

Geochemistry

Notes VIII: Thermodynamics (2)

V. Enthalpy

VI. Entropy

VII. Gibbs Free Energy

As opposed to internal energy, which is a function of both q and w at constant pressure another type of energy, enthalpy is not. Enthalpy is defined as $H = E + PV$.

(1) What is change in H at constant pressure?

$$dE = dq - dw$$

substitute for dw ($= PdV$)

integrate from state 1 to state 2

use $H = E + PV$ and substitute for $E + PV$

$$\Delta H = q_p$$

(2) Since only relative E 's can be determined, only relative H 's can be determined. Define H of formation for elements (sometimes oxides) in their stable phase at STP to be zero ($H_f^\circ = 0$, for elements).

(3) Measure H for other compounds by measuring the heat evolved when each compound is produced by reaction of its constituent elements. e.g. C (graphite) + O_2 (gas) = CO_2 (gas). Heat evolved in this reaction at STP is the H_f° for CO_2 .

(4) H 's are additive; i.e. one can calculate the change in enthalpy for any reaction (ΔH_R) if one knows the H of all of the products and reactants at the temperature and pressure of the reaction:

$$\Delta H_R = \sum n_i H_i (\text{products}) - \sum n_j H_j (\text{reactants})$$

(5) If $\Delta H_R > 0$, endothermic; if $\Delta H_R < 0$, exothermic.

(6) To this point we've discussed enthalpies at one particular temperature and pressure. If you know the enthalpy of a substance at one temperature, can you determine its enthalpy at another temperature? Remember that a change in H at constant P is simply the heat evolved. Imagine instead of a change in state where a chemical reaction is taking place, one has a system composed of a single substance and the change in state is simply a change in T. Remember the simple example where we calculated the amount of heat transferred between a warmer mass and a cooler mass: $q \approx (m)(c) |T_f - T_i|$. Let's envision that this process is isobaric: then q is q_p and c is C_p , the heat capacity at constant pressure. We had used an approximate sign because C_p is a function of T. For a very small change in T, we can write the exact equation: $dq_p = m C_p dT$. If we then stipulate that we are concerned with a single mole of the substance in question, the equation becomes $dq_p = C_p dT$. We can integrate this equation from state 1 (T_1) to state 2 (T_2):

$$q_p = H(P, T_2) - H(P, T_1) = \int_{T_1}^{T_2} C_p dT$$

Entropy

Second Law of Thermodynamics

If one considers both the system and the surroundings, an entropy increase accompanies all processes.

$$dS = dq/T \text{ or}$$

$$\Delta S = q/T, \text{ for reversible process}$$

$$dS > dq/T \text{ or}$$

$$\Delta S > q/T, \text{ for an irreversible process}$$

If we know the entropy of a substance at one temperature, how do we get entropy at another temperature?

$$dq_p = C_p dT$$

$$dS = C_p dT/T$$

$$S(P, T_2) - S(P, T_1) = \int_{T_1}^{T_2} C_p dT/T$$

Third Law of Thermodynamics

At absolute zero, the entropies of pure crystalline solids are zero.

$$S(P, T) - 0 = \int_0^T C_p dT/T$$

Entropies are also additive:

$$\Delta S_R = \sum n_i S_i (\text{products}) - \sum n_j S_j (\text{reactants})$$

If $\Delta S_R > 0$, the products are more disordered than reactants; if $\Delta S_R < 0$, the products are more ordered than the reactants.

Gibbs Free Energy

$$G = H - TS$$

balances the two tendencies, give off heat and increase disorder, the lower the G, the more likely the material is to be stable.

Free energies are also additive:

$$\Delta G_R = \sum n_i G_i (\text{products}) - \sum n_j G_j (\text{reactants})$$

$\Delta G_R = \Delta H_R - \Delta S_R T$ (calculated from the above equation and the analogous equations for ΔH_R and ΔS_R)

If:

$\Delta G_R > 0$, reactants are stable

$\Delta G_R < 0$, products are stable

$\Delta G_R = 0$, reactants and products are both stable

From the 4 equations above, one can determine that higher entropy phases tend to be stable at higher T's.

How does G change with T and P?

$$G=H-TS$$

$$dG=dH-TdS-SdT$$

$$dG=d(E+PV)-TdS-SdT$$

$$dG=dE+PdV+VdP-TdS-SdT$$

$$dG=dq-dw+PdV+VdP-TdS-SdT$$

$$dG=TdS-PdV+PdV+VdP-TdS-SdT$$

$$dG=VdP-SdT$$

-Have one equation as above for each phase in a reaction. They can be added and subtracted to get the following equation:

$$d\Delta G_R = \Delta V_R dP - \Delta S_R dT$$

Suppose you know the ΔG_R at a particular T and you want to know ΔG_R at the same T, but different P.

$$\int_{\Delta G(P_1, T_1)}^{\Delta G(P_2, T_1)} d\Delta G_R = \int_{P_1}^{P_2} \Delta V_R dP$$

For solids volumes do not change much with pressure and for solid-solid reactions the change in volume for the reaction changes even less with pressure, so we can make the assumption that ΔV_R is constant. If so, the integral reduces to: $\Delta G_R(P_2, T_1) - \Delta G_R(P_1, T_1) \approx \Delta V_R(P_2 - P_1)$ or

$$\Delta G_R(P_2, T_1) - \Delta G_R(P_1, T_1) \approx \Delta V_R(\Delta P)$$

from this equation it can be determined that denser phases are more stable at higher pressures.

Suppose you know the ΔG°_R at a particular P and you want to know ΔG°_R at the same P, but different T.

$$\int_{\Delta G^\circ(P_1, T_1)}^{\Delta G^\circ(P_1, T_2)} d\Delta G^\circ_R = - \int_{T_1}^{T_2} \Delta S_R dT$$

We know that entropies do change with T, but as it turns out, the ΔS_R does not change much with T or P, particularly for solid-solid reactions. If so, the integral reduces to:

$$\Delta G^\circ_R(P_1, T_2) - \Delta G^\circ_R(P_1, T_1) \approx -\Delta S_R(T_2 - T_1) \text{ or}$$

$$\Delta G^\circ_R(P_1, T_2) - \Delta G^\circ_R(P_1, T_1) \approx -\Delta S_R(\Delta T)$$

from this equation it can be determined that high entropy phases tend to be stable at high temperatures.

You can combine the above reaction with the analogous equation (but for change in Gibbs Free Energy with pressure, to determine the following equation:

$\Delta G^\circ_R(P_2, T_2) - \Delta G^\circ_R(P_1, T_1) \approx \Delta V_R(\Delta P) - \Delta S_R(\Delta T)$, which tells you how to calculate ΔG°_R at any P and T, given the ΔG°_R at one particular P and T, ΔV_R , and ΔS_R - under the assumption that ΔV_R and ΔS_R are constants, a reasonably good assumption for solid-solid reactions.

You might ask the question - "At what P's and T's is ΔG°_R equal to zero. Simply set $\Delta G^\circ_R(P_2, T_2)$ to zero:

$$-\Delta G^\circ_R(P_1, T_1) \approx \Delta V_R(P - P_1) - \Delta S_R(T - T_1)$$

after a little algebra you can get:

$$P \approx (\Delta S_R / \Delta V_R)(T) - (\Delta S_R / \Delta V_R)(T_1) + P_1 - \Delta G^\circ_R(P_1, T_1) / \Delta V_R$$

This is a line in P-T space.

The slope of the line is $(\Delta S_R / \Delta V_R)$ - or $dP/dT = \Delta S_R / \Delta V_R$, which is the Clausius - Clapeyron Equation. $\Delta S_R / \Delta V_R$ is called the "Clapeyron Slope".

We derived this assuming that $\Delta S_R / \Delta V_R$ did not change with T or P, but it is easy to derive this in general:

$$0 = d\Delta G_R = \Delta V_R dP - \Delta S_R dT$$

$$\text{so, } dP/dT = \Delta S_R / \Delta V_R$$