Spontaneity and Entropy DCI

Name ______________________________ Section ______

1. Entropy (S) is a second driving force for chemical reactions. Define the word entropy. How is the sign of ΔS for a chemical reaction interpreted?
   Entropy is a measure of the randomness of a chemical system. Randomness is measure in terms of the number of possible positions matter has in a chemical system, and the number of energy states the matter has. The greater the number of possible states in position and energy (number of microstates) the higher/greater the entropy. In a chemical or physical change a positive ΔS means the products are more random, have a greater number of microstates compared to the reactants. If ΔS is negative than the products are less random, have fewer number of microstates compared to the reactants.

2. Predict which of the following thermodynamically favored reactions have an increase in entropy of the system.

a) $H_2O(l) \rightarrow H_2O(g)$ at 25 ˚C +ΔS

The products have a greater number of positional microstates possible because gases are mostly empty space and the gas particles can occupy any of the available positions. In the liquid phase, while the molecules are mobile, the phase is condensed so there is considerably less empty space so there are many fewer positional microstates.

b) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$ –ΔS

The products phase is solid and the reactants are a solid and a gas. So the reactants are less ordered compared to the products. Gases have high entropies because the particles are well separated in space, so there are many more microstates possible. Also there are fewer numbers of product particles compared to the reactants. When there are fewer moles of products there are fewer arrangements/microstates possible. So both the phase change and the number of particles point to a more ordered products compared to reactants.

c) $Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 2NH_3(g) + 10H_2O(l)$ +ΔS

The product phases are aqueous solution, a gas and a liquid and the reactants are both solids. The reactants are more ordered compared to the products. Gases have high entropies because the particles are well separated in space, so there are many more microstates possible. In general a substance dissolved in water with have more disorder compared to a solid phase. In solution ions are hydrated, and are able to distribute throughout the solution. There are 13 moles of product compared to 3 moles of reactants, so there are many more substances that the atoms can be distributed between. When there are more moles of products there are larger arrangements/microstates possible. So

both the phase change and the number of particles point to a more disordered products compared to reactants.

d) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ or (g) $-\Delta S$

The products phase is a liquid and a gas and the reactants are a both gases. So the reactants are more disordered compared to the products. Gases have high entropies because the particles are well separated in space, so there are many more microstates possible. Liquids are much more ordered as a condensed phase. There are fewer positions particles can occupy in the liquid phase compared to the gaseous phase. There are equal numbers of product particles and reactants. So the phase change points to a more ordered products compared to reactants.

e) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $-\Delta S$

The products phase is a liquid and a gas and the reactants are a both gases. So the reactants are more disordered compared to the products. Gases have high entropies because the particles are well separated in space, so there are many more microstates possible. Liquids are much more ordered as a condensed phase. There are fewer positions particles can occupy in the liquid phase compared to the gaseous phase. There are equal numbers of product particles and reactants. So the phase change points to a more ordered products compared to reactants.

f) $Al(s) + \frac{3}{2}Br_2(l) \rightarrow AlBr_3(s)$ $-\Delta S$

The products phase is solid and the reactants are a solid and a liquid. So the reactants are less ordered compared to the products. Liquids are more disordered compared to solids as a condensed phase. In the liquid phase particles are able to move very close to each other, and occupy more positions compared to solids where the particles are static and cannot move. Also there is a wider range of energies for liquids compared to solids. Also there are fewer numbers of product particles compared to the reactants. When there are fewer moles of products there are fewer arrangements/microstates possible. So both the phase change and the number of particles point to a more ordered products compared to reactants.

3. A table of absolute entropies (S°) for selected substances is at the end of this DCI. Identify differences between $\Delta S°$ and $\Delta H°_f$ as thermodynamic values.

   The entropy values are positive, while the enthalpy of formation values are positive and negative. The entropy values for the solids are the lowest and the entropy values for gases are the highest. For enthalpy of formations the same substance in different phases the trend is to become more positive from solid, to liquid to gas.

4. Write the mathematical equation that relates the standard entropy change in a chemical reaction to the absolute entropy of the reactants and products.

$\Delta S^\circ_{rxn} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$

5. Calculate the change in entropy (ΔS°_{rxn}) for the chemical reactions in question 2.

a) $H_2O(l) \rightarrow H_2O(g)$ **ΔS° is positive**

$\Delta S^\circ_{rxn} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$
$\Delta S^\circ_{rxn} = S^\circ(H_2O(l)) - S^\circ(H_2O(s))$
$\Delta S^\circ_{rxn} = 189\ \text{J mol}^{-1}\ \text{K}^{-1} - 70\ \text{J mol}^{-1}\ \text{K}^{-1} = +119\ \text{J mol}^{-1}\ \text{K}^{-1}$

b) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$ **ΔS° is negative**

$\Delta S^\circ_{rxn} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$
$\Delta S^\circ_{rxn} = 2S^\circ(MgO(s)) - [2S^\circ(Mg(s)) + S^\circ(O_2(g))]$
$\Delta S^\circ_{rxn} = 2\cdot 26.9\ \text{J mol}^{-1}\ \text{K}^{-1} - [2\cdot 33\ \text{J mol}^{-1}\ \text{K}^{-1} + 205\ \text{J mol}^{-1}\ \text{K}^{-1}] = -217\ \text{J mol}^{-1}\ \text{K}^{-1}$

c) $Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 2NH_3(g) + 10H_2O(l)$
ΔS° is positive

$\Delta S^\circ_{rxn} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$
$\Delta S^\circ_{rxn} = [S^\circ(BaCl_2(aq)) + 2S^\circ(NH_3(g)) + 10S^\circ(H_2O(l))] - [S^\circ(Ba(OH)_2 \cdot 8H_2O(s)) - 2S^\circ(NH_4Cl(g))]$
$\Delta S^\circ_{rxn} = 123\ \text{J mol}^{-1}\ \text{K}^{-1} + 2\cdot 193\ \text{J mol}^{-1}\ \text{K}^{-1} + 10\cdot 70\ \text{J mol}^{-1}\ \text{K}^{-1} - [427\ \text{J mol}^{-1}\ \text{K}^{-1} + 2\cdot 95\ \text{J mol}^{-1}\ \text{K}^{-1}] = +592\ \text{J mol}^{-1}\ \text{K}^{-1}$

d) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ **ΔS° is negative**

$\Delta S^\circ_{rxn} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$
$\Delta S^\circ_{rxn} = -164\ \text{J mol}^{-1}\ \text{K}^{-1}$

e) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ **ΔS° is negative**

$\Delta S^\circ_{rxn} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$
$\Delta S^\circ_{rxn} = -242\ \text{J mol}^{-1}\ \text{K}^{-1}$

f) $Al(s) + \frac{3}{2}Br_2(l) \rightarrow AlBr_3(s)$ **ΔS° is negative**

$\Delta S^\circ_{rxn} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$
$\Delta S^\circ_{rxn} = -72.6\ \text{J mol}^{-1}\ \text{K}^{-1}$

6. The natural tendency for spontaneous chemical reactions is to increase entropy. Is the entropy an absolute predictor of spontaneity? Defend your answer.

   The entropy of a chemical reaction is not an absolute predictor of the spontaneity of a chemical reaction. In Q5 note that all reactions are spontaneous, however there are some reactions with a negative ΔS and some reactions with a positive ΔS.

7. Predict whether the entropy of the system increases, remains constant or decreases when the following processes occur. Explain your reasoning.

a. Ice melts at 0 ˚C.
$H_2O(s) \rightarrow H_2O(l)$
Liquids are more disordered compared to solids as a condensed phase. In the liquid phase particles are able to move very close to each other, and occupy more positions compared to solids where the particles are static and cannot move. Also there are a wider range of energies for liquids compared to solids. ΔS is positive.

b. A precipitate forms in aqueous solution.
$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
Ions dissolved in water are mobile, therefore they can occupy many more positions compared to the ions in the solid phase. In the solid phase ions are static, so there is effectively one positional microstate. The products are less random compared to the reactants and ΔS is negative.

c. A solid dissolves in water.
$C_6H_{12}O_6(s) \rightarrow C_6H_{12}O_6(aq)$ **A covalent solid like glucose dissolves in water the molecules are more mobile and can move around in the solution. In the solid phase the molecules of glucose are static, there is only one positional microstate compared to the many positional microstates available to a hydrated glucose molecule. ΔS is positive.**

d. A gas condenses to a liquid.
$N_2(g) \rightarrow N_2(l)$ **gases are mostly empty space and the gas particles can occupy any of the available positions. In the liquid phase, while the molecules are mobile, the phase is condensed so there is considerably less empty space so there are many fewer positional microstates. ΔS is negative.**

Substance and State	ΔH°_f (kJ/mol)	Substance and State	ΔH°_f (kJ/mol)
C(*s*) (graphite)	0	HCl(*g*)	-92.3
C(*s*) (diamond)	2	HBr(*g*)	-36.4
CO(*g*)	-110.5	HI(*g*)	26.5
CO_2(*g*)	–393.5	I_2(*g*)	62.25
CH_4(*g*)	–75	O_2(*g*)	0
CH_3OH(*g*)	-201	O(*g*)	249
CH_3OH(*l*)	-239	O_3(*g*)	143
H_2CO(*g*)	-116		
CCl_4(*l*)	-135.4	N_2(*g*)	0
HCOOH(*g*)	-363	NH_3(*g*)	-46
HCN(*g*)	135.1	NH_3(*aq*)	-80
CS_2(*g*)	117.4	NH_4^+(*aq*)	-132
CS_2(*l*)	89.7	NH_4Cl(*s*)	-314.4
C_2H_2(*g*)	227	N_2H_4(*l*)	50.6
C_2H_4(*g*)	52	NO(*g*)	90.25
CH_3CHO(*g*)	-166	NO_2(*g*)	33.18
C_2H_5OH(*l*)	-278	N_2O(*g*)	82.0
$C_2H_5O_2N$(*g*)	-533	N_2O_4(*g*)	9.16
C_2H_6(*g*)	-84.7	N_2O_4(*l*)	20
C_3H_6(*g*)	20.9	HNO_3(*aq*)	-207.36
C_3H_8(*g*)	-104	HNO_3(*l*)	-174.10
C_4H_{10}(*g*)	-126	NH_4ClO_4(*s*)	-295
C_8H_{18}(*l*)	-208		
$CH_2 = CHCN$(*l*)	152		
CH_3COOH(*l*)	-484	S_2Cl_2(*g*)	-18
$C_6H_{12}O_6$(*s*)	-1275	SO_2(*g*)	-296.83
		H_2S(*g*)	-20.6
Cl_2(*g*)	0	$SOCl_2$(*g*)	-213
Cl_2(*aq*)	-23		
Cl^-(*aq*)	-167.5	$SiCl_4$(*g*)	-657
		SiO_2(*s*)	-910.94
		SiF_4(*g*)	-1614.9
H_2(*g*)	0		
H(*g*)	217	$Ba(OH)_2 \cdot 8H_2O$(*s*)	-3342
H^+(*aq*)	0	$BaCl_2$(*aq*)	-872
OH^-(*aq*)	-230	$AlBr_3$(*s*)	-526
H_2O(*l*)	-286		
H_2O(*g*)	-242	ZnS(*s*)	-206

Thermodynamic Values (25°C)

Substance and State	$\Delta H^0{}_f$ $\left(\frac{kJ}{mol}\right)$	$\Delta G^0{}_f$ $\left(\frac{kJ}{mol}\right)$	S^0 $\left(\frac{J}{K \bullet mol}\right)$	Substance and State	$\Delta H^0{}_f$ $\left(\frac{kJ}{mol}\right)$	$\Delta G^0{}_f$ $\left(\frac{kJ}{mol}\right)$	S^0 $\left(\frac{J}{K \bullet mol}\right)$
Aluminum				**Iodine**			
$AlBr_3(g)$	−526.3	−505	184	$I_2(s)$	0	0	116.7
$Al(s)$	0	0	28.32	$I_2(g)$	62.25	19.37	260.57
				$HI(g)$	25.94	1.30	206.3
Barium							
$BaCl_2(aq)$	−872	−823	123	**Magnesium**			
$Ba(OH)_2{\cdot}8H_2O(s)$	−3342	−2793	427	$Mg(s)$	0	0	33
				$Mg^{2+}(aq)$	−492	−456	−118
Bromine				$MgO(s)$	−601	−569	26.9
$Br_2(l)$	0	0	152.231				
$BrCl(g)$	14.64	−0.96	239.99	**Oxygen**			
				$O_2(g)$	0	0	205
Carbon				$O(g)$	249	232	161
$C(s)$ (graphite)	0	0	6	$O_3(g)$	143	163	239
$C(s)$ (diamond)	2	3	2				
$CO(g)$	−110.5	−137	198	**Nitrogen**			
$CO_2(g)$	−393.5	−394	214	$N_2(g)$	0	0	192
$CH_4(g)$	−75	−51	186	$NCl_3(g)$	230	271	−137
$CH_3OH(g)$	−201	−163	240	$NF_3(g)$	−125	−83.6	−139
$CH_3OH(l)$	−239	−166	127	$NH_3(g)$	−46	−17	193
$H_2CO(g)$	−116	−110	219	$NH_3(aq)$	−80	−27	111
$HCOOH(g)$	−363	−351	249	$NH_2CONH_2(aq)$	?	?	174
$HCN(g)$	135.1	125	202	$NO(g)$	90	87	211
$C_2H_2(g)$	227	209	201	$NO_2(g)$	34	52	240
$C_2H_4(g)$	52	68	219	$N_2O(g)$	82	104	220
$CH_3CHO(g)$	−166	−129	250	$N_2O_4(g)$	10	98	304
$C_2H_5OH(l)$	−278	−175	161	$N_2O_5(g)$	$^{-}$42	134	178
$C_2H_6(g)$	−84.7	−32.9	229.5	$N_2H_3CH_3(l)$	54	180	166
$C_3H_6(g)$	20.9	62.7	266.9	$HNO_3(aq)$	−207	−111	146
$C_3H_8(g)$	−104	−24	270	$HNO_3(l)$	−174	−81	156
				$NH_4Cl(s)$	−314	−201	95
Chlorine				$NH_4ClO_4(s)$	−295	−89	186
$Cl_2(g)$	0	0	222.957				
$Cl_2(aq)$	−23	7	121	**Silver**			
$Cl^-(aq)$	−167	−131	57	$Ag(s)$	0	0	42.6
$HCl(g)$	−92	−95	187	$Ag^+(aq)$	105.6	77.1	72.7
				$AgBr(s)$	−100.4	−96.9	107.1
Fluorine				$AgCl_3(s)$	−127.1	−109.8	96.2
$F_2(g)$	0	0	203				
$F^-(aq)$	−333	−279	−14	**Sulfur**			
$HF(g)$	−271	−273	174	S(rhombic)	0	0	31.8
				S(monocl)	0.3	0.1	32.6
Hydrogen				$SO_2(g)$	−296.8	−300.2	248.8
$H_2(g)$	0	0	131	$SO_3(g)$	−395.7	−371.1	256.3
$H(g)$	217	203	115	$H_2S(g)$	−20.17	−33.0	205.6
$H^+(aq)$	0	0	0				
$OH^-(aq)$	−230	−157	−11	**Titanium**			
$H_2O(l)$	−286	−237	70	$TiCl_4(g)$	−763	−727	355
$H_2O(g)$	−242	−229	189	$TiO_2(s)$	−945	−890	50