the canonical ensemble:

$$Q = q^N \qquad \text{or} \qquad Q = \frac{q^N}{N!} \qquad \text{where} \qquad q \equiv \sum_{\mathcal{X}} e^{-\beta\epsilon(\mathcal{X})}$$

Canonical fluctuations:

$$\wp(E) = \frac{\Omega(E,V,N)e^{-\beta E}}{Q(T,V,N)} \qquad \langle E^\nu \rangle = \sum_E E^\nu \wp(E) = \frac{(-1)^\nu}{Q}\frac{\partial^\nu Q}{\partial \beta^\nu} \qquad \sigma_E^2 = C_V k_B T^2$$

Classical systems in the canonical ensemble:

$$\wp(p_x) = (2\pi m k_B T)^{-\frac{1}{2}} \exp\left(-\frac{p_x^2}{2mk_BT}\right) \qquad \langle K \rangle = \frac{3}{2}Nk_BT$$

$$\wp(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{mv^2}{2k_BT}\right) \qquad \langle v \rangle = \int v\wp(v)dv = \left(\frac{8k_BT}{\pi m}\right)^{\frac{1}{2}}$$

$$P = \frac{Nk_BT}{V} + \frac{1}{3V}\left\langle \sum \mathbf{f}_i \cdot \mathbf{r}_i \right\rangle$$

Gibbs entropy formula:

$$S = -k_B \sum_m \wp_m \ln \wp_m$$

Chemical equilibrium:

$$\prod_i P_i^{\nu_i} = K_P(T) \quad \text{where } K_P(T) \equiv \exp\left[-\frac{\sum_i \nu_i \mu_i^0}{k_BT}\right] \qquad \frac{d \ln K_P}{d(1/T)} = -\frac{\Delta h^0}{k_B} \quad \text{where } \Delta h^0 \equiv \sum_i \nu_i h_i^0$$

$$\prod_i \rho_i^{\nu_i} = K_C(T) \quad \text{where } K_C(T) \equiv \exp\left[-\frac{\sum_i \nu_i \mu_i^0}{k_BT}\right](k_BT)^{-\sum_i \nu_i}$$

$$\prod_i x_i^{\nu_i} = K_x(T,P) \quad \text{where } K_x(T,P) \equiv \exp\left[-\frac{\sum_i \nu_i \mu_i^*}{k_BT}\right]$$

$$\prod_i \rho_i^{\nu_i} = K_C(T,P) \quad \text{where } K_C(T,P) \equiv \exp\left[-\frac{\sum_i \nu_i \mu_i^*}{k_BT}\right]\rho_{\text{solvent}}^{\sum_i \nu_i}$$

$$\left(\frac{\partial \ln K_x}{\partial(1/T)}\right)_P = -\frac{\Delta h^*}{k_B} \quad \text{where } \Delta h^* \equiv \sum_i \nu_i h_i^* \qquad \left(\frac{\partial \ln K_x}{\partial P}\right)_T = -\frac{\Delta v^*}{k_BT} \quad \text{where } \Delta v^* \equiv \sum_i \nu_i v_i^*$$

Classical transition state theory:

$$\frac{\text{molecules reacted}}{\text{time} \cdot \text{volume}} = k_f \rho_A \rho_{BC} \qquad \text{where } k_f \equiv \left(\frac{k_BT}{h}\right)e^{-\beta\Delta F_f^\ddagger}$$

$$\Delta F_f^\ddagger \equiv -k_BT \ln\left[\frac{(q^\ddagger/V)}{(q_A/V)(q_{BC}/V)}\right] + U^\ddagger$$

Statistical mechanical ensembles

property	microcanonical	canonical	grand canonical	isothermal-isobaric
constant conditions	E, V, N	T, V, N	T, V, μ	T, P, N
fluctuations	none	E	E, N	E, V
microstate probabilities	$\wp_m = \frac{\delta_{E_m,E}}{\Omega(E,V,N)}$	$\wp_m = \frac{e^{-\beta E_m}}{Q(T,V,N)}$	$\wp_m = \frac{e^{-\beta E_m + \beta\mu N_m}}{\Xi(T,V,\mu)}$	$\wp_m = \frac{e^{-\beta E_m - \beta P V_m}}{\Delta(T,P,N)}$
partition function	$\Omega(E,V,N) = \sum_n \delta_{E_n,E}$	$Q(T,V,N) = \sum_n e^{-\beta E_n}$	$\Xi(T,V,\mu) = \sum_N \sum_n e^{-\beta E_n + \beta\mu N}$	$\Delta(T,P,N) = \sum_V \sum_n e^{-\beta E_n - \beta P V}$
relations to other partition functions	---	$Q = \sum_E e^{-\beta E}\Omega$	$\Xi = \sum_N \lambda^N Q$ $= \sum_N \sum_E \lambda^N e^{-\beta E}\Omega$ $\lambda \equiv \exp[\beta\mu]$	$\Delta = \sum_V e^{-\beta P V} Q$ $= \sum_V \sum_E e^{-\beta E - \beta P V}\Omega$
thermo-dynamic potential	$S = k_B \ln \Omega(E,V,N)$	$A = -k_B T \ln Q(T,V,N)$	$PV = k_B T \ln \Xi(T,V,\mu)$	$G = -k_B T \ln \Delta(T,P,N)$
classical partition function	$\Omega = \frac{1}{h^{3N} N!} \int \delta[H(\mathbf{p}^N, \mathbf{r}^N) - E]\, d\mathbf{p}^N d\mathbf{r}^N$	$Q = \frac{Z(T,V,N)}{\Lambda(T)^{3N} N!}$ $Z \equiv \int e^{-\beta U(\mathbf{r}^N)} d\mathbf{r}^N$ $\Lambda \equiv (h^2/2\pi m k_B T)^{\frac{1}{2}}$	$\Xi = \sum_{N=0}^{\infty} \frac{\lambda^N Z(T,V,N)}{\Lambda(T)^{3N} N!}$ $\lambda \equiv \exp[\beta\mu]$	$\Delta = \frac{1}{\Lambda(T)^{3N} N!} \int_0^\infty e^{-\beta P V} Z(T,V,N)\, dV$

*Sums over n correspond to sums over all microstates at a given V and N.

**Sums over N are from 0 to ∞, for V from 0 to ∞, and for E from $-\infty$ to ∞.

***Classical partition functions are given for a monatomic system of indistinguishable, structureless particles.