

## Thermodynamics Part 2: Second Law and Free Energy

Geochemistry  
DM Sherman, University of Bristol

### State Functions, so far..

We've defined the internal energy,  $U$ , in terms of the first law:

$$dU = dQ + dW$$

Internal energy is heat added at constant  $V$  (hard to do..). For convenience, we defined another state function, enthalpy,  $H$ , as

$$H = U + PV$$

Enthalpy is heat added at constant  $P$ .

However, neither  $\Delta H$  and  $\Delta U$  all us to predict whether a process will happen.

## Entropy and Heat

Q (heat) is not a state function. However, if we divide it by T, we get a state function called **entropy (S)**:

$$dS = \frac{dQ_{rev}}{T}$$

For an irreversible process,

$$dS \geq \frac{dQ}{T}$$

## What is Entropy??

Entropy is a measure of the number of microscopic ways to have a macroscopic state. A macroscopic state will be more probable if there are more microscopic ways to achieve it.

**Configurational entropy** results from the disorder of atoms over equivalent positions.

**Thermal entropy** results from the distribution of thermal energy over the microscopic energy levels of a system.

## The Second Law of Thermodynamics

For any process to occur spontaneously:

$$dS^{Universe} \geq 0$$

This is the **second law of thermodynamics**.

Another statement of the second law:

The macroscopic properties of any isolated system eventually assume constant values. This is called the **equilibrium state**.

## The Second Law of Thermodynamics

How will we know if processes in our *system* will be spontaneous?

Consider a system in thermal equilibrium with its surroundings. If the system transfers heat to the surroundings then:

$$\begin{aligned}dS^{Universe} &= dS^{system} + dS^{surr.} \\ &= dS^{system} + \frac{dQ^{surr.}}{T} \\ &= dS^{system} - \frac{dQ^{system}}{T} \geq 0\end{aligned}$$

Hence, a process will be spontaneous if:

$$TdS^{system} \geq dQ^{system}$$

## Spontaneous Processes: U and H

Suppose heat is exchanged at constant volume ( $dV=0$ ). Then,

$$dU = dQ^{system}$$

It follows that a process will be spontaneous if

$$TdS \geq dU$$

If heat is exchanged at constant pressure ( $dP=0$ ) a process will be spontaneous if

$$TdS \geq dH$$

## Spontaneous Processes and Free Energy

Let us define a new state function called the **Gibbs free energy**:

$$G = H - TS$$

$$dG = dH - TdS + SdT$$

It follows that, at constant  $T$  (i.e.,  $dT = 0$ ) and constant  $P$ , a process will be spontaneous when

$$dG \leq 0 \quad (\text{const. } P, T)$$

This criterion is easier to work with. The free energy change of a system accounts for the entropy of the universe.

## Free Energy and Equilibrium

If a process does not increase the entropy of the universe, then

$$dG = 0 \quad (\text{const. } P, T)$$

This means that the system is in equilibrium with the surroundings. On a microscopic scale, it means that the most probable distribution of thermal energy (and atomic positions) within the system has been reached.

## Practical meaning of free energy

For a general reversible process, we can now express our internal energy in terms of entropy and volume:

$$dU = TdS - PdV + dW_{\text{other}}$$

Where,  $dW_{\text{other}}$  is the non-compression work (work done at constant V).

## Practical meaning of free energy

Since we have defined  $G$  to be

$$G = H - TS = U - TS + PV$$

$$\begin{aligned}dG &= dU - TdS - SdT + PdV + VdP \\ &= -SdT + VdP + dW_{other}\end{aligned}$$

It follows that, at constant  $T$  and  $P$  ( $dT$  and  $dP = 0$ ),

$$dG = dW_{other}$$

This is how chemical reactions do work!

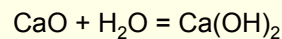
## Using $G$ , $H$ and $S$ for Geochemistry

For a chemical reaction  $A = B$  which occurs at constant  $T$  and  $P$ , we can write:

$$\Delta G = \Delta H - T\Delta S$$

## Free Energy Changes and Chemical Reactions

If we know the enthalpies and entropies of formation for different species, we can predict chemical reactions. Consider the reaction



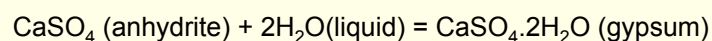
Tabulated values of the free energies of formation from the elements are:

	$\Delta G_f$ kJ/mol	$S_f$ (J/mol-K)
CaO	-604.48	38.21
H <sub>2</sub> O(liq)	-237.14	69.95
Ca(OH) <sub>2</sub>	-894.41	83.39

We find that  $\Delta G = -52.79$  kJ/mol but  $\Delta S = -24.77$  J/mol-K.  
Will the reaction go spontaneously?

## Example: Anhydrite/Gypsum Reaction

**Example:** Calculate the change in Gibb's free energy for the reaction



as a function of temperature from 25 to 100 °C at 1 bar. Will the reaction be spontaneous? The free energies of formation from the elements at 298K, 1 bar are:

Mineral	$\Delta G_f$ (kJ/mol)	$\Delta H_f$ (kJ/mol)	S(kJ/mol-K)
Anhydrite	-1321.7	-1434.1	0.10669
Water	-237.1	-285.8	0.06995
Gypsum	-1797.2	-2022.6	0.1941

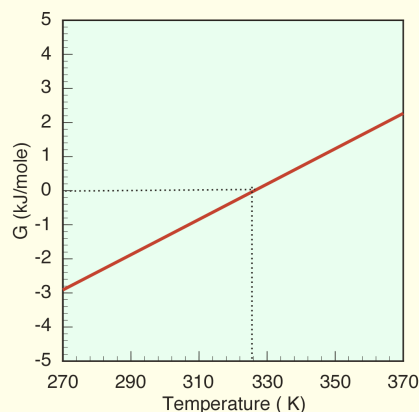
### Anhydrite/Gypsum Reaction (cont.)

$$\Delta H = -2022.6 - (2(-285.8) - 1434.1) = -16.9 \text{ kJ/mole}$$

$$\Delta S = 0.1949 - (2(0.0700) + 0.1067) = -0.0518 \text{ kJ/mol-K}$$

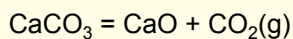
$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= -16.9 + T(0.0518) \text{ kJ/mol} \end{aligned}$$

Gypsum is stable below  
326 K (52 °C).



### Breakdown of CaCO<sub>3</sub> on Venus

**Example:** Given the following thermodynamic data at 1 bar, 298K, work out the phase boundary (P,T along which  $\Delta G = 0$ ) for the reaction



assuming that CO<sub>2</sub> behaves as an ideal gas with  $P=P_{\text{total}}$  and that  $\Delta H$  and  $\Delta S$  are constant with T and P.

Phase	$\Delta H_f$ (kJ/mol)	S (kJ/mol-K)	V (cm <sup>3</sup> /mole)
CaCO <sub>3</sub> (calcite)	-1207.37	0.0917	36.93
CaO	-635.09	0.03821	16.5
CO <sub>2</sub>	-393.51	0.21379	24789.2

## Breakdown of CaCO<sub>3</sub> on Venus

Here, because there is a gas phase,  $\Delta V$  will not be constant with pressure!

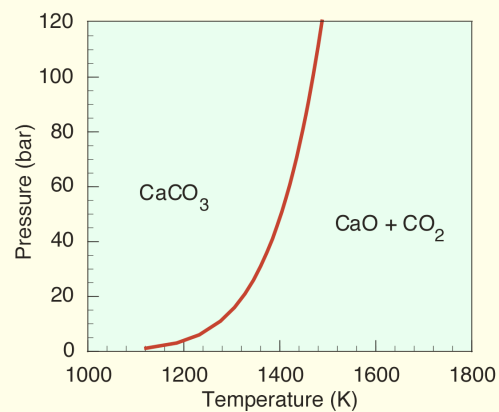
$$\Delta G(P,T) = \Delta H(P_0,T_0) - T\Delta S(P_0,T_0) + \int_{P_0}^P \Delta V(P)dP$$

The volume of the gas phase  $\gg$  volume change of solids. Hence,  $\Delta V \approx V_{\text{CO}_2}$ .

For an ideal gas,

$$\int_{P_0}^P V(P)dP \approx RT \int_{P_0}^P \frac{1}{P} dP = RT \ln\left(\frac{P}{P_0}\right)$$

## Breakdown of CaCO<sub>3</sub> on Venus (cont.)



$$\begin{aligned} \Delta H &= (-393.5 - 635.09) \\ &\quad - (-1207.37) \\ &= 178.8 \text{ kJ/mole} \end{aligned}$$

$$\begin{aligned} \Delta S &= (0.2138 + 0.03821) \\ &\quad - (0.0917) \\ &= 0.1603 \text{ kJ/mole-K} \end{aligned}$$

$$\Delta G = 178.8 - 0.1603T + RT \ln\left(\frac{P}{P_0}\right) = 0$$

## Clapeyron Equation

For a transition from phase 1 to phase 2:

$$dG_1 = V_1 dP - S_1 dT$$

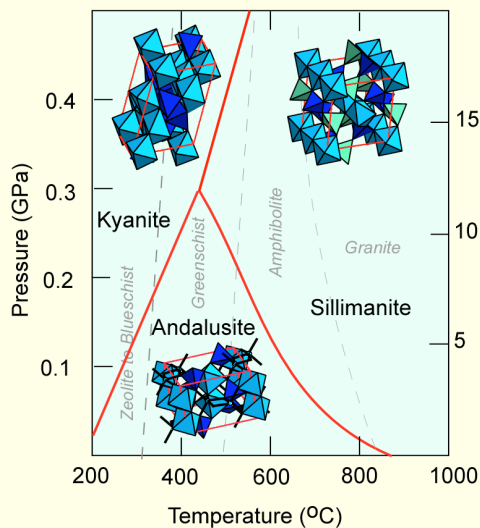
$$dG_2 = V_2 dP - S_2 dT$$

$$dG_2 - dG_1 = d\Delta G = \Delta V dP - \Delta S dT = 0 \quad (\text{at equilibrium})$$

Which gives us the **Clapeyron equation**:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

## The Al<sub>2</sub>SiO<sub>5</sub> Phase Diagram



- The phase with the highest entropy is stable at high T.
- The phase with the lowest V is stable at high P.

	$\Delta H_f$ kJ	S J/K	V cm <sup>3</sup>
Kyanite	-5.3	83.8	44.1
Andalusite	-1.1	93.2	51.5
Sillimanite	0.6	96.1	49.9

## Summary

For a process (chemical reaction) to be spontaneous,  $\Delta G < 0$ . At equilibrium  $\Delta G = 0$ .

If  $\Delta C_p = 0$ , we can write

$$\Delta G(P,T) = \Delta H(P_0,T_0) - T\Delta S(P_0,T_0) + \int_{P_0}^P \Delta V(P)dP$$

For solids, when  $\Delta V$  is constant with  $P$ , this simplifies to

$$\Delta G(P,T) = \Delta H(P_0,T_0) - T\Delta S(P_0,T_0) + (P - P_0)\Delta V$$

## Derivation of $\Delta G(P,T)$

From the definition of  $G$

$$G = H - TS$$

$$G(P,T) = H(P,T) - TS(P,T)$$

The Enthalpy expands as

$$H(P,T) = H(P_0,T_0) + \int_{P_0,T_0}^{P,T} dH$$

$$= H(P_0,T_0) + \int_{P_0,T_0}^{P,T} TdS + \int_{P_0,T_0}^{P,T} VdP$$

### Derivation of $\Delta G(P,T)$ (cont.)

Now the  $TdS$  integral can be evaluated since,

$$dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP$$

$$= \frac{C_p}{T} dT - \alpha V dP$$

The enthalpy is then

$$H(P,T) - H(P_0,T_0) = \int_{P_0,T_0}^{P,T} C_p dT - T \int_{P_0,T_0}^{P,T} \alpha V dP + \int_{P_0,T}^{P,T} V dP$$

### Derivation of $\Delta G(P,T)$ (cont.)

Now we've already evaluated the entropy term

$$S(P,T) - S(P_0,T_0) = \int_{P_0,T_0}^{P,T} \left( \frac{\partial S}{\partial T} \right)_P dT + \int_{P_0,T_0}^{P,T} \left( \frac{\partial S}{\partial P} \right)_T dP$$

$$= \int_{P_0,T_0}^{P,T} \frac{C_p}{T} dT - \int_{P_0,T_0}^{P,T} \alpha V dP$$

### Derivation of $\Delta G(P,T)$ (cont.)

$$G(P,T) = G(P_0T_0) + \int_{P_0T_0}^{PT} C_p dT - T \int_{P_0T_0}^{PT} \alpha V dP + \int_{P_0T_0}^{PT} V dP$$

$$+ T \int_{P_0T_0}^{PT} \frac{C_p}{T} dT + T \int_{P_0T_0}^{PT} \alpha V dP$$

Which simplifies to,

$$G(P,T) = G(P_0T_0) + \int_{P_0T_0}^{PT} C_p dT + T \int_{P_0T_0}^{PT} \frac{C_p}{T} dT + \int_{P_0T_0}^{PT} V dP$$

### Derivation of $\Delta G(P,T)$ (cont.)

For a chemical reaction, we can then write

$$\Delta G(P,T) = \Delta H(P_0T_0) + T\Delta S(P_0T_0) +$$

$$\int_{P_0T_0}^{PT} \Delta C_p dT + T \int_{P_0T_0}^{PT} \frac{\Delta C_p}{T} dT + \int_{P_0T_0}^{PT} \Delta V dP$$

If we assume  $\Delta C_p = 0$  and  $\Delta V$  is constant, we get

$$\Delta G(P,T) = \Delta H(P_0T_0) - T\Delta S(P_0T_0) + (P - P_0)\Delta V$$

## Free Energy as G(P,T)

$$\Delta G(P,T) = \Delta H(P_0, T_0) - T\Delta S(P_0, T_0) + (P - P_0)\Delta V$$

**Warning:** An easy mistake is to get the units wrong!

$$(P - P_0) \text{ bars} \times \frac{\Delta V \text{ cm}^3}{\text{mole}} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times \frac{1 \text{ N}}{\text{m}^2 \text{ Pa}} \times \frac{1 \text{ J}}{\text{N m}} \times \frac{1 \text{ m}^3}{(100 \text{ cm})^3} = 0.1((P - P_0)\Delta V) \text{ J/mole}$$

$$1 \text{ bar} \times 1 \text{ cm}^3 = 0.1 \text{ J}$$