Lecture 6

Chemical Thermodynamics

Pease read White Chapter 4 for today's lecture.

- Non ideality in aqueous mixtures, continued
- Other Types of Solubility (trace element substitution into solids and solid solutions

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Non-Ideality in Chemical Mixtures

Last lecture we discussed that we can estimate γ_I with the Debye-Hückel equation: $-\log \gamma_i = A\, z_i^2\, \mathbf{I}^{\frac{1}{2}}$

For sea water, the major ion content is (almost) constant so the same γ_i parameterization works throughout the oceans.

TABLE 8.1 Major Dissolved Components of Seawater for a Salinity of 35‰

| | Concentration | | | Percent |
Ion	g/kg	mMª	%	Free Ion
Cl⁻	19.354	558	55	100
Na⁺	10.77	479	31	98
Mg⁺⁺	1.290	54.3	3.7	89
SO₄⁻⁻	2.712	28.9	7.7	39
Ca⁺⁺	0.412	10.5	1.2	99
K⁺	0.399	10.4	1.1	98
HCO₃⁻ᵇ	0.12	2.0	0.41	80

ª mM = millimoles per liter at 25°C.
ᵇ For pH = 8.1, P = 1 atm, T = 25°C.
Sources: Wilson 1975; Skirrow 1975; Millero and Schreiber 1982.

A simple Debye-Hückel parameterization turns out to be inadequate for sea water and higher $\mathbf{I}$ situations, so one or another forms of extended Debye-Hückel theory are used.

Non-Ideality in Chemical Mixtures

There are two closely-related γ parameterizations :

a. the "Truesdell- Jones" Equation. $-\log \gamma_i = \dfrac{A z_i^2 I^{\frac{1}{2}}}{1 + B a_i I^{\frac{1}{2}}}$

where a_i is ionic radius, and A and B are temperature dependent constants

TABLE 3-1   VALUES OF CONSTANTS FOR USE IN THE DEBYE-HUCKEL EQUATION[*]

Temperature, °C	A	B ($\times 10^{-8}$)	$\mathring{a} \times 10^8$	Ion
0	0.4883	0.3241	2.5	Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+
5	0.4921	0.3249	3.0	K^+, Cl^-, Br^-, I^-, NO_3^-
10	0.4960	0.3258	3.5	OH^-, F^-, HS^-, BrO_3^-, IO_4^-, MnO_4^-
15	0.5000	0.3262	4.0–4.5	Na^+, HCO_3^-, $H_2PO_4^-$, HSO_3^-, Hg_2^{2+}, SO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}, PO_4^{3-}
20	0.5042	0.3273	4.5	Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}
25	0.5085	0.3281	5.0	Sr^{2+}, Ba^{2+}, Ra^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, WO_4^{2-}
30	0.5130	0.3290	6	Li^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}
35	0.5175	0.3297	8	Mg^{2+}, Be^{2+}
40	0.5221	0.3305	9	H^+, Al^{3+}, Cr^{3+}, trivalent rare earths
45	0.5271	0.3314	11	Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}
50	0.5319	0.3321		
55	0.5371	0.3329		
60	0.5425	0.3338		

[*]Data from Garrels and Christ (1982).

$$\log_{10} \gamma_{Ca^{2+}} = \frac{-A z_i^2 \sqrt{I}}{1 + B \mathring{a} \sqrt{I}}$$

Non-Ideality in Chemical Mixtures

b. the "Davies" Equation

TABLE 2-3
Activity coefficients calculated from Davies' equation

Ionic strength	Ionic charge		
	±1	±2	±3
0.001	0.97	0.87	0.73
0.005	0.93	0.74	0.51
0.01	0.90	0.66	0.40
0.05	0.82	0.45	0.16
0.1	0.78	0.36	0.10
0.2	0.73	0.28	0.06
0.5	0.69	0.23	0.04
0.7	0.69	0.23	0.04

$$-\log \gamma = A z^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.2I \right)$$

$$-\log \gamma_i = A z_i^2 \left[\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2\,I \right]$$

in the Davies equation, the "0.2 **I**" term attempts to account for the "Ba_i" term of the Truesdell-Jones equation.

Notice that the Davies approximation has no solute-specific size parameterization (a_i) whereas Truesdell- Jones does.
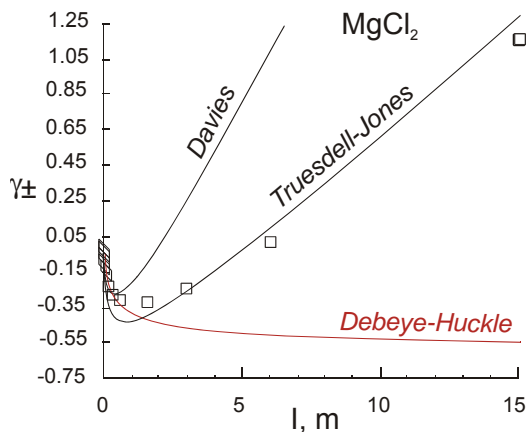
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Non-Ideality in Chemical Mixtures

Figure 4.30. Measured mean ionic activity coefficients in MgCl2 solution as a function of ionic strength compared with values calculated from the Debye-Huckel, Davies and Truesdell-Jones equations. *From White, "Geochemistry"*

A comparison of the "Truesdell-Jones" and Davies equations for a $MgCl_2$ solution shows that Debye-Hückle and Davies work best at low I

and Truesdale-Jones works better at high I, for this particular salt.

Non-Ideality in Chemical Mixtures

Let's calculate true activity of Ca^{2+} in a 0.05 m solution of $CaCl_2$ at 25°C using extended Debye-Hückel theory (Truesdale-Jones).

$$CaCl_{2\ (s)} \rightleftarrows Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$
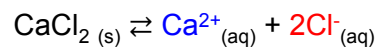
a. First, we calculate Ionic Strength:

$$I = 0.5\ \Sigma m_i\ z_i^2 = 0.5\ [0.05(2)^2 + 0.1(^-1)^2] = 0.15$$
$$\quad\quad\quad\quad\quad\quad\quad Ca^{2+} \quad\quad Cl^-$$

Non-Ideality in Chemical Mixtures

b. next we get γ_{Ca2+} using.... *(get values from this table)*

Ca^{2+}

$- \log \gamma_{Ca2+} = \dfrac{0.5085(2)^2 (0.15)^{\frac{1}{2}}}{1 + (0.3281 \times 10^8)(6 \times 10^{-8})(0.15)^{\frac{1}{2}}}$, $\gamma_{Ca2+} = 0.357$

c. then we get $a_{Ca2+} = \gamma_{Ca2+} \, m_{Ca2+} = 0.357(0.05)$ $a_{Ca2+} = 0.018m$

TABLE 3-1 VALUES OF CONSTANTS FOR USE IN THE DEBYE-HUCKEL EQUATION*

Temperature, °C	A	$B (\times 10^{-8})$	$\overset{\circ}{a} \times 10^8$	Ion
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15	0.5000	0.3262	4.0–4.5	$Na^+, HCO_3^-, H_2PO_4^-, HSO_3^-, Hg_2^{2+}, SO_4^{2-},$ $SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}, PO_4^{3-}$
20	0.5042	0.3273	4.5	$Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}$
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30	0.5130	0.3290	6	$Li^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+},$ Co^{2+}
35	0.5175	0.3297	8	Mg^{2+}, Be^{2+}
40	0.5221	0.3305	9	$H^+, Al^{3+}, Cr^{3+},$ trivalent rare earths
45	0.5271	0.3314	11	$Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}$
50	0.5319	0.3321		
55	0.5371	0.3329		
60	0.5425	0.3338		$\log_{10} \gamma_{Ca^{2+}} = \dfrac{-A \, z_i^2 \sqrt{I}}{1 + B \overset{\circ}{a} \sqrt{I}}$

*Data from Garrels and Christ (1982).

Non-Ideality in Chemical Mixtures

What quantitative effect does ionic strength have on overall solubility of ionic compounds?

Solubility is defined as the total amount of a material that will dissolve into a fixed amount of solvent. If we assume ideal behavior, each mole of a salt that dissolves in a liter of water will result in stoichiometric molal units of solute concentration.

In the case of "ideal" $CaCl_2$: $K_{sp} = m_{Ca2+} \, m_{Cl-}^2$

But with non-ideal ions, the solution upon dissolution reflects ion activities: $K_{sp-ia} = a_{Ca2+} \, a_{Cl-}^2$

note: I've renamed the equilibrium constant for the non ideal case with the "ion-activity" subscript so we can keep track of it in equations on the next page

Non-Ideality in Chemical Mixtures

To quantify the effect of I, we need to calculate γ_{Cl^-} = 0.720 (in the same manner we used for γ_{Ca2+}, but using z =1 and a = 3 x 10^{-8}).

$$K_{sp\text{-}ia} = a_{Ca2+} \, a_{Cl^-} \quad = \quad (\gamma_{Ca2+} \, m_{Ca2+}) \cdot (\gamma_{Cl^-} \, m_{Cl^-})^2$$
$$= \quad \gamma_{Ca2+} \, \gamma_{Cl^-}^2 \cdot m_{Ca2+} m_{Cl^-}^2$$
$$K_{sp\text{-}ia} \quad = \quad \gamma_{Ca2+} \, \gamma_{Cl^-}^2 \cdot K_{sp}$$
$$K_{sp\text{-}ia} \quad = \quad (0.357) \cdot (0.720)^2 \cdot K_{sp}$$

$$K_{sp} \quad = \quad 5.40 \, K_{sp\text{-}ia}$$

thus, at I = 0.15 (a typical stream water value) we predict that the solubility of $CaCl_2$ is 5.4 times higher due to non-ideality than it would be if the dissolved ions behaved ideally.

Non-Ideality in Chemical Mixtures

The last example we looked at was a simplified case, where all of the Ionic Strength of a solution came from one salt.

Systems with multiple salts are more common in nature. Nevertheless, the parameterizations of γ_i work the same.

Our parameterizations predict that double charged ions would have much lower activities than singly charged ones, so that these are the ions that have the biggest non-ideality effects (e.g., Ca2+ and Mg2+ more so than Na+ or K+, and the same for negatively charged ions).

Relative γ_i as a function of I (e.g., going from I = 0.15 to I = 0.7)
γ_i depends on I differently in each parameterization.
However, in general, once can show with these various equations that activity for the same ions goes down by roughly
* 10% for single charged ions
* 35% for doubly charged ions

Thermodynamics of Chemical Mixtures

Other Types of Solubility

Thermodynamics of Chemical Mixtures

Other Types of Solubility
Solutions are not limited to aqueous/gaseous examples.

Mixtures apply to the solid state as well.

We can use chemical potential arguments and solubility relationships any time a solute (or group of solutes) is dissolved in a solvent (the dominant phase in the mixture),.

Thermodynamics of Chemical Mixtures

Other Types of Solubility

One common use of this theory is to solubility of ions in mineral phases. This applies to:

1. **Trace element** substitution into minerals.

2. **Solid solutions** such as in the olivine system of Forsterite, Mg_2SiO_4 -- Fayalite, Fe_2SiO_4

Such solubility is often temperature or pressure dependent, giving us a means to estimate temperature (thermometry) or pressure (barometry) or both (thermobarometry) in some cases.

Thermodynamics of Chemical Mixtures

1. Trace element substitutions are typically at high dilution. Take the example of Co solubility in the minerals biotite and hornblende.

$\mu_{Co} = \mu_{Co}{}^* + RT \ln a_{Co}/a_{tot}$ at high dilution, $a_{tot} \sim 1$ so $\mu_{Co} = \mu_{Co}{}^* + RT \ln a_{Co}$

at chemical equilibrium between biotite and hornblend:

$$\mu_{Co}{}^{Bi} = \mu_{Co}{}^{Hbl} \text{ and } \mu_{Co}{}^{Bi}/\mu_{Co}{}^{Hbl} = 1$$

Thus $1 = (\mu_{Co}{}^{Bi*} + RT \ln a_{Co}{}^{Bi})/(\mu_{Co}{}^{Hbl*} + RT \ln a_{Co}{}^{Hbl})$
rearranging... $1 = (1 + (RT \ln a_{Co}{}^{Bi})/\mu_{Co}{}^{Bi*})/(1 + (RT \ln a_{Co}{}^{Hbl})/\mu_{Co}{}^{Hbl*}$

$\mu_{Co}{}^{Bi*}$, $\mu_{Co}{}^{Hbl*}$, and R are constants, so at constant T this reduces to
$$1 = (1 + C_1 \ln a_{Co}{}^{Bi})/(1 + C_2 \ln a_{Co}{}^{Hbl})$$
then $(1 + C_2 \ln a_{Co}{}^{Hbl}) = (1 + C_1 \ln a_{Co}{}^{Bi})$
$C_2 \ln a_{Co}{}^{Hbl} = C_1 \ln a_{Co}{}^{Bi}$
$C_2/C_1 = \ln a_{Co}{}^{Bi}/\ln a_{Co}{}^{Hbl}$

raising both sides to the e power yields:
$e^{C2/C1} = K$ → $\boxed{K = a_{Co}{}^{Bi}/a_{Co}{}^{Hbl}}$

Thermodynamics of Chemical Mixtures

The resulting K is denoted K_D and is referred to as a **"distribution coefficient"** or **"partition coefficient"** of an element between the phases present. In this case, it is the K_D for Co between biotite and hornblend (K_D^{Co}).

K_D is also sometimes called a *"Henry's law distribution coefficient"* because the equation above is a generalization of $K = P_i/n_i$ (aka Henry's Law).

We will use such K_D relationships frequently this semester.

Non ideality:
We do not have a simple theory for predicting γ_i in mineral systems

We rely on <u>experimentally</u> determined a_i or on values <u>estimated</u> from like-charged elements parameterized as a function of atomic radius and mineral lattice strain considerations (discussed later this semester).

Thermodynamics of Chemical Mixtures

2. Solid solutions The K_D formulation of chemical potential also applies here. Take for example the minerals garnet and mica, which form mineral solid solutions of the type:

	Biotite mica - $K(Z_3)AlSi_3O_{10}(OH)_2$	**garnet -** $Z_3Al_2Si_3O_{12}$
where Z is any one of a number of ions.		
Common igneous forms	**phlogopite** $K(Mg_3)AlSi_3O_{10}(OH)_2$ **annite** $K(Fe_3)AlSi_3O_{10}(OH)_2$	**pyrope** $Mg_3Al_2Si_3O_{12}$ **almandine** $Fe_3Al_2Si_3O_{12}$

Because a range of stoichiometric and non-stoichiometric forms of either mineral are possible (e.g., $(Mg_xFe_{1-x})_3Al_2Si_3O_{12}$), we think of the solid solution as arising from an exchange reaction with

$$K_D = (a_{Fe}/a_{Mg})_{garnet} / (a_{Fe}/a_{Mg})_{biotite}$$

Thermodynamics of Chemical Mixtures

Here's how we derive that equilibrium constant expression:

The simplified chemical reaction is
Mg-garnet + Fe-biotite $\leftrightarrow$ Fe-garnet + Mg-biotite

By the definition of equilibrium constant, we know:

K_{eq} = (a_{Fe}^{garnet} $a_{Mg}^{biotite}$)/(a_{Mg}^{garnet} $a_{Fe}^{biotite}$)

= (a_{Fe}/a_{Mg})$_{garnet}$/(a_{Fe}/a_{Mg})$_{biotite}$

= K_D as on the prior slide.

Thermodynamics of Chemical Mixtures

Pressure and Temperature Effects

Most chemical reactions have temperature and pressure dependent K_{eq}:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^o}{RT^2} \qquad \textbf{at constant P}$$

The change in K_{eq} as a function of temperature is related to the enthalpy change inversely related to Temperature-squared

When ΔH^o is independent of temperature, this becomes
$$\ln K_2/K_1 = \Delta H^o/R \cdot (1/T_2 - 1/T_1)$$

The change in K_{eq} as a function of temperature is related to the enthalpy change divided by the change in Temperature times R

and $\qquad\qquad \dfrac{d(\ln K)}{dP} = \dfrac{\Delta V^o}{RT} \qquad \textbf{at constant T}$

The change in K_{eq} as a function of pressure is related to the volume change divided by the Temperature times R

Thermodynamics of Chemical Mixtures

These **P** and **T** relationships give us a geochemical means for determining the temperatures (*Geothermometry*) and pressures (*Geobarometry*) in which minerals were formed.

3 classes of reactions are used as P-T indicators

a. solid solution substitutions in minerals
(e.g., like we were just discussing)

b. phase boundary changes

c. phase exsolution from a mixture ("unmixing")

The first two types are useful for determining temperatures (or pressures) of many igneous; all three are useful in metamorphic systems.

Thermodynamics of Chemical Mixtures

For instance, the exchange reaction of Fe and Mg between the minerals *garnet* and *biotite* is used as a geothermometer because K_D is temperature dependent @ ln K ∝ 1/T.

$$K_D = (a_{Fe}/a_{Mg})_{garnet}/(a_{Fe}/a_{Mg})_{biotite}$$

It is difficult to calculate the temperature dependence of this exchange from first principles, because of ion non-ideality, and because other elements besides Fe and Mg (i.e., Ca and Ti) can appreciably substitute into these minerals as "Z".

Instead…

Thermodynamics of Chemical Mixtures

Instead, the temperature dependence is parameterized using experimental measurements of K_D^{Mg-Fe} at different temperatures, pressures and ion mixtures (for Z). The resulting data are plotted in in a 1/T vs. ln K diagram (i.e., assuming ΔH_o is not a function of temperature), and a best-fit line through the data is then calculated.

$$K_D = \frac{N_{Fe}^{gar}/N_{Mg}^{gar}}{N_{Fe}^{bio}/N_{Mg}^{bio}}$$
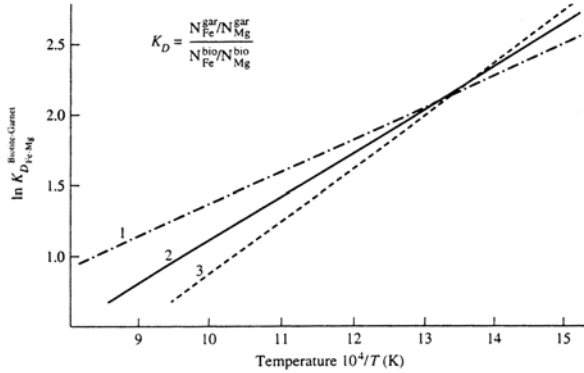
Figure 3-4 Three different calibrations of the biotite-garnet K_D thermometer. Curve one is based on laboratory experimentation [Ferry and Spear (1978)], curve two on field observations [Thompson (1976)], and curve three on comparison with isotopic thermometry [Goldman and Albee (1977)]. Solid solution of components other than iron and magnesium can affect the validity of this and similar geothermometers. N_{Fe}^{gar} is the mole fraction of iron in garnet and so forth. After Essene (1982).

Thermodynamics of Chemical Mixtures

We are not limited only to mineral-mineral substitution reactions.

We can also use certain **mineral-melt** reactions for geothermometry or geobarometry.

For example, another useful geo-thermometer is the Fe-Mg exchange reaction between **basaltic melt** and **olivine**.
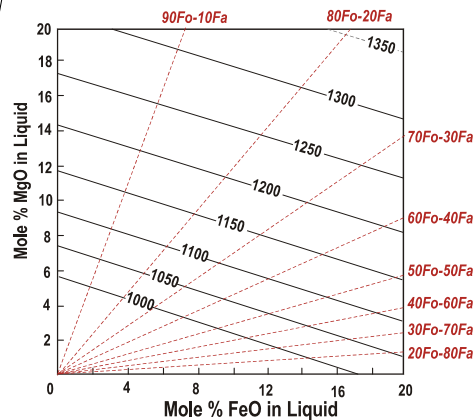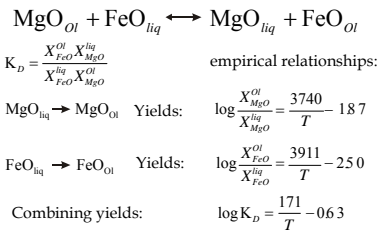
$$MgO_{Ol} + FeO_{liq} \longleftrightarrow MgO_{liq} + FeO_{Ol}$$

$$K_D = \frac{X_{FeO}^{Ol} X_{MgO}^{liq}}{X_{FeO}^{liq} X_{MgO}^{Ol}}$$

empirical relationships:

$MgO_{liq} \rightarrow MgO_{Ol}$ Yields: $\log \frac{X_{MgO}^{Ol}}{X_{MgO}^{liq}} = \frac{3740}{T} - 1.87$

$FeO_{liq} \rightarrow FeO_{Ol}$ Yields: $\log \frac{X_{FeO}^{Ol}}{X_{FeO}^{liq}} = \frac{3911}{T} - 2.50$

Combining yields: $\log K_D = \frac{171}{T} - 0.63$

Fig. 4.18. Olivine saturation surface constructed by Roeder and Emslie (1970).

Thermodynamics of Chemical Mixtures

Solid solution geothermometry is not limited to igneous and metamorphic systems.

For instance, the substitution of Sr^{2+}, Mg^{2+} and U^{+6} into biogenic $CaCO_3$ (both calcite and aragonite) is T-dependent, from which one can estimate past sea surface temperatures (SST) in paleo-oceanographic studies.
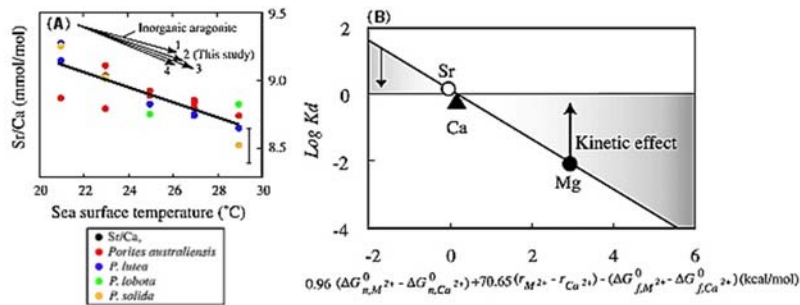
Relationships between the Sr/Ca ratios in *Porites* spp. colonies against (a) incubation temperature for 5 coral colonies cultured at five temperature settings between 21°C and 29°C. The error bar indicates the deviation of triplicate analysis. The formula obtained for the Sr/Ca–temperature relationship was Sr/Ca = 10.31 − 0.057T (°C); r = −0.83; P < 0.01. (b) Diagram of divalent metal partition coefficients (K_d) as a function of metal cation properties. The latter are represented by $\Delta G^0_{n,M}{}^{2+}$, the standard non-solvation energy of cation M^{2+}, $r_M{}^{2+}$, the ionic radius of M^{2+}, and $\Delta G^0_{f,M}{}^{2+}$, the standard Gibbs free energy of formation of cation M^{2+} (from Inoue et al. 2007, Geophys. Res. Lett., vol. 34).

Thermodynamics of Chemical Mixtures

Mineral phase boundary change example:

The presence of just one, any two, or all three of these three phases in a rock gives useful constraints on P and T of formation. This is a very useful system in metamorphosed pelitic (i.e., clay-rich) sediments.
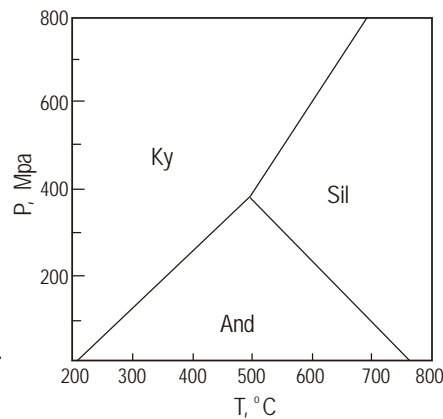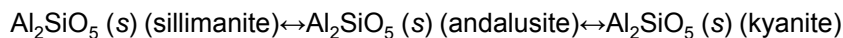

Figure 4.14. Phase diagram for Al_2SiO_5 (kyanite-silli-manite-andalusite) as determined by Holdaway (1971). Due to sluggish reaction kinetics, the exact position of these phase boundaries remains somewhat uncertain.

Al_2SiO_5 (*s*) (sillimanite)$\leftrightarrow Al_2SiO_5$ (*s*) (andalusite)$\leftrightarrow Al_2SiO_5$ (*s*) (kyanite)