

Calculating ΔS and ΔG From a Chemical Reaction

Just as we calculated ΔH_{rxn} from the ΔH_f^0 (enthalpies of formations) of the products and reactants, so too can we calculate the ΔS_{rxn} and ΔG_{rxn} from the ΔS and ΔG_f of the products and reactants. Note that the equation used to solve for ΔH_{rxn} is the same equation used for solving both ΔS_{rxn} and ΔG_{rxn} .

$$\Delta H^{\circ}_{\text{rxn}} = \sum n\Delta H^{\circ}_{\text{f (prod)}} - \sum n\Delta H^{\circ}_{\text{f(react)}}$$

$$\Delta S^{\circ}_{\text{rxn}} = \sum n\Delta S^{\circ}_{\text{f(prod)}} - \sum n\Delta S^{\circ}_{\text{f(react)}}$$

$$\Delta G^{\circ}_{\text{rxn}} = \sum n\Delta G^{\circ}_{\text{f(prod)}} - \sum n\Delta G^{\circ}_{\text{f(react)}}$$

*Remember all the values of the products and the coefficients must be **multiplied by the coefficients**.

So In solving for— $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$, the values for ΔH and/or ΔS can be found if the equation is given for the reaction.

Note: ΔS will have its units in J/K, but ΔH and ΔG will need units in kJ so the units for S will need to be changed to kJ.

Predicting the sign of ΔS

At times, the sign of the entropy is all that is needed to answer the question of whether a reaction will be spontaneous with high, low, all, or no temperatures.

The following characteristics of reactions will tell give the sign (+ or -) of S.

- 1) If substances go from solids to liquids or gases, or if liquids go to gases, the entropy (S) will be (+).
- 2) If substances go from solid to aqueous, the entropy (S) will be (+).
- 3) If there are more gas molecules on the product (right) side of the reaction than on the reactants (left) side, the entropy (S) will be (+).

Likewise, if the opposite occurs the entropy would be negative (-).

Remember that positive entropy is important for spontaneity.

*The Third Law of Thermodynamics states: **The entropy of a perfect crystal at 0 K is zero.**

Free energy is dependent on the pressure on the system if the reaction is all gases. Free energy is dependent on concentration if the system is aqueous. We will limit our concern to systems that are all gases and dependent on pressure, but in thermodynamics, we can have systems using concentration or systems using both pressure and concentration in the same reaction.

Remember, these reactions are equilibrium reactions. They involve an equilibrium constant (K).

We know that the constant that has all pressures given is “ K_p ” and that the constant that has all concentrations is “ K_c ”. With thermodynamics we can have an equilibrium that has both pressure and concentration in the value of k. In this case, the constant is expressed merely as “k” without a subscript.

However, we will be calculating the constant as K_p since we will be limiting our study to pressure. **Remember** $K_p = (\text{product pressures})^n / (\text{reactant pressures})^n$. The “n” is the power of their coefficients.

Remember that a **pressure increase** on a system causes the equilibrium to shift to the side with fewer gas molecules and a **decrease** causes the shift to the side with more gas molecules. If the side with more gas molecules is the right (products) and pressure increases, the shift will be to the left and the entropy will be negative since the side with fewer gas molecules is the reactant side. The same is true for the opposite. Decreases pressure shifts to more gas molecules and if the products have more gas molecules, it shifts right and the entropy for the reaction is positive.

The equation used to represent the **Free Energy** of a reaction is...

$\Delta G = \Delta G^0 + RT \ln(Q)$ ΔG^0 is free energy in standard state. This equation is for ΔG not necessarily at equilibrium.

At equilibrium, $\Delta G = 0$ so the equation can be written

$$0 = \Delta G^0 + RT \ln(Q)$$

$\Delta G^0 = -RT \ln(K_p)$ (R is equal to 8.314×10^{-3} (for kJ) and T is in Kelvin temperature.)

*(k_p changes with temperature. So once ΔG^0 is calculated at a certain temperature calculating ΔG^0 at a new temperature cannot be done using the above equation. Calculating a new ΔG^0 at a different temperature requires using...

$\Delta G^0 = \Delta H^0 - T \Delta S^0$ because ΔH^0 and ΔS^0 do not change significantly with temperature.