

Thermodynamics I (basic equations and relationships))

Gibbs free energy function (G) \Rightarrow thermodynamic potential

G is a state function \Rightarrow a total differential exists (it is path independent)

G is a function of pressure and temperature (in closed systems)

Isolated systems:

Isolated systems are systems that do not exchange heat, matter, and work with its surroundings.

Isochemical systems:

Closed systems are systems that exchange heat and work with its surroundings but not matter.

Allochemical systems:

Open systems are systems exchanging heat and work and matter with its surroundings.

At equilibrium, a rock (system) will be composed of a set of minerals (phases) that constitute the assemblage with the lowest free energy for this total rock composition at a given pressure and temperature.

Example: Aluminosilicates

Al_2SiO_5 occurs as three different minerals (polymorphs), kyanite, andalusite and sillimanite.

Table 1: Thermodynamic data of Ky, And, Sil per mole at 298.15 K (25°C) and 10^5 Pa.

Mineral	ΔG_f (J)	S° (J/K)	V° (J/bar)
Kyanite	- 2'443'370	82.43	4.412
Andalusite	- 2'441'806	91.4337	5.147
Sillimanite	- 2'439'265	95.93	4.983

(from Berman, 1988)

$$1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ N m}^{-2}$$

ΔG_f stands for the free energy of formation from the elements of a phase at T_{ref} and p_{ref} .

Example kyanite: $\Delta G_{f_{\text{kyanite}}} = G_{\text{ky}} - G_{\text{Si}} - 2 G_{\text{Al}} - 2.5 G_{\text{O}_2}$

It follows that kyanite is the most stable polymorph of Al_2SiO_5 , andalusite is less stable (metastable) and sillimanite is more metastable than the other two (at 25°C and 1 bar = 10^5 Pa).

The Gibbs free energy function

Since, $G = f(p, T)$ the stability relationships among the three minerals may change as pressure and temperature changes. We need to know the functional dependency of G on p and T . It is given by the equation (first and second law of thermodynamics):

$$[\text{eq 1}] \quad \mathbf{dG = - S dT + V dp}$$

The bold face variables are extensive variables of the system (= additive), p and T are intensive variables of the system (= not additive in general).

The equation describes that changes in G of a system (phase, group of phases) are related to the exchange of heat ($- S dT$) and volume work ($V dp$) with its surroundings.

Both products on the right hand side of the equation have the dimension of energy (J). It follows that the parameter S must have the dimension $J K^{-1}$ and the parameter V must have the dimension $J \text{ bar}^{-1}$.

Because G is a state function we may write the total differential:

$$[\text{eq 2}] \quad dG = \left(\frac{\partial G}{\partial T} \right)_p dT + \left(\frac{\partial G}{\partial p} \right)_T dp$$

$$[\text{eq 1}] \quad \mathbf{dG = - S dT + V dp}$$

And by comparison with equation 1 we see that:

$$[\text{eq 3}] \quad \left(\frac{\partial G}{\partial T} \right)_p = - S$$

$$[\text{eq 4}] \quad \left(\frac{\partial G}{\partial p} \right)_T = V$$

Equation 3 and 4 are graphically represented on figures 1a and 1b. From the thermodynamic data of the aluminosilicate polymorphs it is immediately clear that: the high-entropy phase andalusite is stable at high- T , the dense phase kyanite (low-volume phase) is stable at high- p .

The slopes of the curves on figure 1a and 1b are directly given by the entropy and volume of the respective minerals (table on page 1). The stable phase on the two figures is indicated by the shaded sections along the curves with the lowest free energy.

Basic relationships of thermodynamics:

Other thermodynamic potentials are **U** (internal energy) and **H** (enthalpy).

The first and second law of thermodynamics states that changes in internal energy of a closed system can be related to exchange of heat and work with its surroundings (energy conservation).

$$\text{[eq 5] } \quad \mathbf{dU = T dS - p dV}$$

Equation 5 represents the fundamental laws of thermodynamics. The term $\{T dS\}$ describes the exchange of thermal energy, the term $\{-p dV\}$ the exchange of mechanical energy. The minus sign in the mechanical energy term reflects the circumstance that energy is added *to* the system if the volume decreases (energy is subtracted from the system during volume expansion).

Defining a new potential (definition of H):

$$\text{[eq 6] } \quad H \equiv U + pV$$

$$\text{[eq 7] } \quad U \equiv H - pV$$

$$\text{[eq 8] } \quad dU \equiv dH - p dV - V dp$$

$$\text{[eq 9] } \quad dH \equiv T dS + V dp$$

Definition of G:

$$\text{[eq 10] } \quad \mathbf{G \equiv H - TS}$$

$$\text{[eq 11] } \quad H \equiv G + TS$$

$$\text{[eq 12] } \quad dH \equiv dG + T dS + S dT$$

$$\text{[eq 1] } \quad dG \equiv -S dT + V dp$$

In geology we are often interested in mineral or reaction properties at a certain pressure and temperature which may be far away from p_{ref} and T_{ref} . The *apparent* standard molal Gibbs free energy of formation from the elements of a mineral α at p and T is given by the relation:

$$\text{[eq. a]} \quad \Delta G^{\circ}_{p,T} \equiv \Delta G^{\circ}_f + (G^{\circ}_{p,T} - G^{\circ}_{p_{\text{ref}},T_{\text{ref}}})$$

Continuing with the aluminosilicate example:

in general:

$$S = f(T,p) \text{ and } V = f(T,p)$$

but let us assume for a moment that:

$$S \neq f(T,p) \text{ and } V \neq f(T,p)$$

Then, at $p = \text{constant} = p_{\text{ref}} = 1 \text{ bar}$, integration of equation 3 leads to ($T_{\text{ref}} = \text{reference temperature} = 298.15 \text{ K}$):

$$\text{[eq 13]} \quad G^{\circ}_{T,p_{\text{ref}}} - G^{\circ}_{T_{\text{ref}},p_{\text{ref}}} = -S^{\circ} (T - T_{\text{ref}})$$

On figure 2, the values of $\Delta G_{T,p_{\text{ref}}}$ have been calculated for kyanite and andalusite in 50° temperature increments using a commercial spreadsheet program on a MAC. Graphical representation of G as a function of T is also shown on figure 2. It is evident from the data that kyanite is more stable at low- T whereas andalusite is more stable at high- T . Figure 3 shows the free energies of kyanite and andalusite versus ΔT in a more elaborate graph. Kyanite has the lowest free energy up to about 200°C ($T_{\text{ref}} + \Delta T$; 25°C + ~ 175°C). At $T > 200^{\circ}\text{C}$ andalusite has a more negative free energy than kyanite and is therefore more stable. Note that the precise location of the intersection is very sensitive to the quality of the data because the difference of the slopes is very small.

Now for the pressure dependence of G we have to integrate equation 4:

$$\text{[eq 14]} \quad G^{\circ}_{T,p} - G^{\circ}_{T,p_{\text{ref}}} = V^{\circ} (p - p_{\text{ref}})$$

Combining equations 13 and 14 gives:

$$\text{[eq 15]} \quad G^{\circ}_{T,p} - G^{\circ}_{T_{\text{ref}},p_{\text{ref}}} = V^{\circ} (p - p_{\text{ref}}) - S^{\circ} (T - T_{\text{ref}})$$

Equation 15 permits us to calculate the free energy of a mineral at any p and T (provided that $S \neq f(T,p)$ and $V \neq f(T,p)$). Figure 4 shows the relationships among the equations 13, 14 and 15.

Let us return to figure 1a. At low-T kyanite is the stable polymorph, at high-T it is andalusite. At the temperature (T_e) where the two G-functions intersect, both minerals are simultaneously stable.

At any temperature (e.g. T^*) the difference between G_{Ky} and G_{And} may be written as:

$$\Delta G = G_{And} - G_{Ky}$$

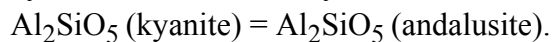
It follows from figure 1a, that:

$$\Delta G > 0 \text{ (kyanite stable), } T < T_e$$

$$\Delta G = 0 \text{ (intersection point), } T = T_e$$

$$\Delta G < 0 \text{ (andalusite stable), } T > T_e$$

T_e must be the temperature where the phase transition occurs. The phase transition from kyanite to andalusite may be written in the form of a chemical reaction equation:



ΔG may therefore be identified as the free energy change of the reaction (or phasetransition) which will be abbreviated by ΔG_r from now on.

Obviously, ΔG_r is equal to zero at the phasetransition (equilibrium of reaction).

$$\text{[eq 16] } \Delta G_r = 0$$

Equation 16 is a fundamentally important equation and represents the equilibrium condition for chemical (mineralogical) reactions (phasetransitions). If ΔG_r is $\neq 0$, the reaction is not in equilibrium (see figure 5).

Since ΔG_r for the reaction (for example) $Ky = And$ is $G_{And} - G_{Ky}$ it follows from equation 15:

$$\text{[eq 17] } \Delta G_{r,T,p} = \Delta G_{r,T_{ref},p_{ref}}^{\circ} + \Delta V_r^{\circ} (p - p_{ref}) - \Delta S_r^{\circ} (T - T_{ref}) = 0$$

Remember that $S = f(T,p)$ and $V = f(T,p)$. However, in solid-solid reactions and phasetransitions ΔV_r and ΔS_r vary very little with p and T. So equation 17 is, in general, a fairly good approximation for that kind of reactions. Equation 17 permits calculation of equilibrium conditions for reactions as a function of p and T, provided G, V, and S is known at reference p and T for all minerals (species) participating in the reaction. We shall explore the potential of equation 17 using some more complex mineral reactions below.

Figure 6 shows two isobaric GT-diagrams for the three Al_2SiO_5 polymorphs kyanite, sillimanite and andalusite. At 1 bar (figure 6a), there are two stable intersections (K=A, and

A=S). However, the intersection which marks the transition from kyanite to sillimanite has a more positive G than andalusite. It is therefore metastable at one bar. At 8 kbar (figure 6b), there is only one stable phasetransition (K=S), the other two are metastable. Evidently, at some definite value of pressure the andalusite curve passes exactly through the intersection of the kyanite and sillimanite curves. It is the pressure of the aluminosilicate triple point, all three polymorphs are stable simultaneously. Keeping these relationships in mind we may now use our quantitative GT-figures to construct a quantitative PT-figure for the Al_2SiO_5 polymorphs. Figure 7 shows all three Als equilibria calculated including $V=f(p,T)$ and $S=f(p,T)$ using data from Berman (1988) and PTXA-software from Liberman (unpublished).

Multiphase equilibria:

The minerals quartz, wollastonite, anorthite, and grossular are connected by the reaction:

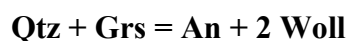


Table 2:

mineral	ΔG_f (J)	S (J/°K)	V (J/bar)
anorthite	-4003221.	200.1861	10.075
grossular	-6270974.	255.1500	12.538
α -quartz	-856287.6	41.46000	2.2690
wollastonite	-1546123.	81.81000	3.9830

$$\sum S_{\text{reactants}} = 296.61 ; \sum S_{\text{products}} = 363.77 \Rightarrow \text{products stable at high-T.}$$

now at equilibrium:

$$\Delta G_r = 0 = G_{\text{An}} + 2 G_{\text{Wo}} - G_{\text{Q}} - G_{\text{Grs}}$$

let us modify equation 17:

$$[\text{eq 17}] \Delta G_{r,T,p} = \Delta G_{r,T_{\text{ref}},p_{\text{ref}}} + \Delta V_r (p - p_{\text{ref}}) - \Delta S_r (T - T_{\text{ref}}) = 0$$

$$[\text{eq 18}] \Delta G_{r,T,p} = \Delta G_{r,T_{\text{ref}},p_{\text{ref}}} + T_{\text{ref}} \Delta S_r - T \Delta S_r + p \Delta V_r$$

Combining eq. 18 with eq. 11 and eq. 16 gives:

$$[\text{eq 19}] 0 = \Delta H_{r_{T_{\text{ref}}, P_{\text{ref}}}} - T \Delta S_r + p \Delta V_r$$

or simply

$$[\text{eq 20}] p = \{ \Delta S_r / \Delta V_r \} T - \{ \Delta H_r / \Delta V_r \}$$

differential:

$$[\text{eq. 21}] dp/dT = \{ \Delta S_r / \Delta V_r \} \quad \text{Clausius-Clapeyron equation.}$$

The position of the equilibrium in pT-space can be calculated if H, S and V data are known for all minerals in the reaction.

Third law entropy and entropy of formation from the elements (oxydes)

Third law entropies of elements at 298.15°K and 1 bar

Ca 41.63

Si 18.81

O₂ 205.15

Ca + Si + 1.5 O₂ = Wollastonite

$\Delta S_f = S_{W_o} - S_{Ca} - S_{Si} - 1.5 S_{O_2}$

$\Delta S_f = -286.355$

Thermodynamic data of wollastonite are tabulated on table 3 (from Robie, Hemingway and Fisher, 1978).

Variation of the Gibbs free energy with composition (the chemical potential)

In the reaction Qtz + Grs = An + 2 Woll two reacting species occur as components in solid-solutions: grossular is a phase component in the garnet solution and anorthite is a component in the plagioclase solution. Above, we derived equations for the calculation of the equilibrium in the pure CaO-Al₂O₃-SiO₂ system.

Two solid-solutions:

Garnet: grossular-andradite

Plagioclase: anorthite-albite

$$[\text{eq 22}] \quad dG = \left(\frac{\partial G}{\partial T} \right)_{p, n_i} dT + \left(\frac{\partial G}{\partial p} \right)_{T, n_i} dp + \sum_{i=1}^{i=k} \left(\frac{\partial G}{\partial n_i} \right)_{T, p} dn_i$$

$$[\text{eq 23}] \quad \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j} \equiv \mu_i$$

Equation 23 defines the chemical potential μ . The chemical potential of a phase component is thus the amount by which the capacity of the phase for doing work is increased per unit amount of substance added, for an infinitesimal addition at constant pressure and temperature.

Now for changes in the composition of a phase:

$$(d\mu_i)_{p, T} = RT \, d(\ln a_i)$$

a_i = **activity** of component i . The activity represents a compositional variable (thermodynamic concentration). The activity is a function of the concentration of component i in the solution phase. For solids: $\mathbf{a} = \mathbf{f}(\mathbf{x})$. The function is called the **solution model**.

The integrated form of the equation above is fundamental:

$$[\text{eq 24}] \quad \mu_i = \mu_i^\circ + R T \ln a_i$$

The integration constant μ_i° is referred to as the **standard state**. In our example reaction the energy balance can be written as:

$$\mu_{\text{grossular}} + \mu_{\text{quartz}} = 2 \mu_{\text{wollastonite}} + \mu_{\text{anorthite}}$$

Or in general:

$$[\text{eq 25}] \quad \sum_i v_i \mu_i = 0 = \Delta G_r$$

where v_i is the **stoichiometric coefficient** of the reacting species i .

By substituting equation 24 into equation 25 we get:

$$0 = (2 \mu_{\text{wollastonite}}^\circ + \mu_{\text{anorthite}}^\circ - \mu_{\text{grossular}}^\circ + \mu_{\text{quartz}}^\circ) + R T \ln [a_{\text{anorthite}} a_{\text{wollastonite}}^2 / a_{\text{grossular}} a_{\text{quartz}}]$$

The term in () brackets may be identified as ΔG_r° ; the term in [] brackets is called the **equilibrium constant K**.

$$[\text{eq 26}] \quad \Delta G_r^\circ = - R T \ln K$$

$$[\text{eq 27}] \quad K = \prod a_i^{v_i}$$

Equations 26 and 27 are of fundamental importance in solving geological problems and should be memorized.

In our example:

$$K_{p,T} = \frac{a_{\text{An}}^{\text{Pl}} a_{\text{Wo}}^2}{a_{\text{Grt}} a_{\text{Grs}} a_{\text{Qtz}}}$$

Since, $a_i \rightarrow 1$ and $\mu_i \rightarrow \mu_i^\circ$; when $x_i \rightarrow 1$ (see figure 8) \Rightarrow the activity terms for quartz and wollastonite may be ignored (activity of pure endmember phase component = 1). In addition, using the simplest possible solution model ($a_i = x_i$; ideal solution), the equilibrium constant expression reduces to:

$$K_{p,T} = \frac{X_{\text{An}}^{\text{Pl}}}{X_{\text{Grs}}^{\text{Grt}}}$$

where, K can be expressed by the ratio of the mole fraction anorthite in plagioclase solid-solution and the mole fraction of grossular in the garnet solution.

Figure 9 shows a GT-graph similar to figure 5. However, it displays ΔG_r° rather than ΔG_r along the vertical axis which allows us to solve equation 26 graphically.

Example:

A rock with excess quartz and wollastonite, contains garnet with 40 mole % grossular and plagioclase with 80 mole % anorthite. The equilibrium constant is then: = 2. Because the gas constant R and T are positive quantities and the logarithm of any number > 1 is also positive, the right hand side of equation 26 is a negative number which increases with T (figure 9).

The intersection of the two curves ($-RT \ln K$ and ΔG_r°) represents the graphical solution of equation 26 and equilibrium of the reaction.

For $K > 1$, the equilibrium temperature (at constant p) is displaced to higher temperatures (case A, figure 9), for $K < 1$, the equilibrium temperature (at constant p) is displaced to lower temperatures (case B, figure 9) relative to the pure endmember equilibrium ($K=1$, all activities = 1).

Remember equation 18;

$$[\text{eq 18}] \Delta G_{r,T,p} = \Delta G_{r,T_{\text{ref}},p_{\text{ref}}} + T_{\text{ref}} \Delta S_r - T \Delta S_r + \Delta V_r (p - p_{\text{ref}})$$

or slightly modified;

$$[\text{eq 18*}] \Delta G_{r,T,p} = \Delta H_{r,T_{\text{ref}},p_{\text{ref}}} - T \Delta S_r + \Delta V_r (p - p_{\text{ref}})$$

in analogy we may write;

$$[\text{eq 28}] \Delta G_{r,T,p}^\circ = \Delta H_{r,T_{\text{ref}},p_{\text{ref}}}^\circ - T \Delta S_r^\circ + \Delta V_r^\circ (p - p_{\text{ref}})$$

substitution into equation 26 gives;

$$[\text{eq 29}] -R T \ln K_{p,T} = \Delta H_{r,T_{\text{ref}},p_{\text{ref}}}^\circ - T \Delta S_r^\circ + \Delta V_r^\circ (p - p_{\text{ref}})$$

or in a rewritten form:

$$[\text{eq 30}] \ln K_{p,T} = -\frac{\Delta H_{r_{\text{ref}}}^\circ}{R T} + \frac{\Delta S_{r_{\text{ref}}}^\circ}{R} - \frac{\Delta V_{r_{\text{ref}}}^\circ}{R T} (p - p_{\text{ref}})$$

Equation 30 demonstrates that the logarithm of the equilibrium constant is a linear function of $1/T$ at constant pressure. Equation 30 is often also expressed in the following form:

$$[\text{eq 30*}] \ln K_{p,T} = -\frac{A}{T} + B - \frac{C}{T} (p - p_{\text{ref}})$$

or for reactions with very small ΔV ;

$$[\text{eq 30**}] \ln K_{p,T} = -\frac{A}{T} + B$$

The meaning of the constants A, B and C may be identified by comparing eq. 30 with eq. 30*.

Our Grt-Pl-Wo-Qtz example:

Using the data given in table 2, the following reaction properties may be readily calculated:

$$\Delta G^\circ = 31'794.6 \text{ J}; \Delta S^\circ = 67.16 \text{ J K}^{-1}; \Delta H^\circ = 51'819.0 \text{ J}; \Delta V^\circ = 3.234 \text{ J bar}^{-1}.$$

$$R = 8.3143 \text{ J K}^{-1} \text{ mole}^{-1}$$

It follows; $A = -6232.5$, $B = 8.0776$, $C = 0.389$

With grossular 40 and anorthite 80 $\Rightarrow K = 2$, $\ln K = 0.6931$, $K = 0.5$, $\ln K = -0.6931$

Equation 30* may be rewritten for constant K as follows (ignoring p_{ref}):

$$0 = -\frac{A}{T} + B^* - \frac{C}{T} p$$

where $B^* = B - \ln K$

it follows the straight line expression for equilibrium of reaction among Wo-Qtz-Grs₄₀-An₈₀;

$$p = -\frac{A}{C} + \frac{B^*}{C} T$$

$A/C = 16'023$, $B/C = 20.767$, $B^*/C = 18.98$ ($K = 2$), $B^*/C = 22.55$ ($K = 0.5$).

$p = 20.767 T - 16'023$. (pure grossular and anorthite)

$p = 18.98 T - 16'023$. (Grs₄₀-An₈₀)

$p = 22.55 T - 16'023$. (Grs₈₀-An₄₀)

The three different equilibria are shown on figure 10.

At e.g. 2 kbar, pure grossular+quartz are stable up to 600°C, garnet with Grs₄₀ in rocks with An₈₀ is stable to about 680°C, garnet with Grs₈₀ in rocks with An₄₀ decomposes to wollastonite at about 530°C.

If we are interested in the relationships at a fixed pressure (e.g. contact metamorphism), we may derive the following thermometric expression:

$$\ln K_{p,T} = -\frac{A^*}{T} + B$$

where $A^* = A + C (p - p_{\text{ref}})$

The equation above can be used in a graphical representation of the thermometer in a $\ln K$ versus $1/T$ diagram.

Example: Hematite-Magnetite, Magnetite-Wüstite, Wüstite-Iron

Variations of H, S, V and G with pressure and temperature

Enthalpy

For any state function a total differential exists and we may write in analogy to equation 2:

$$[\text{eq. 31}] \quad dH = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$

The temperature dependence of the enthalpy is given by:

$$[\text{eq. 32}] \quad \left(\frac{\partial H}{\partial T} \right)_p = c_p$$

c_p is known as the **heat capacity** of a substance. A heat capacity of $121.7 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 for kyanite means that we must add 121.7 J per mole kyanite to rise its temperature by $1 \text{ }^\circ\text{K}$. Consequently, the enthalpy at the temperature of interest may be calculated at constant pressure from:

$$[\text{eq. 33}] \quad H - H_{\text{ref}} = \int_{T_{\text{ref}}}^T c_p dT$$

However, $c_p = c_p(T)$ and the temperature dependence of the heat capacity may be expressed by a suitable power series. One form of such a function is the Maier-Kelley power function:

$$[\text{eq. 34}] \quad c_p = a + b T - c T^{-2}$$

$$[\text{eq. 35}] \quad \int_{T_{\text{ref}}}^T c_p dT = a (T - T_{\text{ref}}) + \frac{b (T^2 - T_{\text{ref}}^2)}{2} + c \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)$$

The isobaric molal heat capacity of kyanite as a function of the temperature is tabulated and shown on table 4 (as an example).

The pressure dependence of the enthalpy is given by:

$$[\text{eq. 36}] \quad \left(\frac{\partial H}{\partial p} \right)_T = \left(V^o - T \left(\frac{\check{Z}V^o}{\check{Z}T} \right)_p \right)_T$$

Entropy

$$[\text{eq. 37}] \quad dS = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp$$

The temperature dependence of the entropy is given by:

$$[\text{eq. 38}] \quad \left(\frac{\partial S}{\partial T} \right)_p = \frac{c_p}{T}$$

The pressure dependence of the entropy is given by:

$$[\text{eq. 39}] \quad \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p = - \alpha V$$

So, in principle:

$$[\text{eq. 40}] \quad S_{p,T}^o - S_{p_{\text{ref}},T_{\text{ref}}}^o = \int_{T_{\text{ref}}}^T C_{p_{\text{ref}}}^o d \ln T - T \int_{p_{\text{ref}}}^p \left(\left(\frac{\check{Z}V^o}{\check{Z}T} \right)_p \right)_T dp$$

The entropy at the temperature of interest may be calculated at constant pressure from:

$$[\text{eq. 39}] \quad S - S_{\text{ref}} = \int_{T_{\text{ref}}}^T c_p d \ln T$$

Using the Maier-Kelley power function, the integration of equation 39 gives:

$$[\text{eq. 40}] \quad \int_{T_{\text{ref}}}^T c_p d \ln T = a \ln \left(\frac{T}{T_{\text{ref}}} \right) + b (T - T_{\text{ref}}) + \frac{c}{2} \left(\frac{1}{T^2} - \frac{1}{T_{\text{ref}}^2} \right)$$

Volume

$$[\text{eq. 41}] \quad dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp$$

$$[\text{eq. 42}] \quad \left(\frac{\partial V}{\partial T} \right)_p = \alpha V$$

Where α represents the isobaric coefficient of **thermal expansion**.

$$[\text{eq. 43}] \quad \left(\frac{\partial V}{\partial p} \right)_T = -\kappa V$$

and κ represents the **isothermal coefficient of compressibility**.

Integration of equations 42 and 43 gives:

$$\int_{T_{\text{ref}}}^T \alpha dT = \int_{V(T=T_{\text{ref}})}^{V(T=T)} \frac{1}{V} dV$$

$$\alpha (T - T_{\text{ref}}) = \ln [V_{\text{pref},T} / V_{\text{pref},T_{\text{ref}}}]$$

or re-arranged:

$$V_{\text{pref},T} = V_{\text{pref},T_{\text{ref}}} \exp [\alpha (T - T_{\text{ref}})]$$

$$-\int_{p_{\text{ref}}}^p \kappa dp = \int_{V(p=p_{\text{ref}})}^{V(p=p)} \frac{1}{V} dV$$

$$-\kappa (p - p_{\text{ref}}) = \ln [V_{p,T} / V_{\text{pref},T}]$$

or re-arranged:

$$V_{p,T} = V_{\text{pref},T} \exp [-\kappa (p - p_{\text{ref}})]$$

Putting the α and κ terms together:

$$V_{p,T} = V_{\text{pref},T_{\text{ref}}} \exp [\alpha (T - T_{\text{ref}})] \exp [-\kappa (p - p_{\text{ref}})] = V_{\text{pref},T_{\text{ref}}} \exp [\alpha (T - T_{\text{ref}}) - \kappa (p - p_{\text{ref}})]$$

The term in square brackets is very small and can be approximated by using $\exp(x) \approx 1 + x$:

$$[\text{eq. 44}] \quad V_{p,T} = V_{\text{pref},T_{\text{ref}}} [1 + \alpha (T - T_{\text{ref}}) - \kappa (p - p_{\text{ref}})]$$

also note that: $dp/dT = \alpha/\kappa$

Gibbs free energy

Integration of the total differential (equation 2) gives:

$$G_{p,T} - G_{p_{\text{ref}},T_{\text{ref}}} = - \int S_{p,T} dT + \int V_{p,T} dp$$

$$[\text{eq. 45}] G_{p,T} - G_{p_{\text{ref}},T_{\text{ref}}} = - S_{p_{\text{ref}},T_{\text{ref}}} (T - T_{\text{ref}}) + \int c_{p(p_{\text{ref}})} dT - T \int c_{p(p_{\text{ref}})} d \ln T + \int V_{p,T} dp$$

The first integral is given in equation 35, the second integral is represented by equation 40. The pressure integral may be derived from equation 44:

$$[\text{eq. 46}] \int V_{p,T} dp = (p - p_{\text{ref}}) V_{p_{\text{ref}},T_{\text{ref}}} [1 + \alpha (T - T_{\text{ref}}) - \kappa/2 (p - p_{\text{ref}})]$$

Substituting eqs. 35, 40 and 46 into 45 leaves us with the final expression for the Gibbs free energy at p and T of interest:

$$[\text{eq. 47}] G_{p,T} - G_{p_{\text{ref}},T_{\text{ref}}} = - S_{p_{\text{ref}},T_{\text{ref}}} (T - T_{\text{ref}}) +$$

$$a (T - T_{\text{ref}} - T \ln (T/T_{\text{ref}})) +$$

$$[(c - b T T_{\text{ref}}^2) (T - T_{\text{ref}})^2] / [2 T T_{\text{ref}}^2] +$$

$$(p - p_{\text{ref}}) V_{p_{\text{ref}},T_{\text{ref}}} [1 + \alpha (T - T_{\text{ref}}) - \kappa/2 (p - p_{\text{ref}})]$$

Table 5: Molar c_p , α and κ data

	a cal K ⁻¹	b cal K ⁻²	c cal K	α K ⁻¹	κ bar ⁻¹
Anorthite	63.311	14.794 x 10 ⁻³	15.44 x 10 ⁵	12 x 10 ⁻⁶	1.5 x 10 ⁻⁶
Wollastonite	26.64	3.60 x 10 ⁻³	6.52 x 10 ⁵	32 x 10 ⁻⁶	1.0 x 10 ⁻⁶
Grossular	104.017	17.013 x 10 ⁻³	27.318 x 10 ⁵	23 x 10 ⁻⁶	0.6 x 10 ⁻⁶
Quartz	11.2	8.20 x 10 ⁻³	2.70 x 10 ⁵	69 x 10 ⁻⁶	2.7 x 10 ⁻⁶

Gasses and dehydration reactions (reactions involving volatiles).

$$[\text{eq. 48}] \Delta V_{\text{reaction}} = \Delta V_{\text{solids}} + V_{\text{gas}}$$

so far for minerals (solids):

assuming $V^\circ \neq f(T,p)$, $\alpha = \kappa = 0$

$$\int_{p_{\text{ref}}}^p V^0 dp = V_{p_{\text{ref}} T_{\text{ref}}}^0 (p - p_{\text{ref}})$$

However for gasses (e.g. H₂O):

V_{gas} complex function of p and T (see figure with isochores in p and T)

Ideal gas:

[eq. 49] **equation of state:** $R T = p V$

$$V = R T / p \quad \text{or} \quad V p / T = R \quad R = \text{universal gas constant; } R = 8.3143 \text{ J K}^{-1}$$

The molar volume of an ideal gas at e.g. 25°C can be calculated from the equation of state given above:

$$V_{1\text{bar}} = 8.3143 \times 298.16 / 1 = 2478.9 \text{ J bar}^{-1} \text{ mole}^{-1} = 24789 \text{ cm}^3 \text{ mole}^{-1}$$

$$V_{10 \text{ kbar}} = 2.48 \text{ cm}^3 \text{ mole}^{-1}$$

For one mole of an ideal gas:

[eq. 50] $\int V dp = R T \ln (p/p_{\text{ref}}) = R T \ln p - R T \ln p_{\text{ref}}$

if p_{ref} is chosen as one bar ⇒ RT ln p_{ref} = 0, however *remember the correct dimensions.*

Real gas:

various approaches are used to express the volume function for geologic gasses:

$$p V / R T = z$$

z = compressibility factor (z=1 for an ideal gas)

$$z = 1 + a p + b P^2 + c P^3 + \dots$$

$$\delta G = R T \int_{p_{\text{ref}}}^p \frac{z}{p} dp$$

alternatively: express V = f(T,p) as a polynomial in p and T

e.g. Burnham, Holloway and Davis:

$$PV = \prod_{j=0}^8 \prod_{i=0}^{8-j} a_{ij} T^i p^{-j}$$

8th degree polynomial (e.g.)

Fugacity and fugacity coefficients:

$$\delta G_{id} = \int V_{id} dp \quad \delta G_{gas} = \int V_{gas} dp$$

$$[\text{eq. 51}] \quad \delta G_{gas} - \delta G_{id} \Rightarrow G_{gas} - G_{id} = G_{gas, p_{ref}} - G_{id, p_{ref}} + \int (V_{gas} - V_{id}) dp$$

if P_{ref} low \Rightarrow gas \rightarrow ideal gas (e.g. 1 bar): $G_{gas, p_{ref}} - G_{id, p_{ref}} = 0$

$V_{gas} - V_{id} \rightarrow$ excess volume (volume difference between ideal and real gas).

dividing by the constant RT ,

$$\frac{G - G_{id}}{RT} = \frac{1}{RT} \int_{p_{ref}}^p \alpha dp$$

$$\alpha = V_{gas} - V_{id} \quad \text{and } V_{id} = RT/p$$

with this: $\delta G_{id} = RT \ln p/p_{ref}$ and [eq. 52] $G_{gas} - G_{id} = RT \ln \gamma$

γ is called the **fugacity coefficient**. It is a quantitative measure of the departure from the ideal gas law. If we know γ for a gas we can calculate G with reference to an ideal gas.

$$[\text{eq. 53}] \quad \delta G_{gas} = \delta G_{id} + (G_{gas} - G_{id}) = RT \ln (p / p_{ref}) + RT \ln \gamma$$

or by combining the terms on the right hand side: $RT \ln (p / p_{ref}) + RT \ln \gamma = RT \ln (f / f_{ref})$

where: $f = p \gamma$, $f =$ **fugacity** of the gas at p and T (dimension = pressure (e.g. bars)).

$$[\text{eq. 54}] \quad G_{gas, T, p} - G_{gas, T, p_{ref}} = RT \ln (f / f_{ref})$$

The fugacity coefficients for many geological gasses are tabulated over wide ranges of pressure and temperature in a number of data compilations.

Figure 11 shows a graphical representation of the fugacity coefficients for H₂O as an example. Table 6 gives polynomial expressions for RT ln f for CO₂ and H₂O (Holland and Powell, 1985).

Table 6:

RT ln f for H₂O and CO₂ are expressed as: $a + bT + cT^2$.

$$\begin{aligned} a &= a_1 + a_2 P + a_3 P^2 \\ b &= b_1 + b_2 P^{-1} + b_3 P^{-2} + b_4 P^{-1/2} \\ c &= c_1 + c_2 P + c_3 P^{-2} + c_4 P^{-1/2} \end{aligned}$$

	H ₂ O	CO ₂
a ₁	-38.261	-9.429
a ₂	1.3854	2.6209
a ₃	-1.228 10 ⁻³	-0.011704
b ₁	0.12716	0.12772
b ₂	0.03977	0.11587
b ₃	-7.8802 10 ⁻³	-0.02725
b ₄	-0.041436	-0.14323
c ₁	-9.8194 10 ⁻⁶	-6.806 10 ⁻⁷
c ₂	6.5419 10 ⁻⁸	-2.3744 10 ⁻⁷
c ₃	1.3849 10 ⁻⁶	0.0
c ₄	-1.390 10 ⁻⁵	-5.677 10 ⁻⁶

The calculated values of RT ln f are shown on figure 12 for a series of temperatures.

Example: H₂O

800°K (527°C) and 10'000 bars (Burnham, Holloway and Davis) $\Rightarrow \gamma_{\text{H}_2\text{O}} = 1$; $f = \gamma p$; $f = 10'000 \text{ bars}$; $\ln f_{\text{H}_2\text{O}} = 9.2103$; $R T \ln f_{\text{H}_2\text{O}} = 61'262 \text{ J mole}^{-1}$.

Reactions involving gasses.

[eq. 55]

$$\begin{aligned} \Delta G^\circ_{r_p T} &= \Delta G^\circ_{r_{p_{\text{ref}} T_{\text{ref}}}} - \Delta S^\circ_{r_{p_{\text{ref}} T_{\text{ref}}}} (T - T_{\text{ref}}) + (c_p, \alpha \text{ and } \kappa \text{ terms}) + \\ &\Delta V^\circ_{\text{solids}_{p_{\text{ref}} T_{\text{ref}}}} (p - p_{\text{ref}}) + \sum \nu_i RT \ln (f_i / f_{i_{\text{ref}}}) \end{aligned}$$

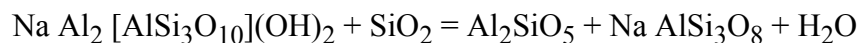
where ν represents the stoichiometric coefficient of the gas in the reaction equation; $f_{\text{ref}} = f_{\text{gas}}$ at 1 bar = 1 bar, so take γ_{gas} at pT from figures or tables then $P \gamma_{\text{gas}} = f_{\text{gas}} \rightarrow RT \ln (f/1)$ or alternatively calculate $RT \ln (f / f_{\text{ref}})$ from equations given by Holland and Powell or any other published equation of state (e.g. MRK).

Or in analogy to equation 30:

$$[\text{eq. 56}] \quad \ln K_{p,T} = -\frac{2 H_{\text{r}}^{\circ}}{R T} + \frac{2 S_{\text{r}}^{\circ}}{R} - \frac{2 V_{\text{r,solids}}^{\circ}}{R T} (p - p_{\text{ref}}) - \nu_{\text{gas}} \ln \left(\frac{f_{\text{gas}}}{f_{T,p_{\text{ref}}}} \right)$$

An example reaction:

paragonite + quartz = kyanite + albite + H₂O (paragonite breakdown reaction)



We may now be interested in finding the equilibrium conditions of the paragonite breakdown reaction in the presence of pure H₂O. In this case we just must solve equation 55 or 56 (the left hand side in both equations must become zero).

However, H₂O may also represent just a component in a fluid phase (mixture of fluid species).

The situation is analogous to the one above where we had anorthite as a component in plagioclase and grossular as a component in garnet. Two basic questions may be asked: 1) what is the equilibrium condition for the reaction if the fluid phase contains a given amount of H₂O (fixed fluid composition, $X_{\text{H}_2\text{O}}$)?; 2) given is the equilibrium pressure and temperature for stable coexistence of paragonite + quartz + kyanite + albite (known for example from conventional thermobarometry), what is the activity of H₂O (fluid composition)?

For simplicity, we consider pure stoichiometric solid phases (paragonite, quartz, kyanite, albite). Let us choose the **standard state** (SST) for the solids: **a=1** for pure solids at any p and T , then:

$$\mathbf{K} = \mathbf{a}_{\text{H}_2\text{O}}$$

$$[\text{eq. 57}] \quad \mathbf{a}_{\text{H}_2\text{O}} = \mathbf{f}_{\text{H}_2\text{O}} (\text{bars}) / \mathbf{f}^*_{\text{H}_2\text{O}} (\text{bars})$$

f^* = fugacity of the pure gas at SST p and T , that is where the activity of the species is chosen to be unity.

(case 1) e.g. if SST $a=1$ is chosen at T and 1 bar pressure $\rightarrow f^* = 1$ bar.
 $a_{\text{gas}} = f_{\text{gas}} / 1\text{bar}$ activity and fugacity are numerically the same

(case 2) e.g. if SST $a=1$ is chosen at T and p $\rightarrow f^* = f$.
 $a_{\text{gas}} = f_{\text{gas}} / f^*_{\text{gas}}$ $0 < \text{activity} < 1$

choice one leads to (case 1): $-RT \ln K + RT \ln f_{\text{H}_2\text{O}}/1 = \Delta G^\circ_r$

choice two leads to (case 2): $-RT \ln K = \Delta G^\circ_r$

$P = 3000$ bars, $T = 600$ °C, $f_{\text{H}_2\text{O}} = ?$

from graph: $\gamma_{\text{H}_2\text{O}} = 0.51$ $f_{\text{H}_2\text{O}} = p \gamma_{\text{H}_2\text{O}} = 1530$ bars

with version 1: $a_{\text{H}_2\text{O}} = 1530/1 = 1530$

with version 2: $a_{\text{H}_2\text{O}} = 1530/1530 = 1$ (same SST as solids)

However: $\delta G = RT \ln f^*_{\text{H}_2\text{O}}/1\text{bar} = 0$ (case 1)

$\delta G = RT \ln f^*_{\text{H}_2\text{O}}/1\text{bar} = 53'224.66$ J (case 2)

so we have two choices again:

$$\Delta G^\circ_r = \sum G^\circ_{\text{solids},p,T} + G^\circ_{\text{gas},p_{\text{ref}}} + \{G_{\text{gas},p,T} - G_{\text{gas},p_{\text{ref}}}\} = -RT \ln K$$

$$RT \ln K + \nu RT \ln f_{\text{gas}} = -A/T + B - C/T (p-p_{\text{ref}}) \quad (\text{case 1})$$

$$RT \ln K = -A/T + B - C/T (p-p_{\text{ref}}) - \nu RT \ln f_{\text{gas}} \quad (\text{case 2})$$

see graphical representations on figures 13a and 13b.

total H₂O-pressure curve: $f_{\text{H}_2\text{O}} = f(p,T)$; $\ln (f_{\text{H}_2\text{O}}/1) = \ln (\gamma_{\text{H}_2\text{O}} \cdot (P/1))$

represents the fugacity of pure H₂O at e.g. 3 kbar and T.

intersection of the two curves: coexistence of paragonite+quartz+kyanite+albite and pure H₂O.

at T below intersection T along the equilibrium curve $P_{\text{H}_2\text{O}} < P_{\text{total}}$

at T above intersection T along the equilibrium curve $P_{\text{H}_2\text{O}} > P_{\text{total}}$; not accessible under

equilibrium conditions.

at $T = T_{\text{intersection}} \rightarrow P_{\text{H}_2\text{O}} = P_{\text{total}}$

Calculated $\ln K$ values for the example reaction are given on figure 14 together with an $\ln K$ vs $1/T$ plot. Equilibrium conditions for the paragonite breakdown reaction are shown on figure 15.