

# GY303 Igneous & Metamorphic Petrology

## Lecture 9: Metamorphic Phase Equilibria



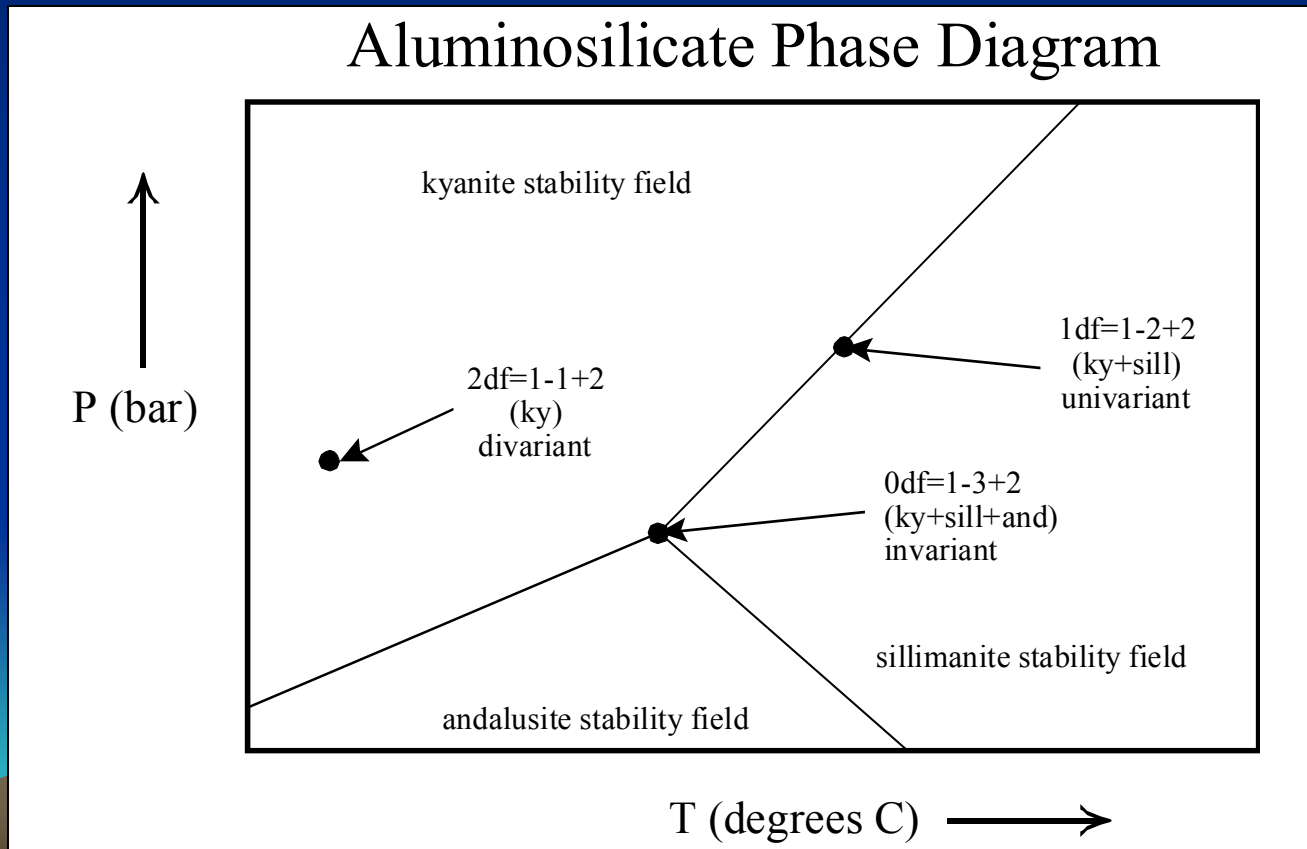
# Phase Rule in Metamorphic Rocks

- $dF = C - P + 2$
- $dF$ : degrees of freedom in the system
- $C$ : number of chemical components
- $P$ : number of phases
- The “2” in the equation is related to  $T$  &  $P$  that are the  $X$  and  $Y$  axes of a phase diagram



# Application of the Phase Rule

- Aluminosilicate ( $\text{Al}_2\text{SiO}_5$ ) Phase stability



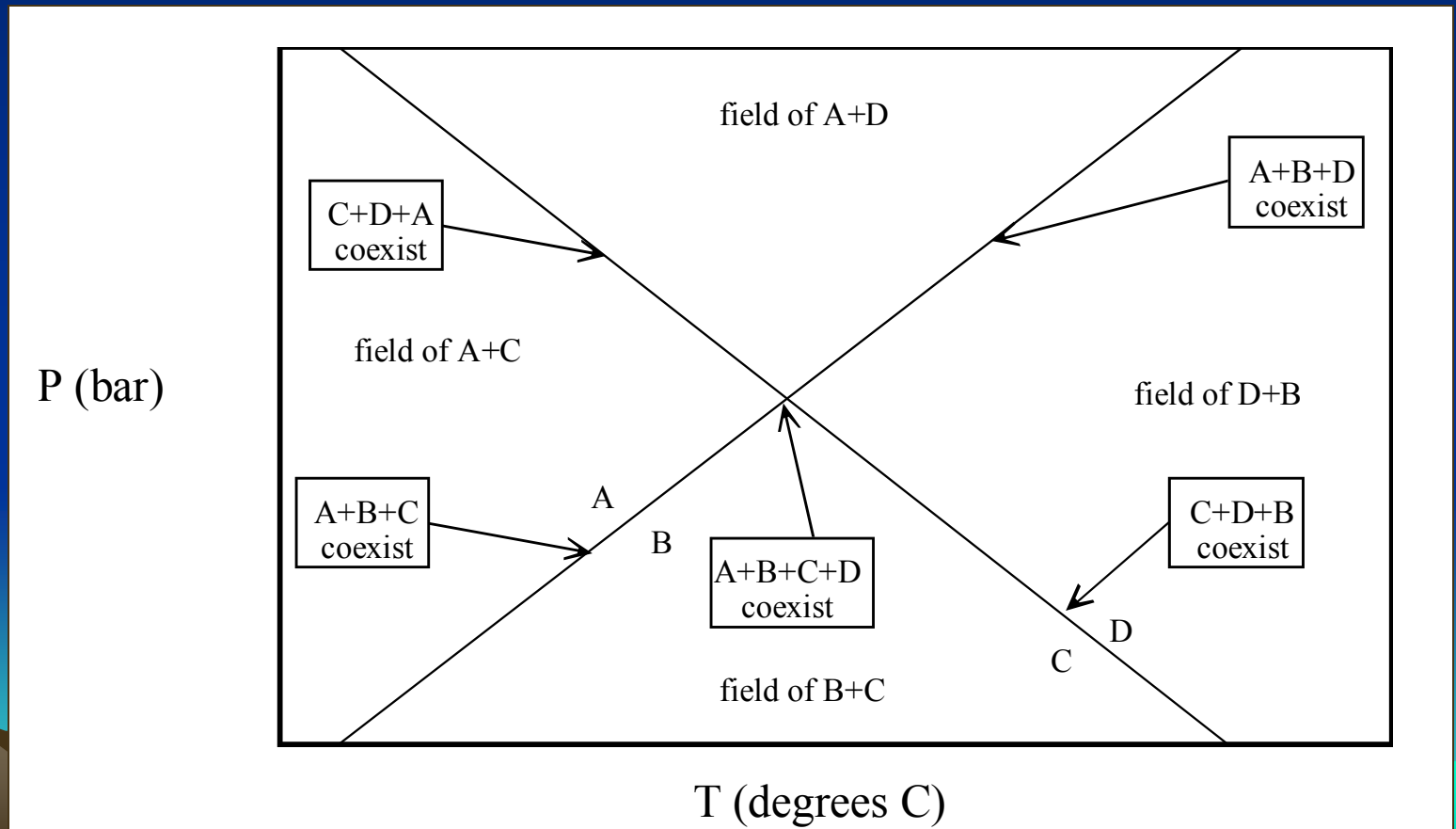
# Eskola's Mineralogical Phase Rule

- Most metamorphic rocks are well represented by 7 chemical components (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, CaO, MgO, K<sub>2</sub>O and Na<sub>2</sub>O)
- A particular rock will most likely undergo metamorphism in a divariant field
- Therefore  $2 = 7 - P + 2$ , so  $P = 7$  (i.e. metamorphic rocks will contain at most 7 or fewer mineral phases)



# A more complex Phase Diagram

- 2 components with 2 possible chemical reactions:
  - $A = B$
  - $C = D$



# Thermodynamics and Metamorphism

- $\Delta G$ : Gibb's Free Energy quantifies the total chemical energy in the defined system. At chemical equilibrium  $\Delta G = 0$
- $\Delta H$ : Enthalpy, the amount of heat energy in the chemical reaction system
- $\Delta S$ : Entropy, the amount of randomness in the chemical system.



# Gibb's Free Energy Equation

- $\Delta G = \Delta H - T \Delta S + P \Delta V$ 
  - T: temperature in degrees K
  - P: pressure in bar
  - $\Delta V$ : change in volume for the reaction
- If  $\Delta G$  is negative the forward reaction will proceed
- Negative  $\Delta H$  reactions are **exothermic** and release heat
- Positive  $\Delta H$  reactions are **endothermic** and absorb heat from the universe



# Gibb's Free Energy cont.

- The free energy is equal to 0 at chemical equilibrium (a good assumption for metamorphic rocks)

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

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

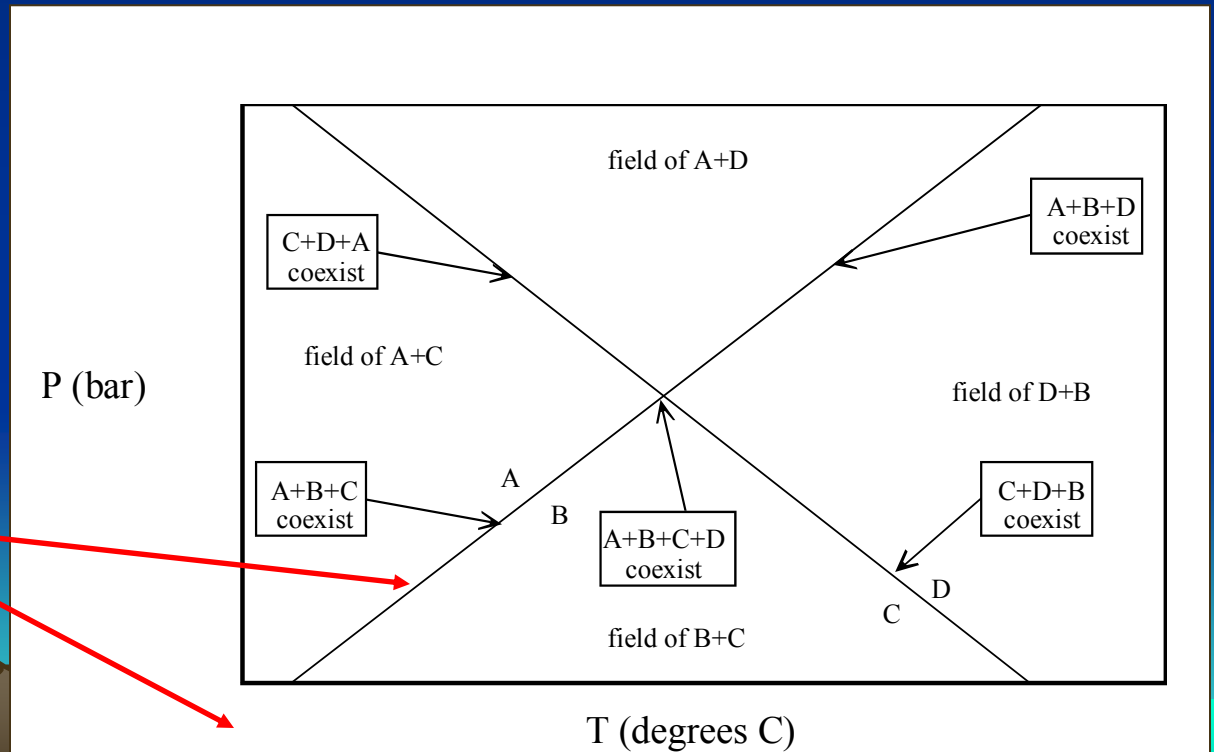
$y = mx + b$  equation of a line

$\Delta S / \Delta V = m = \text{slope}$

$-\Delta H / \Delta V = b = \text{y intercept}$

# $\Delta G$ and P-T Phase Diagrams

- On a P-T graph a reaction can be graphed using Gibb's Free Energy equation



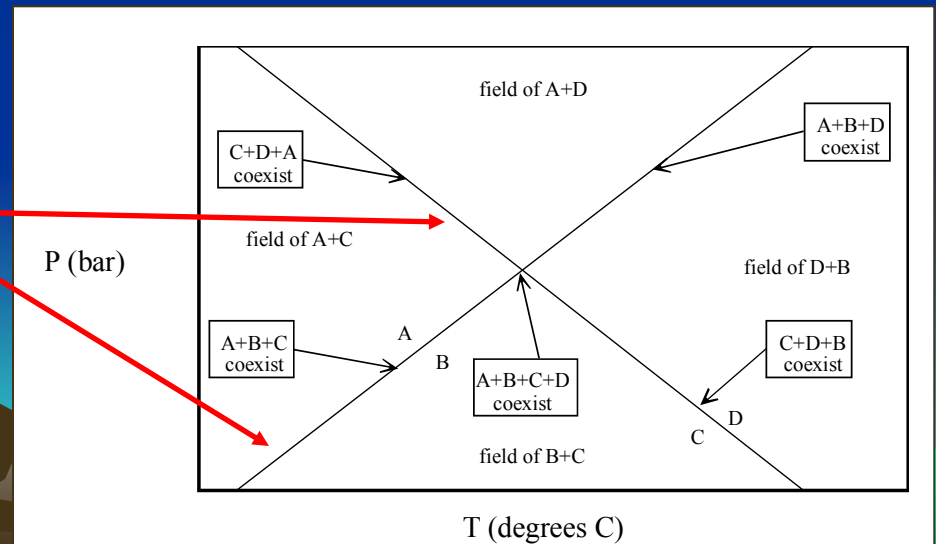
For reaction  $A=B$   
Slope =  $\Delta S / \Delta V$   
Y intercept =  $-\Delta H / \Delta V$

# Clapeyron Equation

- The Clapeyron equation is simply the  $\Delta S / \Delta V$  slope of the Free Energy equation for a reaction:
  - If the slope is  $> 0$  the reaction has a positive slope on a P-T phase diagram graph
  - If the slope is  $< 0$  the reaction has a negative slope on a P-T phase diagram

Clapeyron  $> 0$

Clapeyron  $< 0$



# Clapeyron Aluminosilicate Example

- Goal is to use tabulated values of  $\Delta S$  and  $\Delta V$  to plot the reaction Kyanite = Sillimanite on a P-T graph given the position of the invariant point

	Molar Volume	Entropy
Kyanite	44.09cm <sup>3</sup> mole <sup>-1</sup>	83.76 J mole <sup>-1</sup> K <sup>-1</sup>
Sillimanite	49.90cm <sup>3</sup> mole <sup>-1</sup>	96.11 J mole <sup>-1</sup> K <sup>-1</sup>

$$\Delta S = S(\text{products}) - S(\text{reactants})$$

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

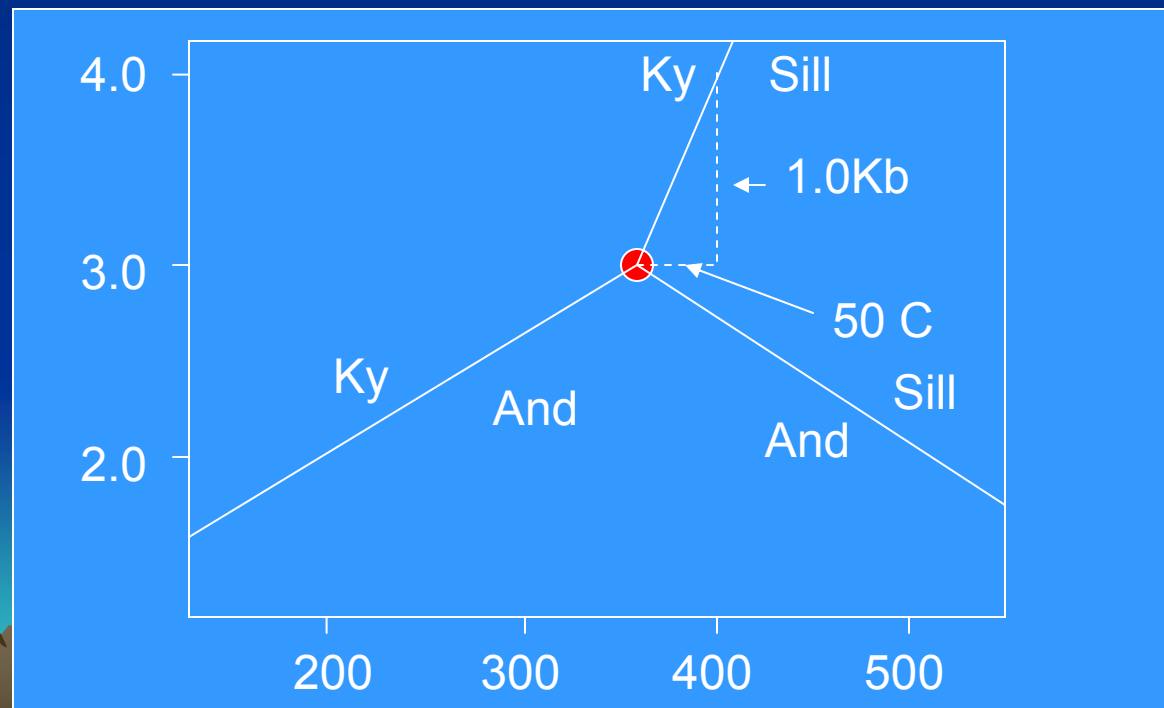
$$\Delta V = V(\text{products}) - V(\text{reactants})$$

$$\Delta V = 49.9 - 44.09 = 5.81 \text{ cm}^3 \text{ mole}^{-1} = 0.581 \text{ J bar}^{-1} \text{ mole}^{-1}$$

$$\text{Slope} = 12.35/0.581 = 21.2 \text{ bar/K} = 0.0212 \text{ Kb/K}$$

# Ky=Sill Univariant Curve

- Assuming that the aluminosilicate invariant point is  $T=350$  C and  $P = 3.0$  Kb



# Univariant Curves for Solid Solution Phases

- Solid solution in minerals such as garnet allows them to persist over a range in T & P
- As a solid solution phase such as garnet experiences different T & P the composition will adjust
- In many cases more than one solid solution phase is required to produce a geothermometer or geobarometer



# Geothermometer Example: Ga+Bi

- Ga+Bi is an excellent geothermometer because these 2 phases are common in medium grade metamorphic rocks
- Almandine + Phlogopite = Pyrope + Annite
- $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$



# Ga+Bi Geothermometer Example

- Given that a microprobe analysis of coexisting biotite and garnet in a thin section yields (X represents mole fraction):
  - (X)Annite = 0.305
  - (X)Almandine = 0.650
  - (X)Phlogopite = 0.416
  - (X)Pyrope = 0.176



# Ga+Bi Geothermometer cont.

- Given the following values:
  - $R$  (gas constant) =  $1.987 \text{ cal mole}^{-1} \text{ K}^{-1}$
  - $\Delta H = 12,454 \text{ cal mole}^{-1}$
  - $\Delta S = 4.662 \text{ cal K}^{-1} \text{ mole}^{-1}$
  - $\Delta V = 0.057 \text{ cm}^3 \text{ mole}^{-1}$
- Note that all of the above values were calculated using the (Products – Reactants) equation
- Molar volume must be converted to appropriate units:
  - $\Delta V = 0.057 \text{ cm}^3 \text{ mole}^{-1} \times [0.0242173 \text{ cal (cm}^3)^{-1} \text{ bar}^{-1}]$
  - $\Delta V = 0.00138 \text{ cal bar}^{-1} \text{ mole}^{-1}$



# Ga+Bi Equilibrium Constant (K)

- For solid solution the Gibb's Free Energy equation includes a term for the equilibrium constant (K)
- K = the ratio of the chemical activity of products over reactants

$$K = \frac{a_{\text{pyrope}} \cdot a_{\text{annite}}}{a_{\text{almandine}} \cdot a_{\text{phlogopite}}}$$

# Activity (a) vs. Concentration (X)

- Chemical activity (a) for ideal solid solution can be assumed to equal mole fraction (X)
- If an element is present in the formula more than once its mole fraction is raised to the occupancy power

$$K = \frac{[X_{pyr}^{ga}]^3 [X_{ann}^{bi}]^3}{[X_{alm}^{ga}]^3 [X_{phl}^{bi}]^3}$$

# Gibb's Free Energy Equation

- For solid solution the equilibrium constant occurs in an additional term:
  - At equilibrium  $\Delta G = 0 = \Delta H - T \Delta S + P \Delta V + RT \ln(K)$
- Re-arranging the equation to solve for T yields:

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

# Units of T Estimate

- The below equation will result in degrees K

$$T = \frac{P\Delta V + \Delta H}{\Delta S - (R)(\ln K)} = \frac{\text{bar} \times \frac{\text{cal}}{\text{bar} \times \text{mole}} + \frac{\text{cal}}{\text{mole}}}{\frac{\text{cal}}{\text{mole} \times ^\circ K} - \left( \frac{\text{cal}}{^\circ K \times \text{mole}} \right) (\text{unitless})} = ^\circ K$$

# Calculation of ln(K)

- The equilibrium constant K is the ratio of the chemical activities of the Products/Reactants

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

# Solving for the T Estimate

- The substitution of all known values into the re-arranged Gibb's Free Energy equation yields T as a function of P
- If this reaction is a good geothermometer it should have a large slope therefore the value of P will have little effect on the result

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

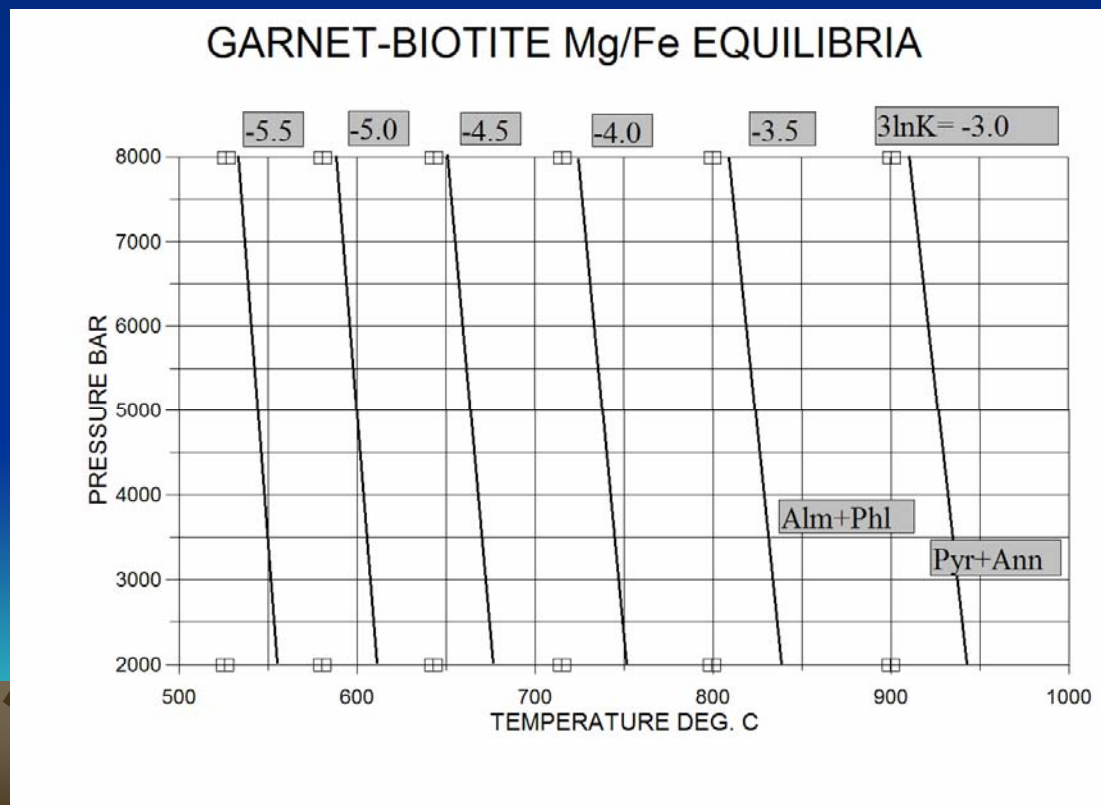
# Ga+Bi T Estimate Result

- Assuming a P=6,000 bar, T = 873.9 K (600.9 C)
- Other P values yield:
  - P = 12,000 bar, T = 874.5 K (601.5 C)
  - P = 1,000 bar, T = 873.4 K (600.4 C)
- Choice of P makes no significant difference therefore Ga+Bi is an excellent geothermometer

$$T = \frac{(6000)(0.00138) + 12454}{14.26} = \frac{12462.3}{14.26} = 873.9^{\circ} K = 600.9^{\circ} C$$

# Graphical Ga+Bi Geothermometer

- T estimate ultimately depends on K since  $\Delta H$ ,  $\Delta S$  and  $\Delta V$  do not change



# Ga+Bi+Ms+Pl Geothermobarometer

- Fe and Mg exchange in Ga+Bi act as thermometer
- 2 other reactions have an intermediate Clapeyron slope so the intersection with the Ga+Bi thermometer defines a single invariant point for P-T



# Ga+Bi+Ms+Pl Reactions

- (1) Pyrope + grossular + muscovite = 3 anorthite + phlogopite



- (2) Almandine + grossular + muscovite = 3 anorthite + annite



- (3) Almandine + Phlogopite = Pyrope + Annite



# Calculation of X (mole fraction)

- Compositional mole fraction is calculated from microprobe data

$$X_{an}^{pl} = \frac{Ca}{Ca + Na + K}$$

$$X_K^{mu} = \frac{K}{K + Na + Ca + Ba}$$

$$X_{phl}^{bi} = \frac{Mg}{Octohedral}$$

$$X_{Al6}^{Mu} = \frac{Al}{Octohedral}$$

$$X_{ann}^{bi} = \frac{Fe}{Octohedral}$$

$$X_{pyr}^{ga} = \frac{Mg}{Mg + Fe + Ca + Mn}$$

# Equilibrium Constants (K)

- Remember that element sites with a “3” subscript are raised to the “3” power in the K ratio

$$K_1 = \frac{[X_{an}^{pl}]^3 [X_{phl}^{bi}]^3}{[X_K^{mu}] [X_{Al6}^{mu}]^2 [X_{pyr}^{ga}]^3 [X_{gr}^{ga}]^3}$$

$$K_3 = \frac{[X_{pyr}^{ga}]^3 [X_{ann}^{bi}]^3}{[X_{alm}^{ga}]^3 [X_{phl}^{bi}]^3}$$

$$K_2 = \frac{[X_{an}^{pl}]^3 [X_{ann}^{bi}]^3}{[X_K^{mu}] [X_{Al6}^{mu}]^2 [X_{alm}^{ga}]^3 [X_{gr}^{ga}]^3}$$

# Thermodynamic Data (H, S and V)

- Thermo data should be from an internally consistent database (Berman, 1992)

<b>Phase</b>	<b>Enthalpy (H) J/mole</b>	<b>Entropy (S) J/(deg. mole)</b>	<b>Molar Volume (V) J/bar</b>	<b>Source</b>
Anorthite	-4228730.0	200.186	10.075	Berman 1992
Annite	-5142000.0	421.010	15.483	Berman 1992
Phlogopite	-6210391.0	334.346	14.977	Berman 1992
Muscovite	-5976740.1	293.157	14.087	Berman 1992
Almandine	-5267216.0	340.007	11.511	Berman 1992
Pyrope	-6286547.6	266.359	11.316	Berman 1992
Grossular	-6632859.4	255.150	12.538	Berman 1992

# Reaction Coefficients

- Slope and Y-intercepts for all 3 reactions
- Note the steep slope on reaction 3 (geothermometer)

Reaction	$\Delta H$ J/mole	$\Delta S$ J/(mole deg. K)	$\Delta V$ J/bar
(1)	-433.9	120.238	7.261
(2)	48625.5	133.254	7.572
(3)	49059.4	13.016	0.311

# Solving for K1

- Solving for equilibrium constant K1 requires substitution of mole fractions into K1 ration (products/reactants)

$$K_1 = \frac{[X_{an}^{pl}]^3 [X_{phl}^{bi}]^3}{[X_K^{mu}] [X_{Al6}^{mu}]^2 [X_{pyr}^{ga}]^3 [X_{gr}^{ga}]^3}$$

$$K_1 = \frac{[0.3233]^3 [0.4425]^3}{[0.871] [0.8991]^2 [0.1836]^3 [0.0788]^3} = 1373.2$$

# Calculation of Reaction (1) Slope

- Remember that slope is derived from rearrangement of Gibb's Free Energy equation

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

$$\text{Slope} = \frac{\Delta S - R \ln K}{\Delta V} = \frac{120.2385 - (8.314)(7.225)}{7.261} = 8.287$$

# Calculation of Reaction (1) Y-intercept

- Derived from Free Energy Equation

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

$$Y\_Intercept = \frac{-\Delta H}{\Delta V} = \frac{433.9}{7.261} = 59.75$$

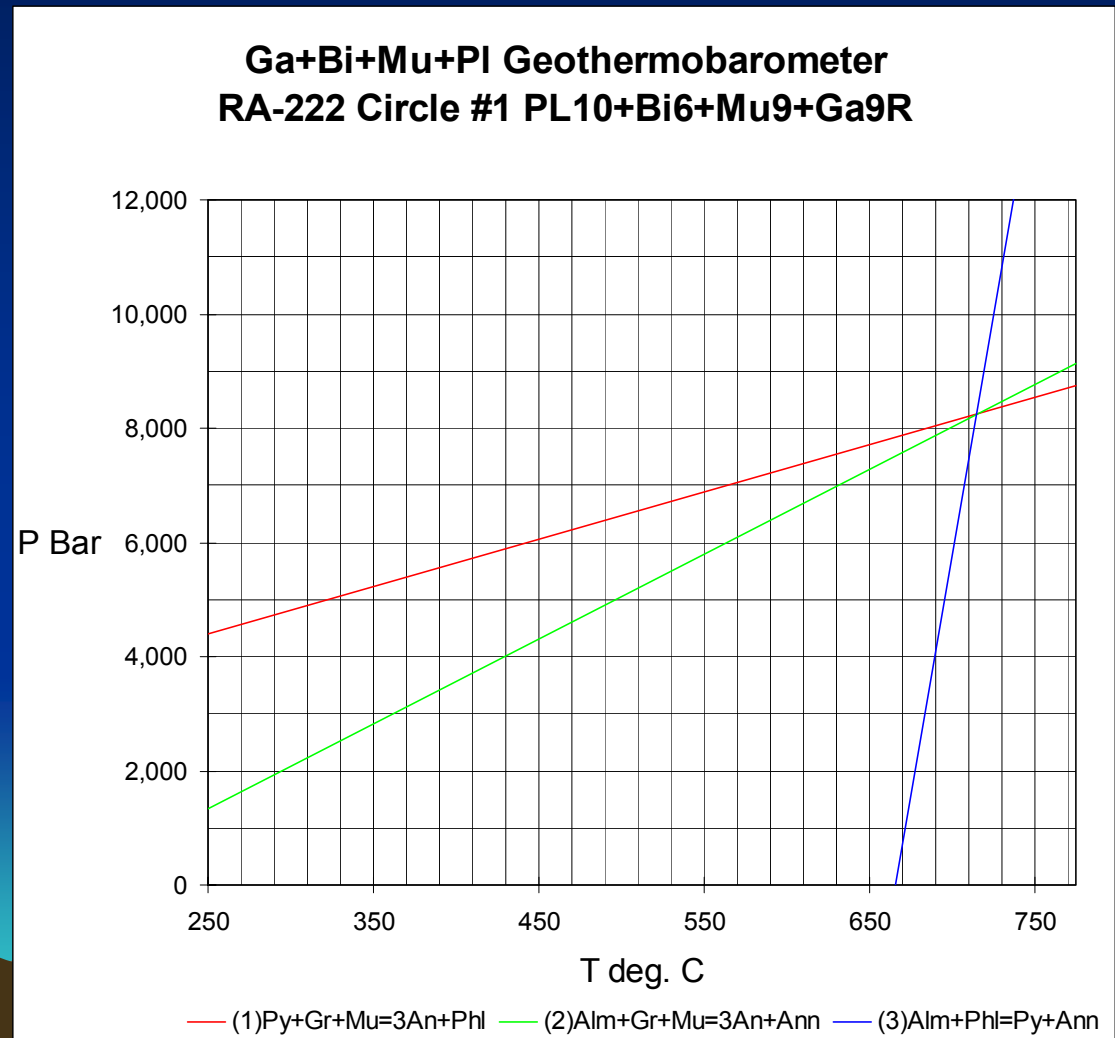
# Summary of Univariant Curves

- The 3 univariant lines intersect at the P-T of recrystallization

	Slope (bar/deg. C)	Y intercept (bar)
Reaction (1)	8.287	59.75
Reaction (2)	14.85	-6421.75
Reaction (3)	168.02	-157747.20

# Graphical Solution for P-T

- Internally consistent thermo database should always intersect at a point
- Ga+Bi thermometer is apparent from high positive slope (reaction 3)



# Summary for Final Exam

- Ternary igneous phase diagram
- Origin of tholeiitic vs. alkaline mafic magma (Ne-Ol-Opx-Q-Pl phase diagram)
- Tholeiitic vs. Calc-Alkaline magma
- Textural and compositional terms for igneous and metamorphic (corona, poikiloblast, etc.)
- Trace element fractionation problem (equation given)
- Phase rule in metamorphic rocks (use aluminosilicates as example)
- Solve for T given the composition of coexisting Garnet and Biotite, Gibb's Free Energy equation, and equation for K
- Norm calculation (quartz normative)
- Metamorphic facies and geotherms
- **Note: Bring CIPW norm calculation rules, calculator and ruler**



# Equations

$$\frac{C_L}{C_O} = F^{(D-1)}$$

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

$$df = C - P + 2$$

$$K = \frac{[X_{pyr}^{ga}]^3 [X_{ann}^{bi}]^3}{[X_{alm}^{ga}]^3 [X_{phl}^{bi}]^3}$$