

## Class Worksheet 15 Key

1. Which of the following processes are spontaneous and which are nonspontaneous:

(a) The melting of ice cubes at  $-5^{\circ}\text{C}$  and 1 atm pressure;

Non Spontaneous

(b) Dissolution of sugar in a cup of hot coffee;

Spontaneous

(c) The reaction of nitrogen atoms to form  $\text{N}_2$  molecules at  $25^{\circ}\text{C}$  and 1 atm;

Spontaneous

(d) Alignment of iron filings in a magnetic field;

Spontaneous

(e) Formation of  $\text{CH}_4$  and  $\text{O}_2$  molecules from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at room temperature and 1 atm pressure?

Non Spontaneous

2. (a) Give two examples of endothermic processes that are spontaneous.

Ammonium nitrate dissolving in water; Naphthalene subliming at room temperature.

(b) Give an example of a process that is spontaneous at one temperature but nonspontaneous at a different temperature.

Melting of a solid.

3. Consider the vaporization of liquid water to steam at a pressure of 1atm.

(a) Is the process endothermic or exothermic?

endothermic

(b) In what temperature range is it a spontaneous process?

At or above  $100^{\circ}\text{C}$

(c) In what temperature range is it a nonspontaneous process?

Below  $100^{\circ}\text{C}$

(d) At what temperature are the two phases in equilibrium?

At  $100^{\circ}\text{C}$

4. (a) What is special about a reversible reaction?

Forward and reverse changes occur by same path; there is only one reversible pathway for a set of conditions.

(b) Suppose a reversible process is reversed, restoring the system to its original state. What can be said about the surroundings after the process is reversed?

There is no net change in the surroundings

(c) Under what circumstances will the vaporization of water to steam be a reversible process?

The vaporization of water to steam is reversible if it occurs at the boiling point for a specific external pressure.

5. For the isothermal expansion of a gas into a vacuum,  $\Delta E = 0$ ,  $q = 0$ , and  $w = 0$ .

(a) Is this a spontaneous process?

Yes

(b) Explain why no work is done by the system during this process.

$$W = -P_{ext}\Delta V; P = 0, w = 0$$

(c) In thermodynamics, what is the "driving force" for the expansion of the gas?

Increase in disorder.

6. (a) What is entropy?

The disorder or randomness of a system.

(b) During a chemical process the system becomes more disordered. What is the sign of  $\Delta S$  for the process?

Positive

(c) Does  $\Delta S$  for a process depend on the path taken from the initial to the final state of the system? Explain.

No,  $\Delta S$  is a state function, so it is independent of path.

6. In a chemical reaction two moles of gaseous reactants are converted to three moles of gaseous products. What do you expect for the sign of  $\Delta S$ ?

$\Delta S$  is positive

7. How does the entropy of the system change when the following occur:

(a) a solid melts;

Increase

(b) a liquid vaporizes;

Increase

(c) a solid dissolves in water;

Increase

(d) a gas liquefies?

Decrease

8. The normal boiling point of  $\text{Br}_2(\text{l})$  is  $58.8^\circ\text{C}$  and its enthalpy of vaporization is  $\Delta H_{\text{vap}} = 29.6\text{kJ/mol}$ .

(a) When  $\text{Br}_2(\text{l})$  boils at its normal boiling point, does its entropy increase or decrease?

Increase

(b) Calculate the value of  $\Delta S$  when 1.00 mol of  $\text{Br}_2(\text{l})$  is vaporized at  $58.8^\circ\text{C}$ .

98.0J/K

9. For each of the following pairs, choose the substance with the higher entropy per mole at a given temperature:

(a)  $\text{Ar}(\text{l})$  or  $\text{Ar}(\text{g})$ ;

$\text{Ar}(\text{g})$

(b) He(g) at 3 atm pressure, or He(g) at 1.5atm pressure;

1.5 atm

(c) 1 mole of Ne(g) in 15.0L or 1 mole of Ne(g) in 1.50L;

15.0L

(d) CO<sub>2</sub>(g) or CO<sub>2</sub>(aq)

CO<sub>2</sub>(g)

10. Predict the sign of the entropy change of the system for each of the following reactions:

(a) 2SO<sub>2</sub>(g) + O<sub>2</sub>(g) → 2SO<sub>3</sub>(g)

negative

(b) Ba(OH)<sub>2</sub>(s) → BaO(s) + H<sub>2</sub>O(g)

positive

(c) CO(g) + 2H<sub>2</sub>(g) → CH<sub>3</sub>OH(l)

negative

(d) FeCl<sub>2</sub>(s) + H<sub>2</sub>(g) → Fe(s) + 2HCl(g)

Positive

11. Using S° values, calculate ΔS° values for the following reactions:

(a) C<sub>2</sub>H<sub>4</sub>(g) + H<sub>2</sub>(g) → C<sub>2</sub>H<sub>6</sub>(g)

-120.5 J/K

(b) N<sub>2</sub>O<sub>4</sub>(g) → 2NO<sub>2</sub>(g)

+176.6 J/K

(c) Be(OH)<sub>2</sub>(s) → BeO(s) + H<sub>2</sub>O(g)

+152.39 J/K

(d) 2CH<sub>3</sub>OH(g) + 3O<sub>2</sub>(g) → 2CO<sub>2</sub>(g) + 4H<sub>2</sub>O(g)

+92.3 J/K

12. For a certain reaction,  $\Delta H^\circ = -35.4 \text{ kJ}$  and  $\Delta S^\circ = -85.5 \text{ J/K}$ .

(a) Is the reaction exothermic or endothermic?

Exothermic

(b) Does the reaction lead to an increase or decrease in the disorder of the system?

Decrease

(c) Calculate  $\Delta G^\circ$  for the reaction at 298K.

-9.9kJ

(d) Is the reaction spontaneous at 298K?

Spontaneous

13. Using thermodynamic tables, calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  at 298K for each of the following reactions. In each case show that  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .

(a)  $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{HF}(\text{g})$

$\Delta G^\circ = -541.40 \text{ kJ}$

(b)  $\text{C}(\text{s, graphite}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g})$

$\Delta G^\circ = -64.0 \text{ kJ}$

(c)  $2\text{PCl}_3(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{POCl}_3(\text{g})$

$\Delta G^\circ = -465.8 \text{ kJ}$

(d)  $2\text{CH}_3\text{OH}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

$\Delta G^\circ = 166.2 \text{ kJ}$

14. Using thermodynamic tables, calculate  $\Delta G^\circ$ . For the following reactions. Indicate whether each reaction is spontaneous.

(a)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

-140 kJ

(b)  $\text{NO}_2(\text{g}) + \text{N}_2\text{O}(\text{g}) \rightarrow 3\text{NO}(\text{g})$

+104.7 kJ

(c)  $6\text{Cl}_2(\text{g}) + 2\text{Fe}_2\text{O}_3(\text{s}) \rightarrow 4\text{FeCl}_3(\text{s}) + 3\text{O}_2(\text{g})$

+146 kJ

(d)  $\text{SO}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{S}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$

-156.7 kJ

15. A particular reaction is spontaneous at 450K. The reaction is endothermic by 34.5kJ. What can you conclude about the sign and magnitude of  $\Delta S$  for this reaction?

$$\Delta S > +76.7 \text{ J/K}$$

16. For a particular reaction,  $\Delta H = -32\text{kJ}$  and  $\Delta S = -98\text{J/K}$ . Assume that  $\Delta H$  and  $\Delta S$  do not vary with temperature.

- (a) At what temperature will  $\Delta G = 0$ ?

$$330\text{K}$$

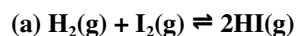
- (b) If T is increased from that in part (a), will the reaction be spontaneous or nonspontaneous?

Spontaneous

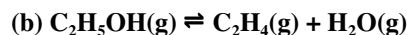
17. For the reaction between nitrogen dioxide and nitrous oxide to form nitric oxide, use thermodynamic data to predict how  $\Delta G^\circ$  varies with increasing temperature.

$\Delta G^\circ$  becomes more negative with increasing temperature.

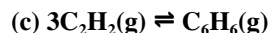
18. Use thermodynamic data to calculate  $K_p$  at 298K for each of the following reaction:



$$870$$



$$0.04$$



$$2 \times 10^{87}$$

19. By using thermodynamic data, calculate the equilibrium pressure of  $\text{CO}_2$  in the decarboxylation of barium carbonate to form barium oxide and carbon dioxide at:

- (a) 298K;

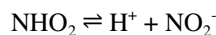
$$6.0 \times 10^{-39} \text{ atm}$$

- (b) 1100K.

$$1.6 \times 10^{-4} \text{ atm}$$

20. The value of  $K_a$  for nitrous acid,  $\text{HNO}_2$ , at  $25^\circ\text{C}$  is  $4.5 \times 10^{-4}$ .

- (a) Write the equilibrium that corresponds to  $K_a$ .



- (b) Use the value of  $K_a$  to calculate  $\Delta G^\circ$  for the dissociation of nitrous acid.

$$19.1 \text{ kJ}$$

- (c) What is the value of  $\Delta G$  at equilibrium?

zero

- (d) What is the value of  $\Delta G$  when  $[\text{H}^+] = 0.05\text{M}$ ,  $[\text{NO}_2^-] = 6.0 \times 10^{-4}\text{M}$ , and  $[\text{HNO}_2] = 0.20\text{M}$ ?

$$-2.72 \text{ kJ}$$