

Gibb's Free Energy Equation

$$\Delta G = 0 = \Delta H - T\Delta S + P\Delta V \quad (\text{At equilibrium conditions})$$

$$P = T \frac{\Delta S}{\Delta V} + \frac{-\Delta H}{\Delta V}$$

Clapeyron Calculation

	Molar Volume	Entropy
Kyanite	4.409 J $\bar{\text{bar}}^{-1}$ mol $^{-1}$	83.76 Jmol $^{-1}$ K $^{-1}$
Sillimanite	4.990 J $\bar{\text{bar}}^{-1}$ mol $^{-1}$	96.11 Jmol $^{-1}$ K $^{-1}$

Parameter = Products - Reactants

$$\Delta V = 4.990 - 4.409 = 0.581 \text{ J}\bar{\text{bar}}^{-1}\text{mol}^{-1}$$

$$\Delta S = 96.11 - 83.76 = 12.35 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$\text{Slope} = 12.35 \text{ Jmol}^{-1}\text{K}^{-1} \div 0.581 \text{ J}\bar{\text{bar}}^{-1}\text{mol}^{-1} = 21.2 \text{ bar}\text{K}^{-1} = 0.0212 \text{ Kilobar}\text{K}^{-1}$$

Continuous Reactions

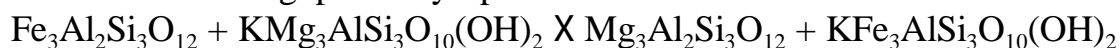
$$0 = \Delta G = \Delta H - T\Delta S + P\Delta V = -RT \ln K$$

$$K = \frac{\text{products}}{\text{reactants}}$$

$$P = T \frac{\Delta S - R \ln K}{\Delta V} + \frac{-\Delta H}{\Delta V}$$

Example: Mg-Fe exchange geothermometer in Garnet+Biotite

Almandine + Phlogopite \rightleftharpoons Pyrope + Annite



$$X_{\text{Annite}} = 0.305$$

$$X_{\text{Almandine}} = 0.650$$

$$X_{\text{Phlogopite}} = 0.416$$

$$X_{\text{Pyrope}} = 0.176$$

For the above reaction (using products - reactants):

$$\Delta H = 12,454 \text{ cal} \cdot \text{mole}^{-1}$$

$$\Delta S = 4.662 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

$$\Delta V = 0.057 \text{ cm}^3 \cdot \text{mole}^{-1}$$

Molar volume must be converted to appropriate units:

$$\Delta V = 0.057 \text{ cm}^3 \cdot \text{mole}^{-1} \cdot [0.0242173 \text{ cal} \cdot (\text{cm}^3)^{-1} \cdot \text{bar}^{-1}] = 0.00138 \text{ cal} \cdot \text{bar}^{-1} \cdot \text{mole}^{-1}$$

$$R \text{ (gas constant)} = 1.987 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

$$K = \frac{a_{\text{pyrope}} \cdot a_{\text{annite}}}{a_{\text{almandine}} \cdot a_{\text{phlogopite}}} \quad (\text{Activities of Products} \div \text{Reactants})$$

$$K = \frac{[X_{\text{pyr}}^{ga}]^3 [X_{\text{ann}}^{bi}]^3}{[X_{\text{alm}}^{ga}]^3 [X_{\text{phl}}^{bi}]^3} \quad (X = \text{site occupancy})$$

$$\ln K = \ln \left[\frac{a_{\text{py}}^{ga} \cdot a_{\text{ann}}^{bi}}{a_{\text{alm}}^{ga} \cdot a_{\text{phl}}^{bi}} \right] = 3 \ln \left[\frac{X_{\text{py}}^{ga} \cdot X_{\text{ann}}^{bi}}{X_{\text{alm}}^{ga} \cdot X_{\text{phl}}^{bi}} \right] = 3 \ln \left[\frac{(0.176)(0.305)}{(0.650)(0.416)} \right] = -4.851$$

$$T = \frac{P\Delta V + \Delta H}{\Delta S - (R)(\ln K)} \quad (\text{Rearrangement of Gibb's Free Energy Equation to solve for } T^\circ\text{K})$$

$$T = \frac{P(0.00138) + 12454}{(4.662) - (1.987)(-4.851)} = \frac{P(0.00138) + 12454}{14.26}$$

Assuming almost any reasonable pressure, for example, 6000 bar allows calculation of T:

$$T = \frac{(6000)(0.00138) + 12454}{14.26} = \frac{12462}{14.26} = 873.9^\circ \text{K} = 600.9^\circ \text{C}$$

As a check on our assumption, let's assume that the pressure of crystallization had been 1000 bar rather than 6000. What difference would that change make?

$$T = \frac{(1000)(0.00138) + 12454}{14.26} = 873.4^\circ \text{K} = 600.4^\circ \text{C}$$

The difference between the two pressure assumptions, 0.5°C , is much less than the accuracy of the geothermometer, estimated to be $\pm 20^\circ\text{C}$.