Appendix III
Summary of Important Equations

Equations of State:

Ideal GasLaw:

$$\mathbf{PV = NRT}$$

Coefficient of Thermal Expansion:

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)$$

Compressibility:

$$\beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)$$

Van der Waals Equation:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

The Laws of Thermdynamics:

First Law:

$$\Delta U = Q + W \qquad 1$$

written in differential form: $$\mathbf{dU = dQ + dW} \qquad 2$$

work done on the system and heat added to the system are positive. The first law states the equivalence of heat and work and the conservation of energy.

Second Law:

$$\mathbf{dQ_{rev} = TdS} \qquad 3$$

Two ways of stating the second law are *Every system left to itself will, on average, change to a condition of maximum probability* and *Heat cannot be extracted from a body and turned entirely into work.*

Third Law:

$$\lim_{T \to 0} S = 0 \qquad 3$$

This follows from the facts that S = R ln Ω and Ω =1 at T = 0 for a perfectly crystalline pure substance.

Primary Variables of Thermodynamics

The leading thermodynamic properties of a fluid are determined by the relations which exist between the volume, pressure, termperature, energy and entropy of a given mass of fluid in a state of thermodynamic equilibrium - J. W. Gibbs

The primary variables of thermodynamics are P, V, T, U, and S. Other thermodynamic functions can be stated in terms of these variables. For various combination of these variables there are characteristics functions. The characteristic function for S and V is one of the primary variables: U. Thus

$$\boxed{dU = TdS + PdV} \qquad 5$$

Other Important Thermodynamic Functions

What then is the use of thermodynamic equations? They are useful precisely because some quantities are easier to measure than others. — M. L. McGlashan

Enthalpy:

$$\boxed{H \equiv U + PV} \qquad 6$$

In differential form in terms of its characteristic variables:

$$dH = TdS + VdP \qquad 7$$

Helmholtz Free Energy:

$$A \equiv U - TS \qquad 8$$

and:

$$dA = -PdV - SdT \qquad 9$$

Gibbs Free Energy:

$$\boxed{G \equiv H - TS} \qquad 10$$

The Gibbs Free Energy change of a reaction at constant temperature and pressure is:

$$\boxed{\Delta G_r = \Delta H_r - T\Delta S_r} \qquad 10a$$

and:

$$\boxed{dG = VdP - SdT} \qquad 11$$

Your choice of which of these functions to use should depend on what the independent variables in your system are. In geochemistry, P and T are the most common independent variables, so the Gibbs Free Energy is often the function of choice.

Exact Differentials and the Maxwell Relations

Any expression that may be written:

$$M(x,y)dx+N(x,y)dy \qquad 12$$

is an exact differential if there exists a function $z = f(x,y)$ such that

$$f(x,y) = M(x,y)dx+N(x,y)dy \qquad 13$$

The total differential of the function $z(x,y)$ is written:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = Mdx + Ndy \qquad 14$$

If dz is an exact differential, then

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \qquad 15$$

which is equivalent to:

$$\left(\frac{\partial M}{\partial y}\right)_y = \left(\frac{\partial N}{\partial x}\right)_x \qquad 16$$

All thermodynamic <u>variables of state</u> are exact differentials. Thus the practical application of the properties of exact differentials can be illustrated as follows. Equation 11 (dG = VdP - SdT) has the form dz = M(x,y)dx+N(x,y)dy since V and S are functions of temperature and pressure. Equation 11 may also be written as

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT \qquad 17$$

and comparing equations 11 and 16, we conclude that

$$\boxed{\left(\frac{\partial \mathbf{G}}{\partial \mathbf{P}}\right)_{\mathbf{T}} = \mathbf{V} \quad \textbf{and} \left(\frac{\partial \mathbf{G}}{\partial \mathbf{T}}\right)_{\mathbf{P}} = -\mathbf{S}} \qquad 18,\ 19$$

Applying the rule embodied in Equation 15, we can conclude that:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \qquad 20$$

Playing similar games with Equations 5 through 9, we can develop a series of relationships:

from dE $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad 21$$

from dH $$\left(\frac{\partial T}{\partial P}\right)_V = \left(\frac{\partial V}{\partial S}\right)_P \qquad 22$$

from dA $$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad 23$$

Equations 20 - 23 are known as the Maxwell Relations.

Derivatives of Entropy

pressure: $$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V \qquad 24$$

temperature: $$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad 25,\ 26$$

volume $$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta} \qquad 27$$

Derivatives of Enthalpy

pressure $$\left(\frac{\partial H}{\partial P}\right)_T = V(1 - \alpha T) \qquad 28$$

temperature $$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad 29$$

Derivatives of Energy

temperature: $$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \text{and} \quad \left(\frac{\partial U}{\partial T}\right)_P = C_P - P\alpha V \qquad 30,\ 31$$

volume: $$\left(\frac{\partial U}{\partial V}\right)_T = \frac{T\alpha}{\beta} - P \qquad 32$$

Difference between Cp and Cv

$$C_P - C_V = \frac{TV\alpha^2}{\beta} \qquad 33$$

The Gibbs Phase Rule:

The Gibbs Phase Rule is a rule for determining the *degrees of freedom* of a system.

$$\boxed{\mathbf{f = c - p + 2}} \qquad 34$$

f is the number of degrees of freedom, c is the number of components, and p is the number of phases. The minimum number of components needed to describe a system is:

$$c = N - R$$

where N is the number of species, and R is the number of reactions possible between these species.

The Clapeyron Equation

The slope of a phase boundary in P-T space is:

$$\boxed{\frac{\mathbf{dT}}{\mathbf{dP}} = \frac{\Delta \mathbf{V_r}}{\Delta \mathbf{S_r}}} \qquad 35$$

Solutions

Raoult's Law: applies to ideal solutions:

$$\boxed{\mathbf{P_i = X_i P_{total}}} \qquad 36$$

Henry's Law: applies to very dilute solutions, and state that the partial pressure of a component in solution is proportional to it mole fraction:

$$\boxed{\mathbf{P_i = hX_i \quad for\ X_i << 1}} \qquad 37$$

Chemical Potential

Chemical potential is defined as:

$$\boxed{\mu_i = \left(\frac{\partial \mathbf{G}}{\partial \mathbf{n_i}}\right)_{\mathbf{P,T,n}}} \qquad 38$$

where n_i is the number of moles of the i^{th} component.
In multicomponent systems, the full expression for the Gibbs Free Energy is:

$$dG = VdP - SdT + \sum_i \mu_i dn_i \qquad 39$$

The Gibbs-Duhem Relation

At equilibrium and at constant pressure and temperature:

$$\sum_i n_i d\mu_i = 0 \tag{40}$$

Thermodynamic Variables in Ideal Solutions

$$\mu_{i,\,ideal} = \mu_i^0 + RT \ln X_i \tag{41}$$

$\Delta V_{ideal\ mixing} = 0$ and therefore: $\overline{V}_{ideal} = \sum_i X_i v_i = \sum_i X_i \overline{V}_i$

$\Delta H_{ideal\ mixing} = 0$ and therefore: $\overline{H}_{ideal} = \sum_i X_i h_i = \sum_i X_i \overline{H}_i$

$$\Delta S_{ideal\ mixing} = -R\sum_i X_i \ln X_i$$

$$S_{ideal\ solution} = \sum_i X_i \overline{S}_i - R\sum_i X_i \ln X \tag{42}$$

$$\Delta G_{ideal\ mixing} = RT\sum_i X_i \ln X_i \tag{43}$$

$$\overline{G}_{ideal\ solution} = \sum_i X_i \mu_i^o + RT\sum_i X_i \ln X \tag{44}$$

Thermodynamic Variables in Non-Ideal Solutions

Fugacity: Fugacity can be thought of as the escaping tendency of a gas in non-ideal solutions. Because systems tend toward ideal at low pressure, it has the property:

$$\lim_{P \to 0} \frac{f_i}{P_i} = 1 \tag{45}$$

and

$$\mu_i = \mu_i^o + RT \ln \frac{f_i}{f_i^o} \tag{46}$$

Activity: Activity is defined as:

$$\mathbf{a_i \equiv \frac{f_i}{f_i^o}} \tag{47}$$

hence:

$$\mu_i = \mu_i^o + RT \ln a_i \tag{48}$$

The activity in an ideal solution is:

$$a_{i,ideal} = X_i \quad 49$$

The activity coefficient, λ, is defined as:

$$a_i = X_i \lambda_i \quad 50$$

When Henry's Law law holds: $\lambda_i = h_i$ 51

The **Debye-Hückel equation** is used to calculate activity coefficients in aqueous solutions. It is:

$$\log_{10} \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + B\mathring{a}\sqrt{I}} \quad 52$$

where z is charge, I is ionic strength, å is the hydrated ionic radius (significantly larger than ionic radius), and A and B are solvent parameters. I is calculated as:

$$I = \frac{1}{2}\sum_i m_i z_i^2 \quad 53$$

Excess Free Energy and activity coefficients:

$$\bar{G}_{excess} = RT\sum_i X_i \ln\lambda_i \quad 54$$

Excess Free Energy and Margules Parameters of a Regular Solution:

$$\bar{G}_{ex} = X_1X_2W_G \quad 55$$

Excess Free Energy and Margules Parameters of an Asymmetric Solution:

$$G_{excess} = \left(W_{G_1}X_2 + W_{G_2}X_1\right)X_1X_2 \quad 56$$

Equilibrium Constant

The equilibrium constant is defined as:

$$\mathbf{K = \prod_i a_i^{\nu_i}} \quad 57$$

It is related to the Gibbs Free Energy change of the reaction by:

$$\mathbf{K = e^{-\Delta G^\circ/RT}} \quad 58$$

It is related to enthalphy and entropy changes of the reaction by:

$$\ln K = -\frac{\Delta H_r^o}{RT} + \frac{\Delta S_r^o}{R} \quad 59$$

Pressure and temperature dependencies of the equilibrium constant are:

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V_r^o}{RT} \quad 60$$

Oxidation and Reduction:

The redox potential is related to the Gibbs Free Energy change of reaction as:

$$\mathbf{\Delta G = -nFE} \quad 61$$

where E is the redox potential, n is the number of electrons exchanged and F is the Faraday constant. The Nernst Equation is:

$$E = E^{\circ} - \frac{RT}{nF} \ln \Pi a_i^{\nu_i} \qquad 62$$

The pε is defined as:

$$\mathbf{p\varepsilon = -\log a_{e^-}} \qquad 63$$

and is related to hydrogen scale redox potential, E_H, as:

$$\mathbf{p\varepsilon = \frac{FE_H}{2.303RT}} \qquad 64$$

Kinetics

Reaction Rates: For a reaction such as:

$$aA + bB \rightleftarrows cC + dD$$

A general form for the rate of a reaction is:

$$\frac{1}{a}\frac{dA}{dt} = \frac{1}{b}\frac{dB}{dt} = -\frac{1}{c}\frac{dC}{dt} = -\frac{1}{d}\frac{dD}{dt} = k\, A^{n_A} B^{n_B} C^{n_C} D^{n_D} \qquad 65$$

where n_A, etc. can be any number. For an elementary reaction, this reduces to:

$$\frac{1}{a}\frac{dA}{dt} = \frac{1}{b}\frac{dB}{dt} = -\frac{1}{c}\frac{dC}{dt} = -\frac{1}{d}\frac{dD}{dt} = k\, A^a B^b \qquad 66$$

The temperature dependence of the rate constant is given by the Arrhenius Relation:

$$k = A \exp\left(-\frac{E_B}{RT}\right) \qquad 67$$

Rate constants of elementary reactions are related to the equilibrium constant as:

$$\frac{k_+}{k_-} = \frac{[B]_{eq}}{[A]_{eq}} = K^{app} \qquad 68$$

Diffusion: Fick's First Law is:

$$J = -D\left(\frac{\partial c}{\partial x}\right) \qquad 69$$

where J is the diffusion flux and D is the diffusion coefficient. Fick's Second Law is:

$$\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t \qquad 70$$

The temperature dependence of the diffusion coefficient is:

$$D = D_o \exp\left(-\frac{E_A}{RT}\right) \qquad 71$$

Diagentic Equation: $$\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial F_i}{\partial x}\right)_t + \sum R_i \qquad 72$$

Trace Elements

Equilibrium or Batch Partial Melting:

$$\frac{C_i^\ell}{C_i^o} = \frac{1}{D^{s/\ell}(1-F)+F} \qquad 73$$

Fractional Partial Melting: $$\frac{C_i^\ell}{C_i^o} = \frac{1}{D}(1-F)^{1/D-1} \qquad 74$$

Zone Refining: $$\frac{C_i^\ell}{C_i^o} = \frac{1}{D} - \left(\frac{1}{D} - 1\right)e^{-DR} \qquad 75$$

Equilibrium Crystallization: $$\frac{C_i^l}{C_i^o} = \frac{1}{DX + (1-X)} \qquad 76$$

Fractional Crystallization: $$\frac{C_i^l}{C_i^o} = (1-X)^{D-1} \qquad 77$$

Isotope Geochemistry

Binding Energy per Nucleon: $$E_b = \left[\frac{W-M}{A}\right]c^2 \qquad 78$$

Basic Equation of Radioactive Decay: $$\frac{dN}{dt} = -\lambda N \qquad 79$$

Isotope Growth (or Isochron) Equation:

$$R = R_0 + R_{P/D}(e^{\lambda t} - 1) \qquad 80$$