Worksheet – Free Energy

According to the ***3rd Law of Thermodynamics***, the spontaneity of a reaction depends on the entropy change of the universe. We defined a new function, Gibbs' Free Energy, **G**, which reflects $\mathbf{\Delta S_{universe}}$. The change in free energy during a chemical process is given by

$$\Delta G^o = \Delta H^o - T\Delta S^o < 0 \text{ for a spontaneous process}$$

Whether or not a reaction will proceed, under standard conditions, at given T depends on whether it is endothermic or exothermic, **and** whether the entropy of the system increases or decreases during the reaction.

When $\Delta G^o < 0$, the reaction, as written, will be **spontaneous**.

When $\Delta G^o > 0$, the **reverse reaction** will be **spontaneous**.

Using only the signs of ΔH^o and ΔS^o, predict the signs and temperature dependence for problems 1 and 2.

1. $CH_3OH\ (l) + 3/2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g)$

   Methanol (CH_3OH) is used as rocket fuel. Look at the reactants and products an predict the sign of ΔS^o.

   ΔS^O (> or <) 0

   Predict the sign of ΔH^o knowing that this is a combustion reaction.

   ΔH^o (> or <) 0

   Is the sign of ΔG^o temperature depend for this reaction?

2. Predict the signs of ΔG^o, ΔH^o and ΔS^o for:

   a) the vaporization of water above 100°C

   b) the vaporization of water at 100°C

   c) Does ΔH^o or ΔS^o favor the vaporization process?

3. For the rection

$$CO\ (g) + H_2O\ (g) \rightarrow CO_2\ (g) + H_2\ (g)$$

$\Delta H^o = -41.2$ kJ and $\Delta S^o = -135$ J/K

a) Calculate ΔG^o at room temperature, 298K.

b) Calculate ΔG^o at 700 K, assuming that ΔH^o and ΔS^o are temperature independent.

c) Does raising the temperature favor this reaction, as written?

d) Which factor, entropy or enthalpy, favors this reaction at high and low T?

e) Calculate ΔG^o at 305 K. Which reaction, forward or reverse, is spontaneous at this temperature?

When **$\Delta G^o = 0$**, the system is at **equilibrium** and **both** the forward and reverse reaction are proceeding, at the same rate. This is the case during **phase transitions**. Since $\Delta G^o = 0$, **$\Delta H^o = T\Delta S^o$**. This can be re-arranged:

$T = \Delta H^o / \Delta S^o$	which allows the determination of melting or boiling points
$\Delta S^o = \Delta H^o / T$	which demonstrates that all of the heat added at the transition temperature goes to raise the entropy of the system

4. Calculate the boiling point for BCl_3:

$$BCl_3\ (l) \leftrightarrows BCl_3\ (g)$$

given the following information:

	ΔH^o_f (kJ/mol)	S^o (J/mol K)
BCl_3 (l)	-418	209
BCl_3 (g)	-395	290

5. The heats of combustion of carbon, in the forms of graphite and diamond are shown below.

$C\ (gr) + O_2\ (g) \rightarrow CO_2\ (g)$ $\Delta H^o = -393.5$ kJ/mol
$C(d) + O_2\ (g) \rightarrow CO_2\ (g)$ $\Delta H^o = -394.4$ kJ/mol

a) What is the heat of reaction in going from graphite to diamond (hint: use Hess' Law)

$C\ (gr) \rightarrow C\ (d)$

b) The absolute entropy of graphite is 5.69 J/mol K and for diamond, 2.44 J/mol K, both at 298 K. Calculate ΔS^o for this reaction.

c) Calculate ΔG^o for this reaction. Are diamonds thermodynamically stable at 298 K?

The value of $\mathbf{\Delta G^o}$ is related to the **equilibrium constant**, **K**, by the expression:

$$\mathbf{\Delta G^o = - RT \ln K}$$

6. What is ΔG^o for the following reaction at 298 K?

$$2\ NH_3\ (g) \leftrightarrows N_2\ (g) + 3\ H_2\ (g) \quad \Delta H^o = 92.4\ kJ$$
$$\Delta S^o = 198\ J/K$$

a) Under standard conditions (1 atm of NH_3, N_2 and H_2) and at 298 K, what will be formed?

b) Calculate the equilibrium constant for this reaction at 298 K.

c) Calculate the equilibrium **temperature** for this standard reaction. Will product or reactant be formed above this temperature?

7. For the reaction

$$CO\ (g) + 2\ H_2O\ (g) \rightarrow CO_2\ (g) + H_2\ (g)$$

at 770 K, $K_{eq} = 5.10$. Calculate the ΔG^o for the reaction at 770 K.

Reactions are most commonly carried out under **non-standard** conditions. The non-standard free energy, **ΔG** is calculated using the equation:

$$\mathbf{\Delta G = -RT \ln (K/Q)} \text{ or } \mathbf{\Delta G = \Delta G^o + RT \ln Q}$$

K is the **equilibrium constant** = $\dfrac{[\text{products}]^p_{\text{equilibrium}}}{[\text{reactants}]^r_{\text{equilibrium}}}$

Q is the **reaction quotient** = $\dfrac{[\text{products}]^p_{\text{initial}}}{[\text{reactants}]^r_{\text{initial}}}$

where p and r are the stoichiometric coefficients of the products and reactants. **K** is calculated using the **equilibrium** concentrations and **Q** is calculated using the **initial** concentrations.

8. Calculate ΔG for the following sets of **initial** concentrations (M) to see how this influences the sign and magnitude of ΔG. Use the equation for the decomposition of ammonia shown in question 6.

	[N_2]	**[H_2]**	**[NH_3]**	**Q**	**ΔG**
a)	1.0	1.0	1.0		
b)	0	0	1.0		
c)	0.01	0.01	0.1		
d)	1.0	1.0	845		
e)	1.4	0.01	1.0		

Use the data given below to answer the next three questions.

$$2\ N_2O\ (g) + 3\ O_2\ (g) \rightarrow 4\ NO_2\ (g) \qquad \Delta H^o = -31.6\ kJ$$
$$\Delta S^o = -98.0\ J/K$$

9. Calculate the equilibrium constant at 298 K for this reaction.

   a) First calculate ΔG^o at 298.

   b) Solve for K, given that $\Delta G^o = -RT \ln K$

10. When 1.00 M NO_2 (g), 0.50 M O_2 (g) and 0.50 M N_2O are mixed in a container, which of the following species will **increase** in concentration at 298 K, *N_2O*, *O_2*, *NO_2*, *none of them will change*

    a) First solve for Q, with the given initial conditions.

    Q = ____________

    b) Next solve for ΔG, the **non-standard** free energy

    c) Given the sign of ΔG, which will proceed spontaneously?

    forward or *reverse* reaction

    d) Which species will be formed under these non-standard conditions?

11. Which of the following changes will make the reaction **less** spontaneous?
    - i) increasing $[N_2O]_i$ by a factor of 2
    - ii) increasing $[NO_2]_i$ by a factor of 2 and the $[N_2O]_i$ by 4
    - iii) increasing the temperature
    - iv) decreasing the temperature

The two expressions for ΔG^o can be combined to give the van't Hoff equation, which explains the temperature dependence of K, the equilibrium constant. $\Delta G^o = \Delta H^o - T\Delta S^o$ and $\Delta G^o = -RT \ln K$. Rearranged, this gives:

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

$$y = \quad m \quad x \; + \; b$$

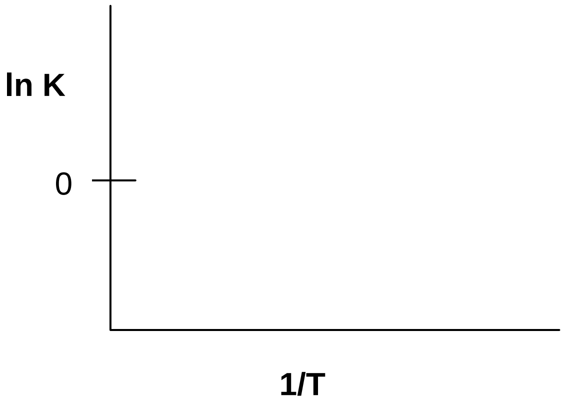
a linear equation that plots ln K vs 1/T.
The slope of the line is related to the standard enthalpy of the reaction and the intercept is related to the standard entropy change.

12. For the previous reaction:

$2\ NO_2\ (g) + 3\ O_2\ (g) \rightarrow 4\ NO_2\ (g)$ $\Delta H^o = -31.6$ kJ

$\Delta S^o = -98.0$ J/mol

draw the approximate shape of the van't Hoff curve.



a) As you increase the temperature, what happens to the value of K?

b) How does this relate to Le Chatelier's principle?