

APPENDIX: A Summary of Important Thermodynamic Fundamentals

REFERENCES:

H.F. Franzen, *Physical Chemistry of Inorganic Crystalline Solids*, Springer-Verlag, New York, 1986D.R. Gaskell, *Introduction to Metallurgical Thermodynamics*, Taylor & Francis, USA, 1983States and Processes:

A *microscopic state* is described by masses, velocities, positions, and all modes of motion of all constituent particles in the system.

A *macroscopic state* is described by the averaged / most probable / aggregated properties. Therefore, a macroscopic property can be defined without recognizing the particulate nature of matter.

Reversible processes are hypothetical changes through a succession of macroscopic states at equilibrium.

Equilibrium macroscopic states are characterized by *state variables*, such as temperature, pressure, composition, entropy, volume, and internal energy. These variables are related to each other by equations of state. These functions and their partial derivatives are continuous except at certain isolated points that correspond to phase transitions.

State Variables (Symbols; Units) and Functions:

Temperature (T ; Kelvin) = measure of the tendency for energy to leave a system as heat

Pressure (p ; Pascal, atmosphere) = measure of the tendency toward mass movement from a system

Chemical potential (μ ; Joule/mole) = measure of the tendency for a chemical species to leave a system

Entropy (S ; Joule/mole·Kelvin) = measure of the intrinsic randomness (disorder) of a system

Volume (V ; Liter) = measure of the intrinsic space occupied by matter in the system

Moles (N_i ; mole) = number of particles of species i in the system

Mole Fractions ($x_i = N_i/N$) = fraction of species i in the system; $0 \leq x_i \leq 1$

Simple systems have no arbitrary barriers to the flow of heat or matter and exchange p - V work with their surroundings:

$$\text{Internal energy:} \quad U(S, V, N_i) \quad dU = TdS - pdV + \sum_{i=1}^C \mu_i dN_i$$

$$\text{Enthalpy:} \quad H(S, p, N_i) = U + pV \quad dH = TdS + Vdp + \sum_{i=1}^C \mu_i dN_i$$

$$\text{Helmholtz free energy:} \quad A(T, V, N_i) = U - TS \quad dA = -SdT - pdV + \sum_{i=1}^C \mu_i dN_i$$

$$\text{Gibbs free energy:} \quad G(T, p, N_i) = U - TS + pV \quad dG = -SdT + Vdp + \sum_{i=1}^C \mu_i dN_i$$

$$\text{Richard's rule:} \quad \Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_f \sim 8-16 \text{ J/mol} \cdot \text{K}; \quad T_f = \text{melting/freezing point}$$

$$\text{Trouton's rule:} \quad \Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T_b \sim 88 \text{ J/mol} \cdot \text{K}; \quad T_f = \text{boiling point}$$

$$\text{Ideal Gas:} \quad pV = nRT; \quad U(T) - \text{internal energy is a function of temperature only}$$

$$G(T, p) = G^\circ(T) + RT \ln p \quad (G^\circ(T) \text{ for standard state, 1 atm})$$

Temperature Dependencies (Constant Pressure):

$$\text{Volume:} \quad \alpha = (1/V)(\partial V/\partial T)_p \quad (\text{thermal expansion coefficient})$$

$$\text{Heat capacity:} \quad C_p(T) = (dH/dT)_p \sim a + bT + cT^{-2} \quad (a, b, c \text{ are numerically fit parameters})$$

$$\text{Enthalpy:} \quad H(T_2, p) = H(T_1, p) + \int_{T_1}^{T_2} C_p(T) dT$$

$$\text{Entropy:} \quad S(T_2, p) = S(T_1, p) + \int_{T_1}^{T_2} (C_p(T)/T) dT$$

$$\text{Gibbs free energy:} \quad d(G/T)/dT = -H/T^2 \quad (\text{Gibbs-Helmholtz equation})$$

Pressure Dependencies (Constant Temperature):

Volume: $\beta = -(1/V)(\partial V/\partial p)_T$ (isothermal compressibility)

Enthalpy: $H(T, p_2) = H(T, p_1) + \int_{p_1}^{p_2} V(1 - \alpha T) dp$

Entropy: $S(T, p_2) = S(T, p_1) + \int_{p_1}^{p_2} \alpha V dp$

Gibbs free energy: $G(T, p_2) = G(T, p_1) + \int_{p_1}^{p_2} V dp$

Mixtures/Solutions:

Chemical potentials: $\mu_i = \mu_i^\circ + RT \ln p_i$ (p_i = vapor pressure of component i)

Ideal solutions: $\Delta H_{\text{mix}} = 0$, $\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}}$

Raoult's law: $p_i = x_i p_i^\circ$; as $x_i \rightarrow 1$, solvent obeys Raoult's law
(p_i° = vapor pressure of pure component i)

Henry's law: $p_i = k_i x_i$; as $x_i \rightarrow 0$, solute obeys Henry's law

Activity: $a_i = p_i/p_i^\circ$.

Raoultian behavior: $a_i = x_i$; Non-Raoultian: $a_i = \gamma_i x_i$, γ_i = activity coefficient.

Gibbs free energy of mixing: $\Delta G_{\text{mix}} = RT \sum_{i=1}^C x_i \ln a_i$

Some General References:

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