Gibb's Free Energy

1.   What is Gibb's free energy? What is its symbol?

This value represents the maximum amount of useful work (non PV-work) that can be obtained by a system.

It is symbolized by G. We only really discuss changes in free energy so you will normally deal with ΔG.

2.   What is the equation for Gibbs Free Energy (ΔG)?

$$\Delta G = \underset{\text{enthalpy}}{\Delta H} - \underset{\text{Temperature in K}}{T} \underset{\text{entropy}}{\Delta S}$$

3.   Why is it such a useful state function?

It can be used to indicate the direction of spontaneity of a reaction, based only on values of the system. Compare this to entropy, which must be viewed from the perspective of the entire universe – a much more complicated endeavor.

4.   What sign must ΔG have to indicate a spontaneous process?

ΔG must be negative.

1. At what temperatures would the following processes be spontaneous?

In order to answer these questions you will have to determine what sign of ΔG would result from the signs of ΔH and ΔS indicated. Remember for a reaction to be spontaneous you need the resulting sign for ΔG to be

negative.

a. $+\Delta S, -\Delta H$

$$\Delta G = \Delta \overset{-}{H} - T \Delta \overset{+}{S}$$

As you can see, a positive entropy when multiplied by the negative sign preceding it will result in an overall negative value (positive time negative = negative). This means that we can have this reaction occur at any temperature and the value will always come out to be negative (remember we are dealing with the Kelvin scale which does not go below zero.)

So we would say that this reaction is spontaneous at all temperatures.

b. $-\Delta S, -\Delta H$

$$\Delta G = \Delta \overset{-}{H} - T \Delta \overset{-}{S}$$

In this case the negative entropy, results in a perpetually positive value. So in order to get a $-\Delta G$ value, we need the $-\Delta H$ to be larger than the $+T\Delta S$ term. This means that this reaction would be spontaneous at sufficiently low temperatures.

c. $+\Delta S, +\Delta H$

$$\Delta G = \Delta \overset{+}{H} - T \Delta \overset{+}{S}$$

In this case the positive entropy, results in a perpetually negative value. So in order to get a $-\Delta G$ value, we need the $+\Delta H$ to be smaller than the $+T\Delta S$ term. This means that this reaction would be
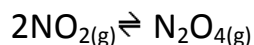
spontaneous at sufficiently high temperatures.

a. -ΔS, +ΔH

$$\Delta G = \overset{+}{\Delta H} - T\overset{\overset{+}{\overline{}}\,-}{\Delta S}$$

In this case there are no values of T that will result in a negative number. This means that this reaction is not spontaneous.

It is important to note that if the reaction was reversed, it would be spontaneous.

5.   For

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

a. ΔH° is -58.03 kJ and ΔS° is -176.6J/K. What is the value of ΔG° at 298K?

For this problem we simply have to plug the given information into the

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

Which would result in

$$\Delta G° = (\text{-}58030 \text{ J}) - (298K)(\text{-}176.6\,\tfrac{J}{K}) = \boxed{\text{-}5403 \text{ J}}$$

b. At what temperature is ΔG° = 0 (assume ΔH° and ΔS° are not temp. dependent).

We will solve using
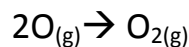
$$\Delta G° = \Delta H° - T\Delta S°$$

Setting ΔG° = 0, we are able to solve for T

$$\Delta G° = 0 = (-58030 \text{ J}) - (T)(-176.6 \tfrac{J}{K})$$

$$T = \frac{(-58030 \text{ J})}{(-176.6 \tfrac{J}{K})} = \boxed{328.6K}$$

c. Would ΔG° be negative above or below that temp?

ΔG° would be negative at temperatures below 328.6K. Anything above would cause the positive TΔS° term override the negative ΔH° term.

6. For the following constant pressure process

$$2O_{(g)} \rightarrow O_{2(g)}$$

a. Sign of ΔH?

-ΔH. We know that when bonds are broken the process is endothermic and when bonds are formed the process is exothermic. In the case of the example above, there are only bonds formed. This means that this reaction must have been exothermic, indicated by a

negative enthalpy value.

b. Sign of ΔS?

-ΔS. We are losing entropy in this reaction. We are moving from 2 separate atoms to one molecule → less disordered = less entropy.

c. Would this process be spontaneous at low or high temperatures?

This process would be spontaneous at sufficiently low temperatures. Sufficiently low meaning that the temperature plugged in would have to result in the -ΔH value being greater than the positive TΔS value.

7. ΔG° gives us important information about the equilibrium position of a reaction.

8. The value of ΔG depends on the concentration and pressure of reactants and products. Therefore the value of ΔG changes as a reaction proceeds.

9. At equilibrium the value for ΔG is zero.

10. Provide an equation for the following relationships:

a. ΔG (non-standard) to concentrations/pressures of reactants/products.

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

$8.3145 \frac{J}{mol\,K}$ Reaction Quotient

i. When would you use this equation?

When you need to solve for the free energy for a system not

under standard conditions.

b. Relates ΔG° to K

$$\Delta G^{0} = -RT \ln (K)$$

8.3145 $\frac{J}{mol\ K}$ equilibrium constant

  i. When would you use this equation?

When solving for the standard free energy of a system or for the equilibrium constant given the standard free energy.

c. Relates K to T

$$\ln K = -\frac{\Delta H^{0}}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^{0}}{R}$$

  i. What is important about the format of this equation?

It is written in y = mx + b format – the equation of a line. This means a line can be described and values of K, ΔH° and ΔS° and T can be determined.
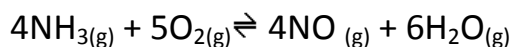
d. Van't Hoff Equation

$$\ln \left|\frac{K_2}{K_1}\right| = -\frac{\Delta H^{0}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

  i. When would you use this equation?

To calculate K at any temperature for a reaction if you know K at another temperature.

11.   Consider

$$4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$$

Calculate K at 825°C if ΔH° is -908kJ and ΔS° is 181J/K

Based on the information provided in this question we will use the following equation to solve this problem:

$$\ln K = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

It may be helpful to view the rearranged version of this equation as we will be solving for K.

$$K = e^{\left(-\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}\right)}$$

Now we just have to plug the information in and solve

$$K = e^{\left(\frac{-(-908000\ J)}{8.3145\ \frac{J}{mol\ K}}\left(\frac{1}{1098\ K}\right) + \frac{181\ \frac{J}{K}}{8.3145\ \frac{J}{mol\ K}}\right)} = e^{121} = 4.49 \times 10^{52}$$

12.   What is free energy of formation?

The free energy of formation is the amount of energy required to form a molecule from its elements in their standard states.

13.   What is the symbol for the free energy of formation?

$(\Delta G_f{}^o)$

14.   What is the free energy of formation for an element in its standard state?

Zero. It would not require any energy to get an element in its standard state.

15.   What is the equation used to solve for the free energy of reaction using the free energy of formation?

$$\Delta G^o{}_{rxn} = \sum \Delta G^o{}_{f\ (product)} - \sum \Delta G^o{}_{f\ (reactant)}$$