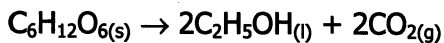


# AP Chemistry: Thermodynamics

AP Chemistry Thermodynamics WS 0809.doc

Name: Key Date: \_\_\_\_\_ Per: \_\_\_\_\_

1. The following equation represents the essential change that takes place during the fermentation of glucose to ethanol:



Is  $\Delta S^\circ$  positive or negative? Explain.

Since the glucose molecules break into smaller molecules and also a gas is formed, the prediction is that entropy increases and  $\Delta S^\circ$  is positive.

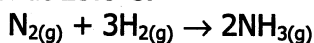
2. Calculate the change of entropy,  $\Delta S^\circ$ , at 25.0°C for the reaction in which urea is formed from  $\text{NH}_3$  and  $\text{CO}_2$ .



The standard entropy of urea is 174 J/molK. See the text appendices for additional values.

$$\Delta S^\circ = [(174 + 70) - (2 \times 193 + 214)] \text{ J/K} = \boxed{-356 \text{ J/K}}$$

3. Using values of  $\Delta H^\circ_f$  and  $S^\circ$ , calculate the standard free energy change,  $\Delta G^\circ$ , for the following reaction at 25.0°C.

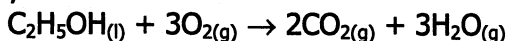


$$\Delta H^\circ = [2 \times (-45.9) - 0] \text{ kJ} = -19.8 \text{ kJ}$$

$$\Delta S^\circ = [2 \times 192.7 - (191.6 + 3 \times 130.6)] \text{ J/K} = -198.0 \text{ J/K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -91.8 \text{ kJ} - (298 \text{ K})(-0.1980 \text{ kJ/K}) = \boxed{-32.8 \text{ kJ}}$$

4. Using standard free energies of formation, calculate  $\Delta G^\circ$  for the combustion of 1 mol of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , at 25.0°C.



$$\Delta G^\circ = [2(-394.4) + 3(-228.6) - (-174.9)] \text{ kJ} \\ = \boxed{-1299.7 \text{ kJ}}$$

5. Calculate  $\Delta H^\circ$  and  $\Delta G^\circ$  for the reaction



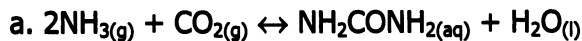
Interpret the signs obtained for  $\Delta H^\circ$  and  $\Delta G^\circ$ . Values of  $\Delta H^\circ_f$  (in kJ/mol) are as following:  $\text{KClO}_3(\text{s}) = -397.7$ ;  $\text{KCl}(\text{s}) = -436.7$ . Similarly, values of  $\Delta G^\circ_f$  (in kJ/mol) are:  $\text{KClO}_3(\text{s}) = -296.3$ ;  $\text{KCl}(\text{s}) = -408.8$ . Note that  $\text{O}_2(\text{g})$  is the reference form of the element, so  $\Delta H^\circ_f = \Delta G^\circ_f = 0$  for it.

$$\Delta H^\circ = [2 \times (-436.7) - 2 \times (-397.7)] \text{ kJ} = \boxed{-78.0 \text{ kJ}}$$

$$\Delta G^\circ = [2 \times (-408.8) - 2 \times (-296.3)] \text{ kJ} = \boxed{-225.0 \text{ kJ}}$$

Rxn is exothermic liberating 78.0 kJ of heat  
Large  $\Delta G^\circ$  indicates equilibrium is mostly towards product side.

6. Write expressions for the "thermodynamic" equilibrium constants for each of the following reactions:

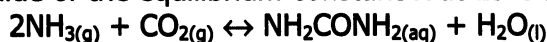


$$a. K = \frac{[\text{NH}_2\text{CONH}_2]}{P_{\text{NH}_3}^2 P_{\text{CO}_2}}$$



$$K = [\text{Ag}^+][\text{Cl}^-]$$

7. Find the value of the equilibrium constant K at 25°C (298K) for the reaction



The standard free energy change,  $\Delta G^\circ$ , at 25.0°C equals -13.6 kJ

$$\Delta G^\circ = -RT \ln K \quad \ln K = \Delta G^\circ / -RT$$

$$\ln K = \left( \frac{-13.6 \times 10^3}{-8.31 \times 298} \right) = 5.49 \quad K = e^{5.49} = 2.4 \times 10^2$$

8. Calculate the equilibrium constant  $K_{\text{sp}}$  at 25.0°C for the reaction:



using standard free energies of formation.

$$\Delta G^\circ = [(77.1 - 131.3) - (-109.8)] \text{ kJ} = 55.6 \text{ kJ} = 5.56 \times 10^4 \text{ J}$$

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{5.56 \times 10^4}{-8.31 \times 298} = -22.45 \quad K = e^{-22.45} = 2 \times 10^{-10}$$

9. a. What is  $\Delta G^\circ$  at 1,000.°C for the following reaction?



Is this reaction spontaneous at 1,000.°C and 1.00 atm?

$$\Delta H^\circ = [(-635.1 - 393.5) - (-1206.9)] \text{ kJ} = 178.3 \text{ kJ}$$

$$\Delta S^\circ = [(38.2 + 213.7) - (92.9)] \text{ J/K} = 159.0 \text{ J/K}$$

$$\Delta G^\circ_{1273} = \Delta H^\circ - T\Delta S^\circ = 178.3 \text{ kJ} - (1273 \text{ K} \times 0.1590 \text{ kJ/K}) = -24.1 \text{ kJ}$$

Should be spontaneous @ 1000°C (negative  $\Delta G^\circ$ )

b. What is the value of  $K_p$  at 1,000.°C for this reaction? What is the partial pressure of  $\text{CO}_2$ ?

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-2.41 \times 10^4}{-8.31 \times 1273} = 2.278 \quad K = K_p = e^{2.278} = 9.8$$

$$K_p = P_{\text{CO}_2} \text{ partial pressure of } \text{CO}_2 = 9.76 (9.8) \text{ atm}$$

10. To what temperature must magnesium carbonate be heated to decompose it to MgO and  $\text{CO}_2$  at 1.00 atm? Values of  $\Delta H^\circ_f$  (in kJ/mol) are:  $\text{MgO}(\text{s}) = -601.2$ ;  $\text{MgCO}_3(\text{s}) = -1111.7$ . Values of  $S^\circ$  (in J/K) are:  $\text{MgO}(\text{s}) = 26.9$ ;  $\text{MgCO}_3(\text{s}) = 65.9$



$$\Delta H^\circ = [(-393.5 + (-601.2)) - (-1111.7)] = 117 \text{ kJ} = 117,000 \text{ J}$$

$$\Delta S^\circ = [(213.7 + 26.9) - (65.9)] = 174.7 \text{ J}$$

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$0 = 117,000 \text{ J} - T(174.7 \text{ J})$$

$$T = 669.71 = 670 \text{ K}$$