Geology 633
Metamorphism and Lithosphere Evolution

Thermodynamic calculation of mineral reactions I:
Reactions involving pure phases

The formulation for the free energy change of any reaction *involving pure phases* (which is why we use the '°') at elevated P and T is calculated as follows:

$$\Delta_r G^\circ_{P,\,T} \qquad = \Delta_r H^\circ_{P,\,T} - T\,\Delta_r S^\circ_{P,\,T}$$

where 'Δ_r' is the change in $G^\circ_{P,\,T}$, $H^\circ_{P,\,T}$ and $S^\circ_{P,\,T}$ in the reaction.

At equilibrium:

$$\Delta_r G^\circ_{P,\,T} \qquad = \Delta_r H^\circ_{P,\,T} - T\,\Delta_r S^\circ_{P,\,T} \qquad = 0$$

thus

$$\Delta_r G^\circ_{P,\,T} = 0 \quad = [\,\Delta_r H^\circ_{1,\,298} + {}_{298}\!\int^{T} (\partial \Delta_r H^\circ/\partial T)_P\, dT + {}_{1}\!\int^{P} (\partial \Delta_r H^\circ/\partial P)_T\, dP]$$

$$- T\,[\Delta_r S^\circ_{1,298} + {}_{298}\!\int^{T} (\partial \Delta_r S^\circ/\partial T)_P\, dT + {}_{1}\!\int^{P} (\partial \Delta_r S^\circ/\partial P)_T\, dP\,]$$

we will assume that the variation of S with pressure is negligible (ie, ${}_{1}\!\int^{P} (\partial \Delta_r S^\circ/\partial P)_T\, dP = 0$), and substitute in expressions for the other variation terms:

$$= [\,\Delta_r H^\circ_{1,\,298} + {}_{298}\!\int^{T} \Delta_r C_p\, dT + {}_{1}\!\int^{P} \Delta_r V^\circ\, dP]$$

$$- T\,[\Delta_r S^\circ_{1,298} + {}_{298}\!\int^{T} \Delta_r C_p/T\, dT\,]$$

1. Solids-only reactions

If we are dealing with a solids-only reaction, we will assume that the molar volume of crystalline solids (minerals) does not change significantly with P and T (ie, $\alpha \approx \beta \approx 0$), so that ${}_{1}\!\int^{P} \Delta_r V\, dP = \Delta_r V^\circ_s\,(P - 1)$. (By adding the subscript '$_s$' to $\Delta_r V^\circ_s$, we remind ourselves that this approximation only holds for solid phases, not fluids). Note that in this expression, pressure units are in bars.

$$= [\,\Delta_r H^\circ_{1,\,298} + {}_{298}\!\int^{T} \Delta_r C_p\, dT + \Delta_r V^\circ_{s\;1,\,298}\,(P - 1)]$$

$$- T\,[\Delta_r S^\circ_{1,298} + {}_{298}\!\int^{T} \Delta_r C_p/T\, dT\,]$$

To complete the formulation, we need to know the formula for $\Delta_r C_p$, the heat capacity expression. Heat capacity in general is a complex function of T, such as:

$$C_p = a + bT + cT^2 + dT^{-0.5} + eT^{-2}$$

or, for the reaction:

$\Delta_r C_p = \Delta_r a + \Delta_r bT + \Delta_r cT^2 + \Delta_r dT^{-0.5} + \Delta_r eT^{-2}$

This expression is substituted in the two places in the above formula for '$\Delta_r C_p$'. The expression must then be broken into its parts, integrated and solved between the limits of 298K and T, similar to what you did in Glgy 429. Note that we are concerned with $\mathbf{\Delta_r C_p}$, so that each term in the general expression below (a, b, c, etc.) has to be calculated for the reaction (ie, $\Delta_r a$, $\Delta_r b$, $\Delta_r c$, etc.).

Simplifications for first order analysis of a solids-only reaction involving pure phases

For a solids-only *reaction,* it turns out that the **change** in the heat capacities between reactants and products going from 1, 298 to P,T is usually small. So, for **first order analysis** of a solids-only reaction, we can make the assumption that $\Delta_r C_p = 0$. Note that this is NOT the same as saying that the enthalpy and entropy of an individual phase involved in the reaction does not change with T – they do! It is just that the changes between the reactant phases and product phases is often about the same, which algebraically is the same as setting $\Delta_r C_p = 0$.

Thus, the above equation simplifies considerably to:

$$\Delta_r G^\circ_{P,T} = \Delta_r H^\circ_{P,T} - T\,\Delta_r S^\circ_{P,T} = 0 \text{ at equilibrium}$$

$$= \Delta_r H^\circ_{1,298} + \Delta_r V^\circ_{s\,1,298}\,(P-1) - T\,\Delta_r S^\circ_{1,298}$$

Note that this simplified formula is used for first-order calculations only. With the widespread use of computers, it is not that complicated to code in the full expressions and these will provide more accurate results.

Finally, to obtain two extremely useful relations in determining the general slope of a reaction, recall the Gibbs-Helmholtz relation:

$dG = -SdT + VdP$

which when compared to the total differential of G:

$dG = (\partial G/\partial T)_P\,dT + (\partial G/\partial P)_T\,dP$

gives the following two key relations:

$\mathbf{(\partial G/\partial T)_P = -S}$ (or, for a reaction: $(\partial \Delta_r G^\circ_{P,T}/\partial T)_P = -\Delta_r S^\circ_{P,T}$)
$\mathbf{(\partial G/\partial P)_T = V}$ (or, for a reaction: $(\partial \Delta_r G^\circ_{P,T}/\partial P)_T = \Delta_r V^\circ_{P,T}$)

In using these expressions for solids-only reactions, it is usually sufficient to assume that:

$$\Delta_r V^\circ_{s\,P,\,T} = \Delta_r V^\circ_{s\,1,\,298} \text{ and } \Delta_r S^\circ_{P,\,T} = \Delta_r S^\circ_{1,298}$$

finally, to calculate the slope of a reaction (meaning, at equilibrium where $dG = 0$):

$$\boldsymbol{(\partial P/\partial T)_{P,T} = \Delta_r S^\circ_{P,\,T} / \Delta_r V^\circ_{P,\,T}}$$

but for our assumptions about S and V in solids, this end up being:

$$(\partial P/\partial T)_{P,T} \sim (\partial P/\partial T)_{1,\,298} = \Delta_r S^\circ_{1,\,298} / \Delta_r V^\circ_{1,\,298}$$

Data

Below are thermochemical data for each of the minerals from Robie et al. (1978). In Robie's tabulation, variation of heat capacity with temperature may be expressed by the equation:

$$C_p = a + bT + cT^2 + dT^{-0.5} + eT^{-2}$$

Parameter	Units	Anorthite	Quartz	Grossular	Wollastonite
$V^\circ_{(1,298)}$	$cm^3\ mol^{-1}$	100.79	22.688	125.30	39.93
$\Delta_f H^\circ_{(1,298)}$	$kJ\ mol^{-1}$	-4243.04	-910.70	-6656.70	-1635.22
$S^\circ_{(1,298)}$	$J\ K^{-1}\ mol^{-1}$	199.3	41.46	255.5	82.01
C_p constants:					
a		516.83	44.603	1529.3	111.25
b		-9.2492×10^{-2}	3.7754×10^{-2}	-0.69900	1.4373×10^{-2}
c		4.1883×10^{-5}	0	2.53×10^{-4}	0
d		-4.5885×10^{3}	0	-1.8943×10^{4}	16.936
e		-1.4085×10^{6}	-1.0018×10^{6}	7.4426×10^{6}	-2.7779×10^{6}

Exercise

1. Balance a reaction between the pure, solid phases grossular (Grs - $Ca_3Al_2Si_3O_{12}$), wollastonite (Wo- $CaSiO_3$), quartz (Qtz - SiO_2) and anorthite (An - $CaAl_2Si_2O_8$). *(You must do this right, or the rest of the exercise will fail!)*

2. Let's do some first order analysis using the heat capacity simplifications to get a feel for the approximate slope and position of the reaction. Answer the following questions:

(a) Which assemblage is more stable at 1 bar, 298K?

(b) Which assemblage is favoured by increasing pressure?

(c) Which assemblage is favoured by increasing temperature?

(d) What is the slope of the reaction?

(e) At P = 1 bar, what is the equilibrium temperature of the reaction?

(f) Based on all of the above, plot on some graph paper the position of the reaction, correctly labelled (ie, reactant and product phases placed on the correct side of the reaction). (Don't make your plot go above 10 kbar)

3. Now let's be more rigorous. Using the full expression for $\Delta_r G^\circ_{P,\,T}$, calculate and plot the P-T position of the reaction using Excel (again, don't go above 10 kbar). For temperature, don't extrapolate beyond the limits of applicability of the heat capacity equations, which is 300 –1800 K.

4. By plotting the equilibrium curves on one chart/graph, how do the two curves compare? In this case, is the heat capacity simplification justified?

5. You will now use above results (recognizing that what you have calculated is a *thermodynamic model* of the real reaction) to make some interesting geological inferences.

(a) For a temperature of 950 K (a temperature typically found for this assemblage), estimate the depth in the earth at which the full assemblage involved in the reaction would be found (ie, where the equilibrium occurs). Use the curve obtained in (3) to get your pressure. Assume an average rock density of 2.6 g cm^{-3}. (Recall that $P = \rho g h$).

(b) What would be the average geothermal gradient, in K (or °C) km^{-1}? How does this compare to the earth's average geothermal gradient? What sort of geological setting might provide the temperature conditions necessary for the formation of this assemblage at this depth?

2. Thermodynamic calculations of reactions with fluids

Recall from above that, at equilibrium:

$$\Delta_r G^\circ_{P,\,T} = 0 \quad = [\, \Delta_r H^\circ_{1,\,298} + {}_{298}\!\int^{T} (\partial \Delta_r H^\circ/\partial T)_P \, dT + {}_{1}\!\int^{P} (\partial \Delta_r H^\circ/\partial P)_T \, dP]$$

$$- T\, [\Delta_r S^\circ_{1,298} + {}_{298}\!\int^{T} (\partial \Delta_r S^\circ/\partial T)_P \, dT \; + {}_{1}\!\int^{P} (\partial \Delta_r S^\circ/\partial P)_T \, dP\,]$$

$$= [\, \Delta_r H^\circ_{1,\,298} + {}_{298}\!\int^{T} \Delta_r C_p \, dT + {}_{1}\!\int^{P} (\partial \Delta_r H^\circ/\partial P)_T \, dP]$$

$$- T\, [\Delta_r S^\circ_{1,298} + {}_{298}\!\int^{T} \Delta_r C_p/T \, dT\,]$$

Whereas we assumed, for *solids-only reactions*, that:

$$_1\int^P (\partial\Delta_r H°/\partial P)_T \, dP] = {_1\int^P} \Delta_r V_s° \, dP = \Delta_r V°_{s\,1,\,298} \, (P - 1)$$

we cannot do this for fluids because they are so compressible.

Instead, for fluids, we must use the expression:

$$_1\int^P V_f° \, dP \qquad = RT \ln f° \,^P\big|_1 \qquad \text{(using bars as units of P and } f\text{)}$$

in which f stands for fugacity of a gas, and $f°$ stands for fugacity of a pure gas.

Because the properties of gases at a pressure of 1 bar (any T) are close to those of an ideal gas, the fugacity of a gas at a pressure of 1 bar (any T) is assumed to equal to 1 bar (ie, the fugacity coefficient is 1). Thus:

$$RT \ln f° \,^P\big|_1 \quad = RT \ln f°_P - RT\ln f°_{1\ bar} = RT\ln (f°_P/ f°_{1\ bar}) = RT(\ln f°_P/1)$$

$$= RT\ln f°_P$$

Because the degree of non-ideality, and thus the fugacity, of gases depends on P as well as T, the general expression becomes:

$$= RT\ln f°_{P,T}$$

where $f°_{P,T}$ stands for the fugacity of a pure fluid at any P and T. If you do a units check for the above term, you might conclude that the units are J-bar, rather than J as we want! The reason is that in evaluating the integral between P and 1 bar, units of P ($f°_{P,T}$) are divided by units of P ($f°_{1\ bar,T}$) (look inside the natural log term), such that the P units cancel. Thus, you must be aware that the term $RT\ln f°_{P,T}$ as written implies division by a P term whose value is 1 bar, such that the units do ultimately work out to be in J.

Values of $f°_{P,T}$ are obtained directly from tables, or can be calculated from:

$$f°_{P,T} = \Gamma_{P,T} \; P$$

where $\Gamma_{P,T}$ is the fugacity coefficient. You can think of the fugacity coefficient as a term that accounts for the non-ideal-gas behaviour of a real gas. Values of Γ can be calculated or obtained from tables. In this lab, values of $\Gamma_{P,T}$ are provided for you.

** ***Note that for an ideal gas, $f°_{P,T} = P$.*** **

Calculation of an equilibrium involving fluids at elevated P and T

For a reaction involving solids and fluids, in order to calculate:

$$_1\int^P (\partial\Delta_r H°/\partial P)_T \, dP] = {_1\int^P} \Delta_r V° \, dP$$

we separate the solids from the fluids as follows:

$$_1\int^P \Delta_r V° \, dP = \Delta_r V°_{s\,1,\,298}\,(P-1) \;\; + \textit{or} - \;\; _1\int^P V_f° \, dP$$

The '+ *or* –' refers to the fact that if the fluid is a *reactant* in the reaction, one *subtracts* the fluid term, whereas if the fluid is a *product*, one *adds* the term.

Because $_1\int^P V_f° \, dP = RT \ln f°_{P,T}$ (see above), this results in:

$$_1\int^P \Delta_r V° \, dP = \Delta_r V°_{s\,1,\,298}\,(P-1) \;\; + \textit{or} - \;\; RT \ln f°_{P,T}$$

Substituting into the full free energy equation:

$$\Delta_r G°_{P,\,T} = \Delta_r H°_{P,\,T} - T\,\Delta_r S°_{P,\,T} = 0 \textit{ at equilibrium}$$

$$\mathbf{\Delta_r G°_{P,\,T} = [\,\Delta_r H°_{1,\,298} + {}_{298}\int^T \Delta_r C_p\, dT + \Delta_r V°_{s\,1,\,298}\,(P-1) \;\; +\textit{or}- \;\; RT \ln f°_{P,T}]}$$

$$\mathbf{-\,T\,[\Delta_r S°_{1,298} + {}_{298}\int^T \Delta_r C_p/T\, dT\,] = 0} \textit{ at equilibrium}$$

Note: despite having made a big deal about how fluids are special when it comes to their variation with pressure, fluid phases are treated *like any other phase* when calculating the change in the reaction (Δ_r) of heat capacity, entropy, and enthalpy in the above equations.

If we assume that the **change** in the heat capacities between reactants and products going from 1, 298 to P,T is negligible, the above equation simplifies considerably to:

$$\mathbf{\Delta_r G°_{P,\,T} = \Delta_r H°_{1,\,298} - T\,\Delta_r S°_{1,298} + \Delta_r V°_{s\,1,\,298}\,(P-1) \;\; +\textit{or}- \;\; RT \ln f°_{P,T}} = 0$$

Exercise

1. Using the ideal gas law for one mole, PV = RT, calculate the volume of pure H_2O at:

200 °C, 1 bar
200 °C, 1 kbar
400 °C, 1 kbar

The specific volumes of water measured experimentally in cc/g are:

200 °C, 1 bar	2171
200 °C, 1 kbar	1.0811
400 °C, 1 kbar	1.442

Comment on how the values based on the ideal gas law compare with those measured experimentally.

2. You will recall from Glgy 311 that a crucial reaction in metapelites is where muscovite and quartz are no longer stable together, reacting to form Al_2SiO_5 + K-feldspar + hydrous fluid (you may wish to refer to your petrogenetic grid from Glgy 311). This is a type of *devolatilization reaction* (it involves release of a fluid phase). Because the fluid is water, it is more specifically a *dehydration reaction*.

Devolatilization reactions are the most common sort of metamorphic reaction. Thus, the results you obtain for the Ms+Qtz reaction will be useful in illustrating a number of features that are common to all devolatilization reactions.

Note that what you will be calculating is a *thermodynamic model* of the reaction in a simplified chemical system, rather than an actual reaction such as one might infer from the change in mineralogy and texture going across an isograd in the field. It turns out that for this reaction, the thermodynamic model is likely a very good approximation to the reaction that occur in rocks.

a. Assuming that sillimanite is the stable form of Al_2SiO_5, write a balanced chemical reaction between these phases (first find the chemical formulae for the phases!).

b. Using the thermodynamic data from Philpotts (appended to the back of this lab), assuming that $\Delta_r C_p = 0$ and $\Delta_r V_s°_{(P, T)} = \Delta_r V°_{s\ 1, 298}$, and assuming that the *water behaves as an ideal gas (ie,* $f°_{H2O\ P,T} = P$*),* calculate the equilibrium pressures for 300, 350, 400, 450, 500, 550, 600, 650 and 700 °C. Plot the values on a graph (either by hand or using Excel).

Note: *the calculation of P in parts b. and d. have to be done by a trial and error method. This will be speeded up if you have the formulae in the spreadsheet, thereby allowing for rapid calculations for each new P you try.*

c. Can you rationalize the shape of the slope of the reaction? (Hint: what two thermodynamic parameters are divided to obtain the slope of a reaction? How does each vary with P and T? – note that one of the reaction products is a gas!)

d. Repeat part b. for the same set of temperatures, only treat the water as the real gas that it is (ie, use fugacity of water rather than pressure of an ideal gas). To save time, here are the values for the fugacity coefficients that you should use (these are the values for the final P conditions of the equilibrium for each temperature):

T °C	$\Gamma_{P,T}$
300	1
350	0.95
400	0.95

450	0.9
500	0.7
550	0.52
600	0.52
650	0.73
700	1.08

e. Plot the results of b. and d. on the same graph, and comment on the difference between the results.

TABLE 7-1

Thermodynamic data for common minerals at 298.15 K and 10^5 Pa (1 bar)

							C_p° Coefficients				Transition		
Name	*Formula*	*Formula Weight (kg)*	*Volume ($m^3\ mol^{-1} \times 10^3$)*	*S° ($J\ mol^{-1}\ K^{-1}$)*	*ΔH_f° ($kJ\ mol^{-1}$)*	*ΔG_f° ($kJ\ mol^{-1}$)*	*a ($J\ mol^{-1}\ K^{-1}$)*	*$b \times 10^3$ ($J\ mol^{-1}\ K^{-2}$)*	*$c \times 10^{-5}$ ($JK\ mol^{-1}$)*	*Temperature Range (K)*	*ΔV° ($m^3\ mol^{-1} \times 10^3$)*	*ΔS° ($J\ mol^{-1}\ K^{-1}$)*	*ΔH° ($J\ mol^{-1}$)*
Akermanite	$Ca_2MgSi_2O_7$	.27264	.09281	209.33	−3878.304	−3681.092	251.42	47.70	47.70				
Albite	$NaAlSi_3O_8$	.262224	.10025	207.15	−3931.621	−3708.313	258.15	58.16	62.80	298–473			
							342.59	14.87	209.84	473–1200			
Analcite	$NaAlSi_2O_6 \cdot H_2O$	.220155	.0971	234.30	−3306.168	−3088.202	223.80	101.00	37.15				
Andalusite	Al_2SiO_5	.162046	.05153	92.88	−2576.783	−2429.176	172.84	26.33	51.85				
Andradite	$Ca_3Fe_2Si_3O_{12}$	.505184	.13185	293.42	−5778.125	−5428.652	475.02	65.42	129.24				
Annite	$KFe_3(AlSi_3O_{10})(OH)_2$	.51189	.15432	398.32	−5155.504	−4799.701	445.30	124.56	80.79				
Anorthite	$CaAl_2Si_2O_8$	.27821	.10079	205.43	−4216.518	−3992.783	264.89	61.90	64.60				
Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	.780872	.2644	538.06	−12086.526	−11361.359	755.97	253.44	160.93	298–903			
							826.52	174.11	55.82	903–1258			
							834.80	174.11	55.82	1258–1800			
Antigorite	$Mg_{48}Si_{34}O_{85}(OH)_{62}$	4.536299	1.74913	3603.93	−71424.608	−66140.756	5139.83	2149.57	1199.47	298–848			
							5166.53	2097.19	1176.88	848–1000			
Aragonite	$CaCO_3$	.100089	.03415	90.21	−1208.017	−1129.157	84.22	42.84	13.97				
Brucite	$Mg(OH)_2$	.058327	.02463	63.14	−926.296	−835.319	101.13	16.79	25.56				
Calcite	$CaCO_3$	.100089	.036934	92.68	−1208.222	−1130.098	104.52	21.92	25.94				
Carbon dioxide	CO_2	.04401	24.465	213.69	−393.522	−394.392	44.22	8.79	8.62				
Chalcedony	SiO_2	.060085	.022688	41.34	−909.108	−854.691	46.94	34.31	11.30				
Chrysotile	$Mg_3Si_2O_5(OH)_4$	.277134	.1085	221.33	−4364.427	−4037.020	317.23	132.21	73.55				
Clinochlore 14-A	$Mg_5Al(AlSi_3O_{10})(OH)_8$	.555832	.20711	465.26	−8857.377	−8207.765	696.64	176.15	156.77				
Clinochlore 7-A	$Mg_5Al(AlSi_3O_{10})(OH)_8$	.555832	.2115	445.60	−8841.616	−8188.511	681.24	211.79	171.04	298–848			
							694.59	185.60	159.75	848–900			
Clinozoisite	$Ca_2Al_3Si_3O_{12}(OH)$	.622882	.1362	295.56	−6879.421	−6483.861	444.00	105.50	113.57				
Coesite													
α	SiO_2	.060085	.020641	40.38	−906.313	−851.616	46.02	34.31	11.30	298–848			
β							59.37	8.12	.00	848–2000			
Cordierite	$Mg_2Al_3(AlSi_5O_{18})$	.584969	.23322	407.23	−9134.505	−8624.391	601.78	107.95	161.50				
Cordierite (hydr.)	$Mg_2Al_3(AlSi_5O_{18}) \cdot H_2O$	.602984	.24122	466.22	−9437.748	−8875.728	649.48	107.95	161.50				
Corundum	Al_2O_3	.101961	.025575	50.96	−1661.655	−1568.264	115.02	11.80	35.06				
Cristobalite	SiO_2	.060085	.02738	50.05	−902.384	−850.565	72.76	1.30	41.38				
Diopside	$CaMg(SiO_3)_2$	.21656	.06609	143.09	−3203.262	−3029.216	220.92	32.80	65.86				
Dolomite	$CaMg(CO_3)_2$	.184411	.064365	155.18	−2329.865	−2167.228	173.87	100.22	41.35				
Enstatite													
Clino	$MgSiO_3$	.100396	.031276	67.78	−1546.766	−1459.923	102.72	19.83	26.28	298–903	.00002	.770	695
Ortho							120.35	.00	.00	903–1258	.00109	1.297	1632
Proto							122.42	.00	.00	1258–1800			
Epidote	$Ca_2FeAl_2Si_3O_{12}(OH)$	.651747	.1392	314.97	−6461.903	−6072.432	492.13	53.62	133.32				
Fayalite	Fe_2SiO_4	.203778	.04639	148.32	−1481.634	−1381.695	152.76	39.16	28.03				
Ferrosilite													
Clino	$FeSiO_3$	.131931	.032952	94.56	−1195.055	−1117.797	110.83	21.21	23.22	298–413	.000056	.377	155
Ortho							87.86	37.66	.00	413–1400			
Forsterite	Mg_2SiO_4	.140708	.04379	95.19	−2175.680	−2056.704	149.83	27.36	35.65				
Gehlenite	$Ca_2Al_2SiO_7$	.274205	.09024	201.25	−3981.766	−3780.612	266.69	33.47	63.26				
Graphite	C	.012011	.0052982	5.74	0	0	16.86	4.77	8.54				
Grossularite	$Ca_3Al_2Si_3O_{12}$	.450454	.1253	254.68	−6624.933	−6263.310	435.21	71.18	114.30				

Hedenbergite	$CaFe(SiO_3)_2$	.248106	.06827	170.29	−2838.827	−2674.488	229.33	34.18	62.80				
Hematite													
α	Fe_2O_3	.159692	.030274	87.61	−827.260	−745.401	98.28	77.82	14.85	298–950		.703	669
β							150.62	.00	.00	950–1050			
γ							132.67	7.36	.00	1050–1800			
Hydrogen	H_2	.002016	24.465	130.57	0	0	27.28	3.26	−.50				
Hydrogen sulfide	H_2S	.0340799	24.465	205.69	−20.627	−33.539	32.68	12.38	1.92				
Jadeite	$NaAl(SiO_3)_2$	.20214	.0604	133.47	−3021.333	−2842.798	201.50	47.78	49.66				
K-feldspar	$KAlSi_3O_8$	.278337	.10887	213.93	−3971.403	−3746.245	320.57	18.04	125.29				
Kalsilite													
α	$KAlSiO_4$	.158167	.05989	133.26	−2131.363	−2015.642	123.14	72.63	22.26	298–810		.828	669
β							177.82	.00	.00	810–1800			
Kaolinite	$Al_2Si_2O_5(OH)_4$	.258161	.09952	203.05	−4109.613	−3789.089	304.47	122.17	90.04				
Kyanite	Al_2SiO_5	.162046	.04409	83.68	−2581.097	−2430.720	173.19	28.52	53.90				
Laumontite	$CaAl_2Si_4O_{12}\cdot 4H_2O$	.470441	.20755	485.76	−7233.651	−6682.028	515.47	186.06	68.74				
Lawsonite	$CaAl_2Si_2O_7(OH)_2\cdot H_2O$	.3142	.10132	233.47	−4846.428	−4492.060	342.25	97.74	68.03				
							355.60	71.55	56.74				
Magnesite	$MgCO_3$	.084321	.028018	65.69	−1111.396	−1027.833	82.55	52.46	19.87				
Magnetite													
α	Fe_3O_4	.231539	.044524	145.73	−1118.174	−1014.930	91.55	201.67	.00	298–900		.000	0
β							200.83	.00	.00	900–1800			
Margarite	$CaAl_2(Al_2Si_2O_{10})(OH)_2$	.398187	.1294	266.94	−6217.520	−5834.044	428.86	68.41	117.36	298–848			
							415.51	94.60	128.66	848–1000			
Merwinite	$Ca_3Mg(SiO_4)_2$	.328719	.1044	253.13	−4566.652	−4339.586	305.31	50.04	60.42				
Methane	CH_4	.016043	24.465	186.15	−74.810	−50.739	23.64	47.86	1.92				
Microcline (max.)	$KAlSi_3O_8$	.278337	.108741	213.93	−3971.403	−3746.245	267.06	53.97	71.34				
Monticellite	$CaMgSiO_4$	.156476	.05147	110.46	−2262.707	−2145.677	154.05	22.34	33.47				
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	.398313	.14071	287.86	−5972.275	−5591.083	408.19	110.37	106.44				
Nepheline	$NaAlSiO_4$	.145227	.05516	124.35	−2093.008	−1978.496	150.24	27.02	30.66				
Paragonite	$NaAl_2(AlSi_3O_{10})(OH)_2$	.382201	.13253	277.82	−5928.573	−5548.034	407.65	102.51	110.62				
Pargasite	$NaCa_2Mg_4Al(Al_2Si_6O_{22})(OH)_2$	.835858	.2735	669.44	−12623.396	−11912.551	861.07	174.31	210.08				
Periclase	MgO	.040311	.011248	26.94	−601.659	−569.384	42.59	7.28	6.19				
Phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$	.417286	.14966	318.40	−6226.072	−5841.646	420.95	120.42	89.96				
Prehnite	$Ca_2Al(AlSi_3O_{10})(OH)_2$	.412389	.14033	271.96	−6201.060	−5818.007	383.25	158.24	82.01	298–848			
							423.30	79.66	48.12	848–1000			
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	.360316	.1266	239.32	−5628.790	−5255.091	332.34	164.07	72.31				
Pyroxene Ca-Al	$CaAl_2SiO_6$	.218125	.0635	146.44	−3280.310	−3105.729	226.48	26.86	62.34				
Quartz													
α	SiO_2	.060085	.022688	41.34	−910.648	−856.239	46.94	34.31	11.30	298–848	.000372	1.431	1213
β							60.29	8.12	.00	848–2000			
Sanidine (high)	$KAlSi_3O_8$	.277337	.109008	228.15	−3960.315	−3739.400	267.06	53.97	71.34				
Sepiolite	$Mg_4Si_6O_{15}(OH)_2(OH_2)_2\cdot(OH_2)_4$	.647861	.2856	613.37	−10116.912	−9251.627	660.74	436.39	78.16				
Silica (amorphous)	$SiO_2\cdot nH_2O$	.060085	.029	60.00	−897.753	−848.900	24.81	197.48	94.98				
Silica glass	SiO_2	.060085	.02727	47.40	−903.200	−850.559	*	*	*				
Sillimanite	Al_2SiO_5	.162046	.0499	96.78	−2573.574	−2427.101	167.46	30.92	48.84				
Spinel	$MgAl_2O_4$	.142273	.03971	80.63	−2288.008	−2163.153	153.86	26.84	40.62				
Steam	H_2O	.0180153	24.465	188.72	−241.818	−228.589	30.54	10.29	.00				
Sulfur	S_2	.064128	24.465	228.07	128.365	79.329	36.48	.67	3.77				
Talc	$Mg_3Si_4O_{10}(OH)_2$	.379289	.13625	260.83	−5903.289	−5523.667	345.10	174.10	55.81				
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	.81241	.27292	548.90	−12319.696	−11592.546	787.52	239.72	187.54				
Wairakite	$CaAl_2Si_4O_{12}\cdot 2H_2O$	.434411	.18687	439.74	−6608.850	−6182.496	420.07	186.06	68.74				
Wollastonite	$CaSiO_3$	.116164	.03993	82.01	−1630.965	−1545.758	111.46	15.06	27.28				
Zoisite	$Ca_2Al_3Si_3O_{12}(OH)$	.622882	.1359	295.98	−6879.044	−6483.606	444.00	105.50	113.57				

(Modified from Helgeson et al. 1978. Reprinted by permission of American Journal of Science. Data for silica glass from Robie et al. 1978)

* $C_p^0 = 74.639 - (7.2594 \times 10^{-3}T) + (5.5704 \times 10^{-6}T^2) - (3.1140 \times 10^6 T^{-2})$ (valid from 298 to 1500 K).