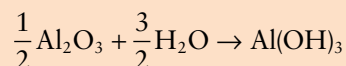## Example 2.5   Enthalpies (or heats) of reaction and Hess's Law

What is the energy consumed or evolved in the hydration of corundum (Al_2O_3) to form gibbsite ($Al(OH)_3$)? The reaction is:

$$\frac{1}{2}Al_2O_3 + \frac{3}{2}H_2O \rightarrow Al(OH)_3$$

Answer: We use *Hess's Law.* To use Hess's Law we need the standard state enthalpies for water, corundum, and gibbsite. These are: Al_2O_3: -1675.70 kJ/mol, H_2O: -285.83 and $Al(OH)_3$: -1293.13. The enthalpy of reaction is $\Delta H_r = -1293.13 - (0.5 \times -1675.70) - (1.5 \times -285.83) = -26.53$ kJ.

This is the enthalpy of reaction at 1 bar and 298 K. Suppose you were interested in this reaction under metamorphic conditions such as 300°C and 50 MPa. How would you calculate the enthalpy of reaction then?

it is not possible to measure the enthalpy for every compound. However, the enthalpies of formation for these compounds can generally be calculated indirectly.

2.10.3   Entropies of reaction

Since

$$dH = dQ_p \qquad (2.62)$$

and

$$dS_{rev} = \frac{dQ}{T} \qquad (2.57)$$

then at constant pressure:

$$dS_{rev} = \frac{dH}{T} \qquad (2.116)$$

Thus at constant pressure, the entropy change in a reversible reaction is simply the ratio of enthalpy change to temperature.

Entropies are additive properties and entropies of reaction can be calculated in the same manner as for enthalpies, so Hess's Law applies:

$$\Delta S_r = \sum_i v_i \Delta S^0_{f,i} \qquad (2.117)$$

The total entropy of a substance can be calculated as:

$$S_{298} = \int_0^{298} \frac{C_P dT}{T} + S_0 + \Delta S_\phi \qquad (2.118)$$

where S_0 is the entropy at 0 K (configurational, or "third law" entropy) and ΔS_Φ is the entropy change associated with any phase change. Compilations for S_{298} are available for many minerals. Table 2.2 lists some heat capacity constants for the power series formula as well as other thermodynamic data for a few geologically important minerals. Example 2.6 illustrates how entropy and enthalpy changes are calculated.

2.11   FREE ENERGY

We can now introduce two free energy functions, Helmholtz free energy and Gibbs free energy. Gibbs free energy is one of the most useful functions in thermodynamics.

2.11.1   Helmholtz free energy

We can rearrange eqn. 2.58 to read $dU - TdS = -PdV$. The $-PdV$ term is the work term and the TdS term is the heat function. TdS is the energy unavailable for work. Therefore $dU - TdS$ is *the amount of internal energy available for work*, or the *free energy*. We define it as A, the *Helmholtz free energy*:

$$A \equiv U - TS \qquad (2.119)$$

As usual, we are interested in the differential form (since we are more interested in changes than in absolutes):

$$dA = dU - d(TS) = dU - SdT - TdS \qquad (2.120)$$

Table 2.2 Standard state thermodynamic data for some important minerals.

Phase/compound	Formula	ΔH°_f (kJ/mol)	S° (J/K-mol)	ΔG°_f (kJ/mol)	$\bar{V}$ (cc/mol)*	C_p a	b	c
H_2O_g	H_2O (gas)	−241.81	188.74	−228.57	24789.00	30.54	0.01029	0
H_2O_l	H_2O (liquid)	−285.84	69.92	−237.18	18.10	29.75	0.03448	0
CO_2	CO_2	−393.51	213.64	−394.39	24465.10	44.22	0.00879	861904
Calcite	$CaCO_3$	−1207.30	92.68	−1130.10	36.93	104.52	0.02192	2594080
Graphite	C	0	5.740		5.298			
Diamond	C	1.86	2.37		3.417			
Aragonite	$CaCO_3$	−1207.21	90.21	−1129.16	34.15	84.22	0.04284	1397456
α-Qz	SiO_2	−910.65	41.34	−856.24	22.69	46.94	0.03431	1129680
β-Qz	SiO_2	−910.25	41.82	−856.24		60.29	0.00812	0
Cristobalite	SiO_2	−853.10	43.40	−853.10	25.74	58.49	0.01397	1594104
Coesite	SiO_2	−851.62	40.38	−851.62	20.64	46.02	0.00351	1129680
Periclase	MgO	−601.66	26.94	−569.38	11.25	42.59	0.00728	619232
Magnetite	Fe_3O_4	−1118.17	145.73	−1014.93	44.52	91.55	0.20167	0
Spinel	$MgAl_2O_4$	−2288.01	80.63	−2163.15	39.71	153.86	0.02684	4062246
Hematite	Fe_2O_3	−827.26	87.61	−745.40	30.27	98.28	0.07782	1485320
Corundum	Al_2O_3	−1661.65	50.96	−1568.26	25.58	11.80	0.03506	3506192
Kyanite	Al_2SiO_5	−2581.10	83.68	−2426.91	44.09	173.18	0.02853	5389871
Andalusite	Al_2SiO_5	−2576.78	92.88	−2429.18	51.53	172.84	0.02633	5184855
Sillimanite	Al_2SiO_5	−2573.57	96.78	−2427.10	49.90	167.46	0.03092	4884443
Almandine	$Fe_3Al_2Si_3O_{12}$	−5265.5	339.93	−4941.73	115.28	408.15	0.14075	7836623
Grossular	$Ca_3Al_2Si_3O_{12}$	−6624.93	254.68	−6263.31	125.30	435.21	0.07117	11429851
Albite	$NaAlSi_3O_8$	−3921.02	210.04	−3708.31	100.07	258.15	0.05816	6280184
K-feldspar	$KAlSi_3O_8$	−3971.04	213.93	−3971.4	108.87	320.57	0.01804	12528988
Anorthite	$CaAl_2Si_2O_8$	−4215.60	205.43	−3991.86	100.79	264.89	0.06190	7112800
Jadeite	$NaAlSi_2O_6$	−3011.94	133.47	−2842.80	60.44	201.67	0.04770	4966408
Diopside	$CaMgSi_2O_6$	−3202.34	143.09	−3029.22	66.09	221.21	0.03280	6585616
Enstatite	$MgSiO_3$	−1546.77	67.86	−1459.92	31.28	102.72	0.01983	2627552
Forsterite	Mg_2SiO_4	−2175.68	95.19	−2056.70	43.79	149.83	0.02736	3564768
Clinozoisite	$Ca_2Al_3Si_3O_{12}(OH)$	−68798.42	295.56	−6482.02	136.2	787.52	0.10550	11357468
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	−12319.70	548.90	−11590.71	272.92	188.22	0.05729	4482200
Chlorite	$MgAl(AlSi_3)O_{10}(OH)_8$	−8857.38	465.26	−8207.77	207.11	696.64	0.17614	15677448
Pargasite	$NaCa_2Mg_4Al_3Si_8O_{22}(OH)_2$	−12623.40	669.44	−11950.58	273.5	861.07	0.17431	21007864
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	−6226.07	287.86	−5841.65	149.66	420.95	0.01204	8995600
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	−5972.28	287.86	−5591.08	140.71	408.19	0.110374	10644096
Gibbsite	$Al(OH)_3$	−1293.13	70.08	−1155.49	31.96	36.19	0.19079	0
Boehmite	$AlO(OH)$	−983.57	48.45	−908.97	19.54	60.40	0.01757	0
Brucite	$Mg(OH)_2$	−926.30	63.14	−835.32	24.63	101.03	0.01678	2556424

Data for the standard state of 298.15 K and 0.1 MPa. ΔH°_f is the molar heat (enthalpy) of formation from the elements; S° is the standard state entropy; V is the molar volume; a, b and c are constants for the heat capacity (C_p) computed as: $C_p = a + bT - cT^{-2}$ J/K-mol. Modified from Helgeson *et al.* (1978). Reproduced with permission of the American Journal of Science.

*cc/mol = J/MPa/mol.

Example 2.6 Calculating enthalpy and entropy changes

If the heat capacity of steam can be represented by a three-term power series:

$$C_p = a + bT + cT^2$$

with constants $a = 36.37$ J/K-mol, $b = -7.84 \times 10^{-3}$ J/K^2-mol, and $c = 9.08 \times 10^{-6}$ J/K^3-mol, and the enthalpy of vaporization at 100°C is 40.6 kJ/mol, calculate the S and H changes when 1 mol of liquid water at 100°C and 1 atm is converted to steam and brought to 200°C and 3 atm. Assume that with respect to volume, steam behaves as an ideal gas (which, in reality, it is certainly not).

Answer: We need to calculate entropy and enthalpy associated with three changes: the conversion of water to steam, raising the steam from 100°C to 200°C, and increasing the pressure from 1 atm to 3 atm. Since both S and H are state variables, we can treat these three processes separately; our answer will be the sum of the result for each of these processes and will be independent of the order in which we do these calculations.

1. Conversion of water to steam. This process will result in ΔH of 40.6 kJ. For entropy, $\Delta S = \Delta H/T = 40.6/373 = 109$ J/K. We converted centigrade to Kelvin, or absolute, temperature.
2. Raising the steam from 100°C to 200°C (from 373 K to 473 K) isobarically. Since heat capacity is a function of temperature, we will have to integrate eqn. 2.81 over the temperature interval:

$$\int_{T_1}^{T_2} C_P dT = \int_{373}^{473} (a + bT + cT^2) dT = a\int_{373}^{473} dT + b\int_{373}^{473} T dT + c\int_{373}^{473} T^2 dT = \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 \right]_{373}^{473}$$

Evaluating this, we find that $\Delta H = (17.20 - 0.88 + 0.32) - (13.57 - 0.55 + 0.16) = 3.469$ kJ. The entropy change is given by:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT = \int_{373}^{473} \frac{a}{T} dT + \int_{373}^{473} b dT + \int_{373}^{473} cT dT = \left[a\ln T + bT + \frac{c}{2}T^2 \right]_{373}^{473}$$

Evaluating this, we find that $\Delta S = (224.01 - 3.71 + 1.02) - (215.37 - 2.93 + 0.63) = 8.24$ J/K.
3. Increasing pressure from 1 atm to 3 atm (0.1 MPa to 0.3 MPa) isothermally. We can use eqn. 2.117 to determine the enthalpy change associated with the pressure change. On the assumption of ideal gas behavior, we can substitute $1/T$ for α. Doing so, we find the equation goes to 0; thus there is no enthalpy change associated with a pressure change for an ideal gas. This is in accord with assumptions about an ideal gas: namely, that there are no forces between molecules, hence no energy is stored as potential energy of attraction between molecules.

The isothermal pressure dependence of entropy is given by eqn. 2.106. We substitute $1/T$ for α and RT/P for V and integrate from P_1 to P_2:

$$\Delta S = \int_{P_1}^{P_2} -\frac{1}{T}\frac{RT}{P} dP = \int_{P_1}^{P_2} -\frac{R}{P} dP = -R[\ln P]_{0.1}^{0.3} = -8.315\left[\ln \frac{0.3}{0.1}\right] \text{J/K} = -9.13 \text{ J/K}$$

The whole enthalpy and entropy changes are the sum of the changes in these three steps:

$$\Delta H = 40.6 + 3.5 + 0 = 44.1 \text{ kJ} \quad \Delta S = 108.8 + 8.2 - 9.1 = 107.9 \text{ J/K}$$

or substituting eqn. 2.58 into 2.120:

$$dA = -SdT - PdV \qquad (2.121)$$

2.11.2 Gibbs free energy

2.11.2.1 Derivation

The Gibbs free energy is perhaps misnamed. By analogy to the Helmholtz free energy, it should be called the free enthalpy (but enthalpy is an energy), because it is derived as follows:

$$\boxed{G \equiv H - TS} \qquad (2.122)$$

and

$$dG = d(H - TS) = dH - d(TS) \qquad (2.123)$$

or

$$dG = TdS + VdP - d(TS)$$
$$= TdS + VdP - SdT - TdS$$

which reduces to:

$$\boxed{dG = VdP - SdT} \qquad (2.124)$$

Notice the similarity to the Helmholtz free energy; in that case we subtracted the *TS* term from the internal energy; in this case we subtracted the *TS* term from the enthalpy. *The Gibbs free energy is the energy available for non-PV work (such as chemical work)*. It has two other important properties: its independent variables are *T* and *P*, generally the ones in which we are most interested in geochemistry, and it contains the entropy term (as does the Helmholtz free energy), and hence can be used as an indication of the direction in which spontaneous reactions will occur.

2.11.2.2 Gibbs free energy change in reactions

For a finite change at *constant temperature*, the Gibbs free energy change is:

$$\boxed{\Delta G = \Delta H - T\Delta S} \qquad (2.125)$$

The free energy change of formation, ΔG_f, is related to the enthalpy and entropy change of reaction:

$$\Delta G_f^0 = \Delta H_f^0 - T\Delta S_f^0 \qquad (2.126)$$

Like other properties of state, the Gibbs free energy is additive. Therefore:

$$\Delta G_r = \sum_i v_i \Delta G_{f,i} \qquad (2.127)$$

In other words, we can use Hess's Law to calculate the free energy change of reaction. Values for ΔG_f at the standard state are available in compilations.

2.11.3 Criteria for equilibrium and spontaneity

The Gibbs free energy is perhaps the single most important thermodynamic variable in geochemistry because it provides this criterion for recognizing equilibrium. This criterion is:

> **Products and reactants are in equilibrium when their Gibbs free energies are equal.**

Another important quality of the Gibbs free energy is closely related:

> **At fixed temperature and pressure, a chemical reaction will proceed in the direction of lower Gibbs free energy (i.e., $\Delta G_r < 0$).**

The reverse is also true: a reaction will not proceed if it produces an increase in the Gibbs free energy.

On an intuitive level, we can understand the Gibbs free energy as follows. We know that transformations tend to go in the direction of the lowest energy state (e.g., a ball rolls down hill). We have also learned that transformations go in the direction of increased entropy (if you drop a glass it breaks into pieces; if you drop the pieces they don't re-assemble into a glass). We must consider both the tendency for energy to decrease and the tendency for entropy to increase in order to predict the direction of a chemical reaction. This is what the Gibbs free energy does. Example 2.7 illustrates how Gibbs free energy of reaction is used to predict an equilibrium.

Example 2.7   Using Gibbs free energy to predict equilibrium

Using the thermodynamic data given in Table 2.2, calculate ΔG_r for the reaction:

$$CaAl_2Si_2O_8 + 2Mg_2SiO_4 \rightleftharpoons CaMgSi_2O_6 + MgAl_2O_4 + 2MgSiO_3$$

$$(Anorthite + 2\ Forsterite \rightleftharpoons Diopside + Spinel + 2\ Enstatite)$$

at 298 K and 0.1 MPa. Which mineral assemblage is more stable under these conditions (i.e., which side of the reaction is favored)? Which assemblage will be favored by increasing pressure? Why? Which side will be favored by increasing temperature? Why?

Answer: We can calculate ΔG_r from ΔH_f and ΔS_f, values listed in Table 2.2:

$$\Delta G = \Delta H - T\Delta S$$

ΔH is calculated as: $\Delta H_{f,Di} + \Delta H_{f,Sp} + 2 \times \Delta H_{f,En} - (\Delta H_{f,An} + 2 \times \Delta H_{f,Fo})$. ΔS is calculated in a similar manner. Our result is −6.08 kJ/mol. Because ΔG_r is negative, the reaction will proceed to the right, so that the assemblage on the right is more stable under the conditions of 298 K and 1 atm.

To find out which side will be favored by increasing pressure and temperature, we use equations 2.128 and 2.129 to see how ΔG will change. For temperature, $\partial \Delta G / \partial T = -\Delta S$. ΔS_r is −36.37/K-mol, and $\partial \Delta G / \partial T = 36.37$. The result is positive, so that ΔG will increase with increasing T, favoring the left side. Had we carried out the calculation at 1000°C and 0.1 MPa, a temperature appropriate for crystallization from magma, we would have found that the anorthite–forsterite assemblage is stable. For pressure, $\partial \Delta G / \partial P = \Delta V$. ΔV for the reaction is −20.01 cc/mol (=J/MPa-mol), so will decrease with increasing pressure, favoring the right side. Reassuringly, our thermodynamic result is consistent with geologic observation. The assemblage on the left, which could be called "plagioclase peridotite", transforms to the assemblage on the right, "spinel peridotite", as pressure increases in the mantle.

2.11.4 Temperature and pressure dependence of the Gibbs free energy

One reason why the Gibbs free energy is useful is that its characteristic variables are temperature and pressure, which are the "external" variables of greatest interest in geochemistry. Since it is a state variable, we can deduce its temperature and pressure dependencies from eqn. 2.124, which are:

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \qquad (2.128)$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \qquad (2.129)$$

Equations 2.128 and 2.129 allow us to predict how the Gibbs free energy of reaction will change with changing temperature and pressure. *Thus we can predict how the direction of a reaction will change if we change temperature and pressure.* To obtain the ΔG_r at some temperature T' and pressure P', we integrate:

$$\Delta G_{T',P'} = \Delta G_{T_{ref},P_{ref}} + \int_{P_{ref}}^{P'} \Delta V_r dP - \int_{T_{ref}}^{T'} \Delta S_r dT$$

$$(2.130)$$

(See Example 2.8.) For liquids and particularly gases, the effects of pressure and temperature on ΔV are significant and cannot be ignored. The reference pressure is generally 0.1 MPa. For solids, however, we can often ignore the effects of temperature and pressure on ΔV so the first integral reduces to: $\Delta V(P'-P_{ref})$ (see Example 2.9). On the other hand, we cannot ignore the temperature dependence of entropy. Hence we need to express ΔS_r as a function of temperature. The temperature dependence of entropy is given by eqn. 2.105. Writing this in integral form, we have:

$$\Delta S(T) = \int_{T_{ref}}^{T} \frac{\Delta C_p}{T} dT$$

This is the change in entropy due to increasing the temperature from the reference state to T.

The full change in entropy of reaction is then this plus the entropy change at the reference temperature:

$$\Delta S_r = \Delta S_{T_{ref}} + \int_{T_{ref}}^{T} \frac{\Delta C_p}{T} dT \quad (2.131)$$

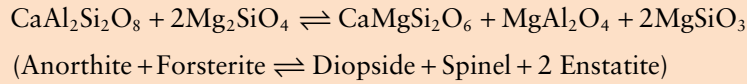Substituting this into 2.130, the second integral becomes:

$$-\int_{T_{ref}}^{T'} \Delta S_r dT = -\Delta S_{ref}(T' - T_{ref})$$

$$-\int_{T_{ref}}^{T'} \int_{T_{ref}}^{T} \frac{\Delta C_p}{T} dT dT = \Delta G_{T'} \quad (2.132)$$

$\Delta G_{T'}$ as we define it here, is the change in free energy of reaction as a result of increasing temperature from the reference state to T´.

Example 2.8   Predicting the equilibrium pressure of a mineral assemblage

Using the thermodynamic reaction and data as in Example 2.7:

$$CaAl_2Si_2O_8 + 2Mg_2SiO_4 \rightleftharpoons CaMgSi_2O_6 + MgAl_2O_4 + 2MgSiO_3$$

(Anorthite + Forsterite $\rightleftharpoons$ Diopside + Spinel + 2 Enstatite)

determine the pressure at which these two assemblages will be in equilibrium at 1000°C. Assume that the volume change of the reaction is independent of pressure and temperature (i.e., α and $\beta = 0$).

Answer: These two assemblages will be in equilibrium if and only if the Gibbs free energy of reaction is 0. Mathematically, our problem is to solve eqn. 2.130 for P such that $\Delta G_{1273,P} = 0$.

Our first step is to find ΔG_r for this reaction at 1000°C (1273 K) using eqn. 2.132. Heat capacity data in Table 2.2 is in the form: $C_p = a + bT - cT^{-2}$. Substituting for ΔC_p, we have:

$$\Delta G_T = -\Delta S_{T_{ref}}(T' - T_{ref}) - \int_{T_{ref}}^{T'} \int_{T_{ref}}^{T} \left(\frac{\Delta a}{T} + \Delta b - \frac{\Delta c}{T^3} \right) dT dT \quad (2.133)$$

Performing the double integral and collecting terms, substituting ΔT for T´ − T_{ref}, this simplifies to:

$$\Delta G_{T'} = -\Delta T \left[\Delta S_{T_{ref}} - \Delta a + \frac{\Delta b}{2} \Delta T - \frac{\Delta c \Delta T}{2T'T_{ref}^2} \right] - \Delta a T' \ln \frac{T'}{T_{ref}} \quad (2.134)$$

Equation 2.134 is a general solution to eqn. 2.132 when the Maier-Kelley heat capacity is used.

We found $\Delta S_{T_{ref}}$ to be −36.37 J/K-mol in Example 2.7. Computing Δa as $(a_{Di} + a_{Sp} + 2a_{En}) - (a_{An} + 2a_{Fo})$, we find $\Delta a = 15.96$ J/mol. Computing Δb and Δc similarly, they are −0.01732 J/K-mol and 1.66×10^6 J-K²/mol respectively. Substituting values into eqn. 2.136, we find $\Delta G_T = 36.74$ kJ/mol.

Since we may assume the phases are incompressible, the solution to the pressure integral is:

$$\Delta G_P = \int_{P_{ref}}^{P'} \Delta V_r dP = \Delta V_r (P' - P_{ref}) \quad (2.135)$$

Equation 2.130 may now be written as:

$$\Delta G_{T',P'} = 0 = \Delta G° + \Delta G_T + \Delta V_r (P' - P_{ref})$$

Let $\Delta G_{1273,0.1} = \Delta G° + \Delta G_T$. $\Delta G°$ is −6.95 kJ/mol (calculated from values in Table 2.2), so $\Delta G_{1273,0.1} = 29.86$ kJ/mol. $\Delta G_{1273,0.1}$ is positive, meaning that the left side of the reaction is favored at 1000°C and atmospheric pressure, consistent with our prediction based on $\partial G/\partial T$.

Solving for pressure, we have

$$P' = \frac{-\Delta G_{T'P_{ref}}}{\Delta V_r} + P_{ref} \quad (2.136)$$

With $\Delta V = -20.01$ cc/mol, we obtain a value of 1.49 GPa (14.9 kbar). Thus assemblages on the right and left will be in equilibrium at 1.49 GPa and 1000°C. Below that pressure, the left is stable, and above that pressure, the right side is the stable assemblage, according to our calculation.

The transformation from "plagioclase peridotite" to "spinel peridotite" actually occurs around 1.0 GPa in the mantle. The difference between our result and the real world primarily reflects differences in mineral composition: mantle forsterite, enstatite and diopside are solid solutions containing Fe and other elements. The difference does not reflect our assumption that the volume change is independent of pressure. When available data for pressure and temperature dependence of the volume change are included in the solution, the pressure obtained is only marginally different: 1.54 GPa.

Example 2.9   Volume and free energy changes for finite compressibility

The compressibility (β) of forsterite (Mg_2SiO_4) is 8.33×10^{-6} MPa^{-1}. Using this and the data given in Table 2.2, what is the change in molar volume and Gibbs free energy of forsterite at 100 MPa and 298 K?

Answer: Let's deal with volume first. We want to know how the molar volume (43.79 cc/mol) changes as the pressure increases from the reference value (0.1 MPa) to 1 GPa. The compressibility is defined as:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{2.12}$$

So the change in volume for an incremental increase in pressure is given by:

$$dV = -V\beta dP \tag{2.137}$$

To find the change in volume over a finite pressure interval, we rearrange and integrate:

$$\int_{V^o}^{V}\frac{dV}{V} = -\int_{P^o}^{P}\beta dP$$

Performing the integral, we have:

$$\ln\frac{V}{V^o} = -\beta(P - P^o) \tag{2.138}$$

where P is the pressure interval, $P' - P^o$. This may be rewritten as:

$$V = V^o e^{-\beta(P-P^o)} \tag{2.139}$$

However, the value of $\beta\Delta P$ is of the order of 10^{-2}, and in this case, the approximation $e^x \approx x + 1$ holds, so that eqn. 2.139 may be written as:

$$V \cong V^o(1 - \beta(P - P^o)) \tag{2.140}$$

Equation 2.140 is a general expression that expresses volume as a function of pressure when β is known, small, and is independent of temperature and pressure. Furthermore, in situations where $P \gg P^o$, this can be simplified to:

$$V \cong V^o(1 - \beta P) \tag{2.141}$$

Using equation 2.141, we calculate a molar volume of 43.54 cc/mol (identical to the value obtained using eqn. 2.139). The volume change, ΔV, is 0.04 cc/mol.

The change in free energy with volume is given by:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

(Continued)

so that the free energy change as a consequence of a finite change is pressure can be obtained by integrating:

$$\Delta G = \int_{P^o}^{P} V dP$$

Into this we may substitute eqn. 2.141:

$$\Delta G = \int_{V^o}^{V'} V^o (1 - \beta P) dP = V^o \left[P - \beta P^2 \right]_{P^o}^{P} \qquad (2.142)$$

Using eqn. 2.142 we calculate a value of ΔG of 4.37 kJ/mol.

2.12   THE MAXWELL RELATIONS

The reciprocity relationship, which we discussed earlier, leads to a number of useful relationships. These relationships are known as the Maxwell Relations.* Consider the equation:

$$dU = TdS - PdV \qquad (2.58)$$

If we write the partial differential of U in terms of S and V we have:

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \qquad (2.143)$$

From a comparison of these two equations, we see that:

$$\left(\frac{\partial U}{\partial S} \right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V} \right)_S = -P \qquad (2.144)$$

And since the cross-differentials are equal, it follows that:

$$\left(\frac{\partial T}{\partial V} \right)_S = \left(\frac{\partial P}{\partial S} \right)_V \qquad (2.145)$$

The other Maxwell Relations can be derived in an exactly analogous way from other state functions. They are:

from dH (eqn. 2.65)

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \qquad (2.146)$$

from dA (eqn. 2.121)

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \qquad (2.147)$$

from dG (eqn. 2.122)

$$\left(\frac{\partial V}{\partial T} \right)_P = -\left(\frac{\partial S}{\partial P} \right)_T \qquad (2.148)$$

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* The Maxwell Relations are named for Scottish physicist James Clerk Maxwell (1831–1879), perhaps the most important figure in 19th century physics. He is best known for his work on electromagnetic radiation, but he also made very important contributions to statistical mechanics and thermodynamics.

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PROBLEMS

1. For a pure olivine mantle, calculate the adiabatic temperature gradient $(\partial T/\partial P)_s$ at 0.1 MPa (1 atm) and 1000°C. Use the thermodynamic data in Table 2.2 for forsterite (Mg-olivine, Mg_2SiO_4), and $\alpha = 44 \times 10^{-6}\,K^{-1}$, and $\beta = 8 \times 10^{-6}\,MPa^{-1}$.
Note that: 1 cc/mol = 1 J/MPa/mol.

2. Complete the proof that V is a state variable by showing that for an ideal gas:

$$\frac{\partial \alpha V}{\partial P} = -\frac{\partial \beta V}{\partial T}$$

3. A quartz crystal has a volume of 7.5 ml at 298 K and 0.1 MPa. What is the volume of the crystal at 840 K and 12.3 MPa if:

   (a) $\alpha = 1.4654 \times 10^{-5}\,K^{-1}$ and $\beta = 2.276 \times 10^{-11}\,Pa^{-1}$, and α and β are independent of T and P.
   (b) $\alpha = 1.4310 \times 10^{-5}\,K^{-1} + 1.1587 \times 10^{-9}\,K^{-2}T$
   $\beta = 1.8553 \times 10^{-11}\,Pa^{-1} + 7.9453 \times 10^{-8}\,P^{-1}$

4. One mole of an ideal gas is allowed to expand against a piston at constant temperature of 0°C. The initial pressure is 1 MPa and the final pressure is 0.04 MPa. Assuming the reaction is reversible,

   (a) What is the work done by the gas during the expansion?
   (b) What is the change in the internal energy and enthalpy of the gas?
   (c) How much heat is gained/lost during the expansion?

5. A typical eruption temperature of basaltic lava is about 1200°C. Assuming that basaltic magma travels from its source region in the mantle quickly enough so that negligible heat is lost to wall rocks, calculate the temperature of the magma at a depth of 40 km. The density of basaltic magma at 1200°C is 2610 kg/m³; the coefficient of thermal expansion is about 10^{-4}/K. Assume a heat capacity of 850 J/kg-K and that pressure is related to depth as 1 km = 33 MPa (surface pressure is 0.1 MPa.).
   (HINT: "negligible heat loss" means the system may be treated as adiabatic.)

6. Show that the C_P of an ideal monatomic gas is 5/2 R.

7. Show that: $\left(\dfrac{\partial P}{\partial T}\right)_V = \dfrac{\alpha}{\beta}$

8. Show that for a reversible process: $\left(\dfrac{\partial U}{\partial V}\right)_T = T\dfrac{\alpha}{\beta} - P$ (2.73)

   (Hint: begin with the statement of the first law (eqn. 2.58), make use of the Maxwell relations, and your proof in problem 7.)

9. Imagine that there are 30 units of energy to distribute among three copper blocks.

   (a) If the energy is distributed completely randomly, what is the probability of the first block having all the energy?

(b) If n_1 is the number of units of energy of the first block, construct a graph (a histogram) showing the probability of a given value of n_1 occurring as a function of n_1.
(HINT: use eqn. 2.37, but modify it for the case where there are three blocks.)

10. Consider a box partitioned into equal volumes, with the left half containing 1 mole of Ne and the right half containing 1 mole of He. When the partition is removed, the gases mix. Show, using a classical thermodynamic approach (i.e., macroscopic) that the entropy change of this process is $\Delta S = 2R \ln 2$. Assume that He and Ne are ideal gases and that temperature is constant.

11. Find expressions for C_P and C_V for a van der Waals gas.

12. Show that β (the compressibility, defined in eqn. 2.12) of an ideal gas is equal to 1/P.

13. Show that $S = \dfrac{\bar{U}}{T} + R \ln Q$

    Hint: Start with equations 2.47 and 2.36a using the approximation that $\ln N! = N \ln N - N$.

14. Show that $\Delta H = \displaystyle\int_{P_1}^{P_2} V(1 - \alpha T)dP$

    Hint: Begin with eqn. 2.63 and express dU as a function of temperature and volume change.

15. Helium at 298 K and 1 atm has $S° = 30.13$ cal/K-mol. Assume He is an ideal gas.

    (a) Calculate V, H, G, α, ß, C_P, C_V, for He at 298 K and 1 atm.
    (b) What are the values for these functions at 600 K and 100 atm?
    (c) What is the entropy at 600 K and 100 atm?

16. Using the enthalpies of formation given in Table 2.2, find ΔH in joules for the reaction:

$$Mg_2SiO_4 + SiO_2 \rightleftharpoons 2MgSiO_3$$

17. Using the data in Table 2.2, calculate the enthalpy and entropy change of diopside as it is heated at constant pressure from 600 K to 1000 K.

18. Calculate the total enthalpy upon heating of 100 g of quartz from 25°C to 900°C. Quartz undergoes a phase transition from α-quartz to β-quartz at 575°C. The enthalpy of this phase transition is $\Delta H_{tr} = 0.411$ kJ/mol. Use the Maier-Kelly heat capacity data in Table 2.2.

19. Calcite and aragonite are two forms of $CaCO_3$ that differ only their crystal lattice structure. The reaction between them is thus simply:

$$Calcite \rightleftharpoons Aragonite$$

    Using the data in Table 2.2:

    (a) Determine which of these forms is stable at the surface of the Earth (25°C and 0.1 MPa).
    (b) Which form is favored by increasing temperature?
    (c) Which form is favored by increasing pressure?

20. Use the data in Table 2.2 to determine the pressure at which calcite and aragonite are in equilibrium at 300°C.

21. Suppose you found kyanite and andalusite coexisting in the same rock, which you had reason to believe was an equilibrium assemblage, and that you could independently determine the temperature of equilibrium to be 400°C. Use the data in Table 2.2 to determine the pressure at which this rock equilibrated.

Chapter 3

Solutions and thermodynamics of multicomponent systems

3.1 INTRODUCTION

In the previous chapter, we introduced thermodynamic tools that allow us to predict the equilibrium mineral assemblage under a given set of conditions. For example, having specified temperature, we were able to determine the pressure at which the assemblage anorthite + forsterite is in equilibrium with the assemblage diopside + spinel + enstatite. In that reaction the minerals had unique and invariant compositions. In the Earth, things are not quite so simple: these minerals are present as solid solutions,* with substitutions of Fe^{2+} for Mg, Na for Ca, and Cr and Fe^{3+} for Al, among others. Indeed, most natural substances are solutions; that is, their compositions vary. Water, which is certainly the most interesting substance at the surface of the Earth and perhaps the most important, inevitably has a variety of substances dissolved in it. These dissolved substances are themselves often of primary geochemical interest. More to the point, they affect the chemical behavior of water. For example, the freezing temperature of an aqueous NaCl solution is lower than that of pure water. You may have taken advantage of this phenomenon by spreading salt to de-ice sidewalks and roads.

In a similar way, the equilibrium temperature and pressure of the plagioclase + olivine $\rightleftharpoons$ clinopyroxene + spinel + orthopyroxene reaction depends on the composition

of these minerals. To deal with this compositional dependence, we need to develop some additional thermodynamic tools, which is the objective of this chapter. This may seem burdensome at first: if it were not for the variable composition of substances, we would already know most of the thermodynamics we need. However, as we will see in Chapter 4, we can use this compositional dependence to advantage in reconstructing conditions under which a mineral assemblage or a hydrothermal fluid formed.

A final "difficulty" is that the valance state of many elements can vary. Iron, for example, may change from its Fe^{2+} state to Fe^{3+} when an igneous rock weathers. The two forms of iron have very different chemical properties; for example Fe^{2+} is considerably more soluble in water than is Fe^{3+}. Another example of this kind of reaction is photosynthesis, the process by which CO_2 is converted to organic carbon. These kinds of reactions are called "oxidation–reduction", or "redox" reactions. The energy your brain uses to process the information you are now reading comes from oxidation of organic carbon – carbon originally reduced by photosynthesis in plants. To fully specify the state of a system, we must specify its "redox" state. We treat redox reactions in the final section of this chapter.

Though Chapter 4 will add a few more tools to our geochemical toolbox, and treat a number of advanced topics in thermodynamics, it is

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* The naturally occurring minerals of varying composition are referred to as plagioclase rather than anorthite, olivine rather than forsterite, clinopyroxene rather than diopside, and orthopyroxene rather than enstatite.

designed to be optional. With completion of this chapter, you will have a sufficient thermodynamic background to deal with a wide range of phenomena in the Earth, and most of the topics in the remainder of this book.

3.2   PHASE EQUILIBRIA

3.2.1   Some definitions

3.2.1.1   Phase

Phases are real substances that are homogeneous, physically distinct, and (in principle) mechanically separable. For example, the phases in a rock are the minerals present. Amorphous substances are also phases, so glass or opal would be phases. The sugar that won't dissolve in your ice tea is a distinct phase from the tea, but the dissolved sugar is not. *Phase* is not synonymous with *compound*. Phases need not be chemically distinct: a glass of ice water has two distinct phases: water and ice. Many solid compounds can exist as more than one phase. Nor need they be compositionally unique: plagioclase, clinopyroxene, olivine, and so on, are all phases even though their composition can vary. Thus a fossil in which the aragonite ($CaCO_3$) is partially retrograded into calcite (also $CaCO_3$) consists of two phases. Systems, and reactions occurring within them, consisting of a single phase are referred to as *homogenous*; those systems consisting of multiple phases, and the reactions occurring within them, are referred to as *heterogeneous*.

3.2.1.2   Species

Species is somewhat more difficult to define than either *phase* or *component*. A species is a chemical entity, generally an element or compound (which may or may not be ionized). The term is most useful in the context of gases and liquids. A single liquid phase, such as an aqueous solution, may contain a number of species. For example, H_2O, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, and OH^- are all species commonly present in natural waters. The term species is generally reserved for an entity that actually exists, such as a molecule, ion, or solid, on a microscopic

scale. This is not necessarily the case with components, as we shall see. The term species is less useful for solids, although it is sometimes applied to the pure end-members of solid solutions and to pure minerals.
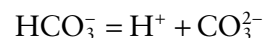
3.2.1.3   Component

In contrast to a species, a *component* need not be a real chemical entity; rather it is simply an algebraic term in a chemical reaction. The *minimum number of components** of a system is rigidly defined as *the minimum number of independently variable entities necessary to describe the composition of each and every phase of a system*. Unlike species and phases, components may be defined in any convenient manner: what the components of your system are and how many there are depend upon your interest and upon the level of complexity you will be dealing with. Consider our aragonite–calcite fossil. If the only reaction occurring in our system (the fossil) is the transformation of aragonite to calcite, one component, $CaCO_3$, is adequate to describe the composition of both phases. If, however, we are also interested in the precipitation of calcium carbonate from water, we might have to consider $CaCO_3$ as consisting of two components: Ca^{2+} and CO_3^{2-}.

There is a rule to determine the minimum number of components in a system once you decide what your interest in the system is; the hard part is often determining your interest. The rule is:

$$c = n - r \qquad (3.1)$$

where *n is the number of species*, and *r is the number of independent chemical reactions possible between these species*. Essentially, this equation simply states that if a chemical species can be expressed as the algebraic sum of other components, we need not include that species among our minimum set of components. Let's try the rule on the species we listed earlier for water. We have six species: H_2O, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, and OH^-. We can write three reactions relating them:

$$HCO_3^- = H^+ + CO_3^{2-}$$

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* Caution: some books use the term *number of components* as synonymous with *minimum number of components*.

$$H_2CO_3 = H^+ + HCO_3^-$$

$$H_2O = H^+ + OH^-$$
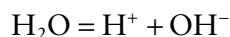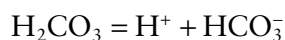
Equation 3.1 tells us we need $3 = 6 - 3$ components to describe this system: CO_3^{2-}, H^+, and OH^-. Put another way, we see that carbonic acid, bicarbonate, and water can all be expressed as algebraic sums of hydrogen, hydroxyl, and carbonate ions, so they need not be among our minimum set of components.

In igneous and metamorphic petrology, components are often the major oxides (though we may often choose to consider only a subset of these). On the other hand, if we were concerned with the isotopic equilibration of minerals with a hydrothermal fluid, ^{18}O would be considered as a different component than ^{16}O.

Perhaps the most straightforward way of determining the number of components is a graphical approach. If all phases can be represented on a one-dimensional diagram (that is, a straight line representing composition), we are dealing with a two-component system. For example, consider the hydration of Al_2O_3 (corundum) to form boehmite ($AlO(OH)$) or gibbsite $Al(OH)_3$. Such a system would contain four phases (corundum, boehmite, gibbsite, water), but is nevertheless a two-component system because all phases may be represented in one dimension of composition space, as shown in Figure 3.1. Because there are two polymorphs of gibbsite, one of boehmite, and two other possible phases of water, there are nine possible phases in this two-component system. Clearly, a system may have many more phases than components.

Similarly, if a system may be represented in two dimensions, it is a three-component system. Figure 3.2 is a ternary diagram illustrating the system Al_2O_3–H_2O–SiO_2. The graphical representation approach reaches its practical limit in a four-component system because of the difficulty of representing more than three dimensions on paper. A four-component system is a quaternary one, and can be represented with a three-dimensional quaternary diagram.

It is important to understand that a component may or may not have chemical reality. For example in the exchange reaction:

$$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+$$
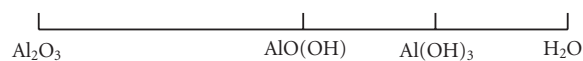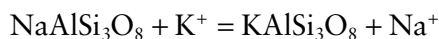
Figure 3.1   Graphical representation of the system Al_2O_3-H_2O.
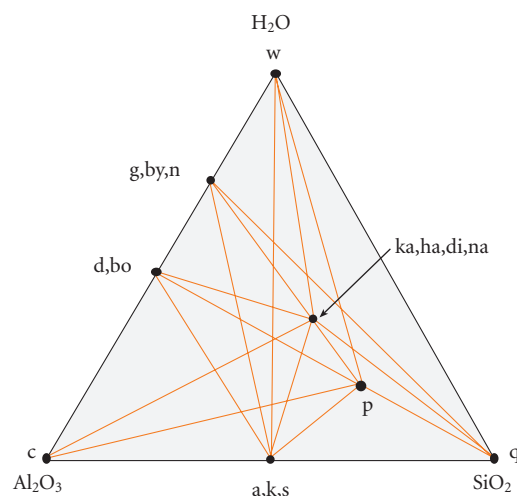
Figure 3.2   Phase diagram for the system Al_2O_3–H_2O–SiO_2. The lines are called *joins* because they join phases. In addition to the end-members, or components, phases represented are *g*: gibbsite, *by*: bayerite, *n*: norstrandite (all polymorphs of $Al(OH)_3$), *d*: diaspore, *bo*: boehmite (polymorphs of $AlO(OH)$), *a*: andalusite, *k*: kyanite, *s*: sillimanite (all polymorphs of Al_2SiO_5), *ka*: kaolinite, *ha*: halloysite, *di*: dickite, *na*: nacrite (all polymorphs of $Al_2Si_2O_5(OH)_4$), and *p*: pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). There are also six polymorphs of quartz, *q* (coesite, stishovite, tridymite, cristobalite, α-quartz, and β-quartz). From Nordstrom and Munoz (1986). With permission from John Wiley & Sons.

we could alternatively define the *exchange operator* KNa_{-1} (where Na_{-1} is $-1\,mol$ of Na ion) and write the equation as:

$$NaAlSi_3O_8 + KNa_{-1} = KAlSi_3O_8$$

In addition, we can also write the reaction:

$$K - Na = KNa_{-1}$$
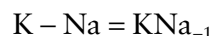
Here we have four species and two reactions and thus a minimum of only two components. You can see that *a component is merely an algebraic term*.

There is generally some freedom in choosing components. For example, in the ternary (i.e., three-component) system SiO_2-Mg_2SiO_4-$MgCaSi_2O_6$, we could choose our components to be quartz, diopside, and forsterite, or we could choose them to be SiO_2, MgO, and CaO. Either way, we are dealing with a ternary system (which contains $MgSiO_3$ as well as the three other phases).

3.2.1.4   Degrees of freedom

The number of degrees of freedom in a system is equal to the sum of the number of independent *intensive* variables (generally temperature and pressure) and independent concentrations (or activities or chemical potentials) of components in phases that must be fixed to define uniquely the state of the system. A system that has no degrees of freedom (i.e., is uniquely fixed) is said to be invariant, one that has one degree of freedom is univariant, and so on. Thus in a univariant system, for example, we need specify the value of only one variable, for example, temperature or the concentration of one component in one phase, and the value of pressure and all other concentrations are then fixed and can be calculated (assuming the system is at equilibrium).

3.2.2   The Gibbs phase rule

The Gibbs* phase rule is a rule for determining the *degrees of freedom*, or *variance*, of a system *at equilibrium*. The rule is:

$$\boxed{f = c - \phi + 2} \qquad (3.2)$$

where f is the degrees of freedom, c is the number of components, and ϕ is the number of phases. The mathematical analogy is that the degrees of freedom are equal to the number of variables minus the number of equations relating those variables. For example, in a system consisting of just H_2O, if two phases coexist, for example, water and steam, then the system is univariant. Three phases coexist

at the triple point of water, so the system is said to be invariant, and T and P are uniquely fixed: there is only one temperature and one pressure at which the three phases of water can coexist (273.15 K and 0.006 MPa). If only one phase is present, for example just liquid water, then we need to specify two variables to describe completely the system. It does not matter which two we pick. We could specify molar volume and temperature and from that we could deduce pressure. Alternatively, we could specify pressure and temperature. There is only one possible value for the molar volume if temperature and pressure are fixed. It is important to remember this applies to intensive parameters. To know volume, an extensive parameter, we would have to fix one additional extensive variable (such as mass or number of moles). And again, we emphasize that all this applies only to systems at equilibrium.

Now consider the hydration of corundum to form gibbsite. There are three phases, but there need be only two components. If these three phases (water, corundum, gibbsite) are at equilibrium, we have only one degree of freedom (i.e., if we know the temperature at which these three phases are in equilibrium, the pressure is also fixed).

Rearranging eqn. 3.2, we also can determine the *maximum* number of phases that can coexist at equilibrium in any system. The degrees of freedom cannot be less than zero, so for an invariant, one-component system, a maximum of three phases can coexist at equilibrium. In a univariant one-component system, only two phases can coexist. Thus sillimanite and kyanite can coexist over a range of temperatures, as can kyanite and andalusite, but the three phases of Al_2SiO_5 coexist only at one unique temperature and pressure.

Let's consider the example of the three-component system Al_2O_3–H_2O–SiO_2 in Figure 3.2. Although many phases are possible in this system, for any given composition of the system only three phases can coexist at equilibrium over a range of temperature and pres-

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* J. Williard Gibbs (1839–1903) is viewed by many as the father of thermodynamics. He received the first doctorate in engineering granted in the US, from Yale in 1858. He was Professor of Mathematical Physics at Yale from 1871 until his death. He also helped to found statistical mechanics. The importance of his work was not widely recognized by his American colleagues, though it was in Europe, until well after his death.

sure. Four phases (e.g., a, k, s, and p) can coexist only along a one-dimensional line or curve in P-T space. Such points are called univariant lines (or curves). Five phases can coexist at invariant points at which both temperature and pressure are uniquely fixed. Turning this around, if we found a metamorphic rock whose composition fell within the Al_2O_3–H_2O–SiO_2 system, and if the rock contained five phases, it would be possible to determine uniquely the temperature and pressure at which the rock equilibrated.

3.2.3   The Clapeyron equation

A common problem in geochemistry is to know how a phase boundary varies in P-T space, for example, how a melting temperature will vary with pressure. At a phase boundary, two phases must be in equilibrium, so ΔG must be 0 for the reaction Phase 1 $\rightleftharpoons$ Phase 2. The phase boundary therefore describes the condition:

$$d(\Delta G_r) = \Delta V_r dP - \Delta S_r dT = 0$$

Thus the slope of a phase boundary on a temperature-pressure diagram is:

$$\boxed{\frac{dT}{dP} = \frac{\Delta V_r}{\Delta S_r}} \qquad (3.3)$$

where ΔV_r and ΔS_r are the volume and entropy changes associated with the reaction. Equation 3.3 is known as the *Clausius-Clapeyron equation*, or simply the *Clapeyron equation*. Because ΔV_r and ΔS_r are functions of temperature and pressure, this is, of course, only an instantaneous slope. For many reactions, however, particularly those involving only solids, the temperature and pressure dependencies of ΔV_r and ΔS_r will be small and the Clapeyron slope will be relatively constant over a large T and P range (see Example 3.1).

Because $\Delta S = \Delta H/T$, the Clapeyron equation may be equivalently written as:

$$\frac{dT}{dP} = \frac{T\Delta V_r}{\Delta H_r} \qquad (3.4)$$

Example 3.1   The graphite-diamond transition

At 25°C the graphite-diamond transition occurs at 1600 MPa (megapascals, 1 MPa = 10 b). Using the standard state (298 K, 0.1 MPa) data below, predict the pressure at which the transformation occurs when temperature is 1000°C.

	Graphite	Diamond
a (K^{-1})	1.05×10^{-05}	7.50×10^{-06}
b (MPa^{-1})	3.08×10^{-05}	2.27×10^{-06}
$S°$ (J/K-mol)	5.74	2.38
V (cm^3/mol)	5.2982	3.417

Answer: We can use the Clapeyron equation to determine the slope of the phase boundary. Then, assuming that ΔS and ΔV are independent of temperature, we can extrapolate this slope to 1000°C to find the pressure of the phase transition at that temperature.

First, we calculate the volumes of graphite and diamond at 1600 MPa as (eqn. 2.140):

$$V = V°(1 - \beta\Delta P) \qquad (3.5)$$

where ΔP is the difference between the pressure of interest (1600 MPa in this case) and the reference pressure (0.1 MPa). Doing so, we find the molar volumes to be 5.037 for graphite and 3.405 for diamond, so ΔV_r is −1.6325 cc/mol. The next step will be to calculate ΔS at 1600 MPa. The pressure dependence of entropy is given by equation 2.148: $\partial S/\partial P)_T = -\alpha V$. Thus to determine the effect of pressure we integrate:

(Continued)

$$S_P = S° + \int_{P_{ref}}^{P_1} \left(\frac{\partial S}{\partial P} \right)_T dP = S° + \int_{P_{ref}}^{P_1} -\alpha V dP \qquad (3.6)$$

(We use S_p to indicate the entropy at the pressure of interest and $S°$ the entropy at the reference pressure.) We need to express V as a function of pressure, so we substitute eqn. 3.5 into 3.6:

$$S_P = S° + \int_{P_{ref}}^{P_1} -\alpha V°(1 - \beta P)dP$$

$$= S° - \alpha V° \left[\Delta P - \frac{\beta}{2}(P_1^2 - P_{ref}^2) \right] \qquad (3.7)$$

The reference pressure, P_{ref}, is negligible compared with P_1 (0.1 MPa vs 1600 PMa), so that this simplifies to:

$$S_P = S° - \alpha V \left[\Delta P - \frac{\beta}{2} P_1^2 \right]$$

For graphite, S_p is 5.66 J/K-mol, for diamond it is 2.34 J/K-mol, so ΔS_r at 1600 MPa is -3.32 J-K^{-1}-mol^{-1}.
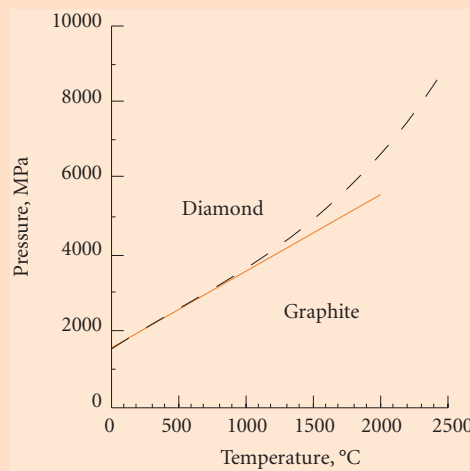
The Clapeyron slope is therefore:

$$\frac{\Delta S}{\Delta V} = \frac{-3.322}{-1.63} = 2.035 \text{ JK}^{-1} \text{ cm}^{-3}$$

One distinct advantage of the SI units is that cm^3 = J/MPa, so the above units are equivalent to K/MPa. From this, the pressure of the phase change at 1000°C can be calculated as:

$$P_{1000} = P_{293} + \Delta T \times \frac{\Delta S}{\Delta V}$$

$$= 1600 + 975 \times 2.035 = 3584 \text{ MPa}$$

The Clapeyron slope we calculated (solid line) is compared with the experimentally determined phase boundary in Figure 3.3. Our calculated phase boundary is linear whereas the experimental one is not. The curved nature of the observed phase boundary indicates ΔV and ΔS are pressure- and temperature-dependent. This is indeed the case, particularly for graphite. A more accurate estimate of the volume change requires that β be expressed as a function of pressure.

Figure 3.3   Comparison of the graphite-diamond phase boundary calculated from thermodynamic data and the Clapeyron slope (solid line) with the experimentally observed phase boundary (dashed line).

Slopes of phase boundaries in P-T space are generally positive, implying that the phases with the largest volumes also generally have the largest entropies (for reasons that become clear from a statistical mechanical treatment). This is particularly true of solid–liquid phase boundaries, although there is one very important exception: water. How do we determine the pressure and temperature dependence of ΔV_r and why is ΔV_r relatively T- and P-independent in solids?

We should emphasize that application of the Clapeyron equation is not limited to reactions between two phases in a one-component system, but may be applied to any univariant reaction.

3.3   SOLUTIONS

Solutions are defined as homogenous phases produced by dissolving one or more substances in another substance. In geochemistry we are often confronted by solutions: as gases, liquids, and solids. Free energy depends not only upon T and P, but also upon composition. In thermodynamics it is generally most convenient to express compositions in terms of mole fractions, X_i, the number of moles of i divided by the total moles in the substance (moles are weight divided by atomic or molecular weight). The sum of all the X_i fractions must, of course, total to 1.

Solutions are distinct from purely mechanical mixtures. For example, salad dressing (oil and vinegar) is not a solution. Similarly, we can grind anorthite ($CaAl_2Si_2O_8$) and albite ($NaAlSi_3O_8$) crystals into a fine powder and mix them, but the result is not a plagioclase solid solution. The Gibbs free energy of mechanical mixtures is simply the sum of the free energy of the components. If, however, we heated the anorthite-albite mixture to a sufficiently high temperature that the kinetic barriers were overcome, there would be a reordering of atoms and the creation of a true solution. Because this reordering is a spontaneous chemical reaction, there must be a decrease in the Gibbs free energy associated with it. This solution would be stable at 1 atm and 25°C. Thus we can conclude that the solution has a lower Gibbs free energy than the mechanical mixture. On the other hand, vinegar will never dissolve in oil at 1 atm and 25°C because the Gibbs free energy of that solution is greater than that of the mechanical mixture.

3.3.1   Raoult's Law

Working with solutions of ethylene bromide and propylene bromide, Raoult* noticed that the vapor pressures of the components in a solution were proportional to the mole fractions of those components:

$$P_i = X_i P_i^o \qquad (3.8)$$

where P_i is the vapor pressure of component i above the solution, X_i is the mole fraction of i in solution, and P_i^o is the vapor pressure of pure i under standard conditions. Assuming the partial pressures are additive and the sum of all the partial pressures is equal to the total gas pressure ($\Sigma P_i = P_{total}$):

$$P_i = X_i P_{total} \qquad (3.9)$$

Thus partial pressures are proportional to their mole fractions. *This is the definition of the **partial pressure** of the ith gas in a mixture.*

Raoult's Law holds only for *ideal solutions*, that is, substances where there are no intermolecular forces. It also holds to a good approximation where the forces between like molecules are the same as between different molecules. The two components Raoult was working with were very similar chemically, so that this condition held and the solution was nearly ideal. As you might guess, not all solutions are ideal. Figure 3.4 shows the variations of partial pressures above a mixture of water and dioxane. Significant deviations from Raoult's Law are the rule except where X_i approaches 1.

3.3.2   Henry's Law

Another useful approximation occurs when X_i approaches 0. In this case, the partial

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* Francois Marie Raoult (1830–1901), French chemist, chaired the Chemistry Department at the Université de Grenoble from 1867 until his death.
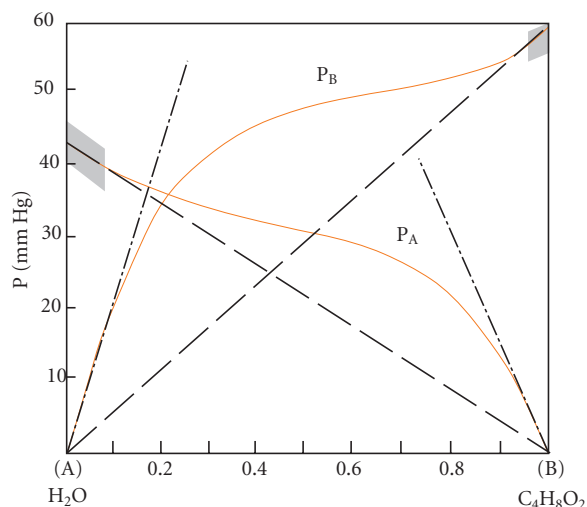
Figure 3.4   Vapor pressure of water and dioxane in a water-dioxane mixture showing deviations from ideal mixing. Shaded areas are areas where Raoult's Law (dashed lines). Henry's Law slopes are shown as dot-dashed lines. After Nordstrom and Munoz (1986). With permission from John Wiley & Sons.

pressures are not equal to the mole fraction times the vapor pressure of the pure substance, but they do vary linearly with X_i. This behavior follows Henry's Law,* which is:

$$P_i = hX_i \text{ for } X_i \ll 1 \qquad (3.10)$$

where h is known as the Henry's Law constant.

3.4   CHEMICAL POTENTIAL

3.4.1   Partial molar quantities

Free energy and other thermodynamic properties are dependent on composition. We need a way of expressing this dependence. For any extensive property of the system, such as volume, entropy, energy, or free energy, we can define a *partial molar value*, which expresses how that property will depend on changes in amount of one component. For example, we define the partial molar volume of component *i* in phase ϕ as:

$$v_i^\phi = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j,j\neq i}} \quad \text{such that} \quad V = \sum_i n_i v_i$$

$$(3.11)$$

(we will use small letters to denote partial molar quantities; the superscript refers to the phase and the subscript refers to the component). The English interpretation of eqn. 3.11 is that *the partial molar volume of component* i *in phase ϕ tells us how the volume of phase ϕ will vary with an infinitesimal addition of component* i, *if all other variables are held constant.* For example, the partial molar volume of Na in an aqueous solution such as seawater would tell us how the volume of that solution would change for an infinitesimal addition of Na. In this case *i* would refer to the Na component and ϕ would refer to the aqueous solution phase. In Table 2.2, we see that the molar volumes of the albite and anorthite end-members of the plagioclase solid solution are different. We could define v_{Ab}^{pl} as the partial molar volume of albite in plagioclase, which would tell us how the volume of plagioclase would vary for an infinitesimal addition of albite. (In this example, we have chosen our component as albite rather than Na. While we could have chosen Na, the choice of albite simplifies matters because the replacement of Na with Ca is accompanied by the replacement of Si by Al.)

The second expression in eqn. 3.11 says that the volume of a phase is the sum of the partial molar volumes of the components times the number of moles of each component present. Thus the volume of plagioclase would be the sum of the partial molar volumes of the albite and anorthite components weighted by the number of moles of each.

Another example might be a solution of water and ethanol. The variation of the partial molar volumes of water and ethanol in a binary solution is illustrated in Figure 3.5. This system illustrates very clearly why the qualification "for an infinitesimal addition" is always added: the value of a partial molar quantity of a component may vary with the amount of that component present.

Equation 3.11 can be generalized to all partial molar quantities and also expresses an

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* Named for English chemist William Henry (1775–1836), who formulated it.
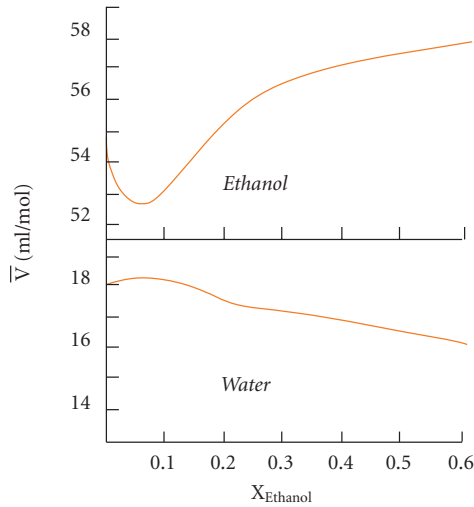
Figure 3.5 Variation of the partial molar volumes of water and ethanol as a function of the mole fraction of ethanol in a binary solution. This figure also illustrates the behavior of a very non-ideal solution. After Nordstrom and Munoz (1986). With permission from John Wiley & Sons.

important property of partial molar quantities: *an extensive variable of a system or phase is the sum of its partial molar quantities for each component in the system*. In our earlier example, this means that the volume of plagioclase is the sum of the partial molar volume of the albite and anorthite components.

Generally, we find it more convenient to convert extensive properties to intensive properties by dividing by the total number of moles in the system, Σn. Dividing both sides of eqn. 3.11 by Σn we have:

$$\bar{V} = \sum_i X_i v_i \qquad (3.12)$$

This equation says that the molar volume of a substance is the sum of the partial molar volumes of its components times their mole fractions. *For a pure phase, the partial molar volume equals the molar volume since X = 1.*

3.4.2 Definition of chemical potential and relationship to Gibbs free energy

We define μ as the *chemical potential*, which is simply the partial molar Gibbs free energy:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j,j\neq i} \qquad (3.13)$$

The chemical potential thus tells us how the Gibbs free energy will vary with the number of moles, n_i, of component i holding temperature, pressure, and the number of moles of all other components constant. We said that the Gibbs free energy of a system is a measure of the capacity of the system to do chemical work. Thus the chemical potential of component i is the amount by which this capacity to do chemical work is changed for an infinitesimal addition of component i at constant temperature and pressure. In a NiCd battery (common rechargeable batteries), for example, the chemical potential of Ni in the battery (our system) is a measure of the capacity of the battery to provide electrical energy per mole of additional Ni for an infinitesimal addition.

The total Gibbs free energy of a system will depend upon composition as well as on temperature and pressure. The equations we introduced for Gibbs free energy in Chapter 2 fully describe the Gibbs free energy only for single component systems or systems containing only pure phases. The Gibbs free energy change of a phase of variable composition is fully expressed as:

$$dG = VdP - SdT + \sum_i \mu_i dn_i \qquad (3.14)$$

3.4.3 Properties of the chemical potential

We now want to consider two important properties of the chemical potential. To illustrate these properties, consider a simple two-phase system in which an infinitesimal amount of component i is transferred from phase β to phase α, under conditions where T, P, and the amount of other components is held constant in each phase. One example of such a reaction would be the transfer of Pb from a hydrothermal solution to a sulfide mineral phase. The chemical potential expresses the change in Gibbs free energy under these conditions:

$$dG = dG^\alpha + dG^\beta = \mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta \qquad (3.15)$$

since we are holding everything else constant, atoms gained by α must be lost by β, so $-dn_i^\alpha = dn_i^\beta$ and:

$$dG = \left(\mu_i^\alpha - \mu_i^\beta\right) dn_i \qquad (3.16)$$

At equilibrium, $dG = 0$, and therefore

$$\mu_i^\alpha = \mu_i^\beta \qquad (3.17)$$

Equation 3.17 reflects a very general and very important relationship, namely:

> **In a system at equilibrium, the chemical potential of every component in a phase is equal to the chemical potential of that component in every other phase in which that component is present.**

Equilibrium is the state toward which systems will naturally transform. The Gibbs free energy is the chemical energy available to fuel these transformations. *We can regard differences in chemical potentials as the forces driving transfer of components between phases*. In this sense, the chemical potential is similar to other forms of potential energy, such as gravitational or electromagnetic. Physical systems spontaneously transform so as to minimize potential energy. Thus for example, water on the surface of the Earth will move to a point where its gravitational potential energy is minimized – downhill. Just as gravitational potential energy drives this motion, the chemical potential drives chemical reactions, and just as water will come to rest when gravitational energy is minimized, chemical reactions will cease when chemical potential is minimized. So in our earlier example, the spontaneous transfer of Pb between a hydrothermal solution and a sulfide phase will occur until the chemical potentials of Pb in the solution and in the sulfide are equal. At this point, there is no further energy available to drive the transfer.

We defined the chemical potential in terms of the Gibbs free energy. However, in his original work, Gibbs based the chemical potential on the internal energy of the system. As it turns out, however, the quantities are the same:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j, j \neq i} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j, j \neq i} \qquad (3.18)$$

It can be further shown (but we won't) that:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j, j \neq i} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j, j \neq i} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j, j \neq i}$$

$$= \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j, j \neq i}$$

3.4.4   The Gibbs-Duhem relation

Since μ is the partial molar Gibbs free energy, the Gibbs free energy of a system is the sum of the chemical potentials of each component:

$$G = \sum_i n_i \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j, j \neq i} = \sum_i n_i \mu_i \qquad (3.19)$$

The differential form of this equation (which we get simply by applying the chain rule) is:

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \qquad (3.20)$$

Equating this with eqn. 3.14, we obtain:

$$\sum_i n_i d\mu_i + \sum_i \mu_i dn_i = VdP - SdT + \sum_i \mu_i dn_i \qquad (3.21)$$

Rearranging, we obtain the *Gibbs-Duhem relation*:

$$\boxed{VdP - SdT - \sum_i n_i d\mu_i = 0} \qquad (3.22)$$

The Gibbs-Duhem equation describes the relationship between simultaneous changes in pressure, temperature and composition in a single-phase system. In a closed system at equilibrium, net changes in chemical potential will occur only as a result of changes in temperature or pressure. *At constant temperature and pressure*, there can be no net change in chemical potential at equilibrium:

$$\boxed{\sum_i n_i d\mu_i = 0} \qquad (3.23)$$

This equation further tells us that the chemical potentials do not vary independently, but change in a related way. In a closed system, only one chemical potential can vary inde-