Thermodynamics in petrology

Thermodynamics = *heat + work*

We can study *energy transfer* during reactions in chemical systems.

Reactions
- reversible
- irreversible

Cautions and limitations
Thermodynamics in petrology

Want to answer questions such as:

• How are phase diagrams made?
• How do we evaluate phase equilibria?
• How do mineral compositions relate to P & T?
• What do we need to know to make a P-T or T-X diagram?
• What are the thermodynamic properties of minerals?

Shortly we will apply these principles to:

• Metamorphic mineral reactions
• Activity models
• Thermobarometry
• P-T-t paths
Le Châtelier’s Principle

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to **counter-act the imposed change**.
Equilibrium

Equilibrium
no observed change

stable

unstable

metastable

Mechanical energy

Chemical energy

-5°C

water

ice

stable

unstable

+5°C

water

ice

free energy of reaction
Enthalpy of reaction (H)

- as $T \uparrow$, $H \uparrow$
- relation of $T$ & $H$ define *heat capacity* $(C_P)$
- discontinuity of $\Delta H$ shows energy gained by system at constant $T$ during fusion reaction

$\Delta H_{\text{melting}} = 144 \text{ kJ/mol}$

$\frac{dH}{dT}_P = C_P$

$T_{\text{melting}} \sim 1400 \, ^\circ\text{C}$

$\text{CaMgSi}_2\text{O}_6$  
Constant $P$

Di crystals  
Melt

$H (\text{kJ/mol})$

$T (\, ^\circ\text{C})$
Configurational entropy ($S$)

ordered

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\begin{array}{ccc}
\bullet & \circ & \bullet \\
\circ & \bullet & \circ \\
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\end{array}
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\begin{array}{ccc}
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disordered

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\begin{array}{ccc}
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\end{array}
\]
Gibbs free energy (G) of a phase

\[ G = H - TS \]

Enthalpy (H)

TS

Gibbs free energy (G)

\[ \frac{\partial G}{\partial T} = -S \]

(slope)
Gibbs free energy ($G$) of melting for two phases melt and solid

$H_{\text{melt}}$  
$H_{\text{solid}}$  

$S_{\text{melt}} > S_{\text{solid}}$  
(note different slopes)

$T_{\text{liquidus}}$  

$G_{\text{melt}}$  
$G_{\text{solid}}$  

Monday, September 28, 2009
Dependence on P & T

\[ \frac{\partial G}{\partial P} = V \]
\[ \frac{\partial G}{\partial T} = -S \]

\( \text{slope} = -S \)
\( \text{slope} = V \)
Gibbs free energy (G) of a reaction

for two phases A & B

$\Delta_r G^\circ = 0$

$G_A > G_B$

$\therefore B$ is stable

$G_A < G_B$

$\therefore A$ is stable
Gibbs free energy (G) of a phase

\[ G = H - TS \]

Enthalpy (H)

Gibbs free energy (G)

\[ \frac{\partial G}{\partial T} = -S \]

(slope)

T

Gibbs free energy (G) of a reaction

for two phases A & B

\[ H_A \quad H_B \]

\[ S_A > S_B \]

(note different slopes)

T_{equilibrium}

T

Monday, September 28, 2009
Al-silicate phase diagram (system $\text{Al}_2\text{SiO}_5$)
Al-silicate phase diagram (system Al$_2$SiO$_5$)
Clapeyron relations

\[ \frac{\Delta S}{\Delta V} = \frac{dP}{dT} = \frac{\Delta S}{\Delta V} \]

P

phase A

phase B

T

Monday, September 28, 2009
Clapeyron example:

if we know one point on a reaction equilibrium, can we determine the whole thing?

grossular + corundum = anorthite + gehlenite

If we know one point (760-780°C @ 1 kbar), how can we get the rest?

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>V</th>
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<td>125.3</td>
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<tr>
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<td>25.58</td>
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<tr>
<td>An</td>
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<td>100.79</td>
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<tr>
<td>Ge</td>
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</table>

\[
dP = \frac{\Delta S}{dT} = \frac{\Delta V}{dT}
\]
How do we interpret the Clapeyron slope?

- **solid-solid reaction**
- equilibrium is a straight line because $\Delta S/\Delta V = \text{constant}$ for reactions with no compressible fluid phase

- **devolatilization or melting reaction**
- at low $T$, initial devolatilization and low $\Delta S/\Delta V$ (low slope)
- fluids are highly expandable, so $\Delta V$ is high when going to higher $T$ at low $P$
- $\Delta S$ is low because just beginning to make volatiles

- at high $T$, have high $\Delta S/\Delta V$
- more volatiles are released, so have high $\Delta S$
- $\Delta V$ is low because fluids compress at high $P$