Spring 2009

2. The reaction of an elemental halogen with an alkane is a very common reaction. The reaction between chlorine and butane is provided below. (NOTE: Questions a – d and f pertain to this reaction.)

$$C_4H_{10}(g) + 2Cl_2(g) \rightarrow C_4H_8Cl_2(l) + 2HCl(g)$$

a) Calculate ΔH°_{rxn} for the reaction above. (8 points)

	$C_4H_{10}(g)$	$2Cl_2(g)$	$C_4H_8Cl_2(l)$	$2HCl(g)$
$\Delta H^\circ_f \left(\frac{kJ}{mol}\right)$	**–125**	**0**	**-229**	**-92**

$$\mathbf{\Delta H^\circ_{rxn} = \Sigma \Delta H^\circ_f \text{ (products)} - \Sigma \Delta H^\circ_f \text{ (reactants)}}$$

$$\mathbf{= [\Delta H^\circ_f (C_4H_8Cl_2(l)) + 2\Delta H^\circ_f (HCl(g))] - [\Delta H^\circ_f (C_4H_{10}(g)) + 2\Delta H^\circ_f (2Cl_2(g))]}$$

$$\mathbf{= [(-229\ kJ\ mol^{-1}) + 2(-92\ kJ\ mol^{-1})] - [(-125\ kJ\ mol^{-1}) + 2(0\ kJ\ mol^{-1})]}$$

$$\mathbf{= -2.88 \times 10^2\ kJ\ mol^{-1}}$$

b) Predict the sign of ΔS°_{rxn} for the reaction above. Provide an explanation to support the sign of ΔS°_{rxn}. (5 points)

ΔS°_{rxn} is negative for the reaction. Three moles of gas in the reactants form two moles of gas and one mole of liquid in the products. Liquids occupy a much smaller volume compared to gases. Gases are composed of mostly empty space so there are many more positional microstates compared to liquids, which have very empty space so there are few positional microstates. So in the reaction there are fewer microstates in the products compared to the reactants so ΔS° is negative.

c) Which factor, the change in enthalpy, ΔH°, or the change in entropy, ΔS°, provides the principal driving force for the reaction at 298 K? Explain. (6 points)

In this reaction both ΔH° and ΔS° are negative. ΔS° does not favor spontaneity in the reaction, while ΔH° does. So ΔH° favors spontaneity and is the driving force in the reaction.
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
spontaneous reactions have ΔG° that are negative. According to the above equation a ΔH° that is negative and a ΔS° that is positive favor ΔG° that is negative.

d) For the reaction, how is the value of the standard free energy, ΔG°, and the spontaneity of the reaction affected by an increase in temperature? You may wish to use a mathematical relationship to help in your explanation. (6 points)

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

In the reaction ΔS° is negative, so as T increases $T\Delta S^\circ$ becomes more negative and when subtracted from a negative ΔH° makes ΔG° more positive. The reaction become less spontaneous with increasing temperature.

(15) 1. Given the reaction

$$CO_{2(g)} + 2NH_{3(g)} \rightarrow 2\ CO(NH_2)_{2(s)} + H_2O_{(l)} \quad \Delta H^\circ = -134\ kJ\ mol^{-1}$$

a) For the reaction, indicate whether the standard entropy change, ΔS°, is positive, negative or zero. Support your response with a brief explanation. (5)

ΔS° is negative in this reaction. Three moles of gases in the reactants are forming two moles of solid and one mole of gas. Gases are primarily empty space and have a large number of microstates, while solids and liquids have very little empty space so there are very few microstates.

b) Which factor, the change in enthalpy, ΔH°, or the change in entropy, ΔS°, provides the principal driving force for the reaction at 298 K. Explain. (5)

In this reaction both ΔH° and ΔS° are negative. ΔS° does not favor spontaneity in the reaction, while ΔH° does. So ΔH° favors spontaneity and is the driving force in the reaction.
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
spontaneous reactions have ΔG° that are negative. According to the above equation a ΔH° that is negative and a ΔS° that is positive favor ΔG° that is negative.

c) For the reaction, how is the value of the standard free energy change, ΔG° affected by an increase in temperature? Explain. (5)

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

In the reaction ΔS° is negative, so as T increases $T\Delta S^\circ$ becomes more negative and when subtracted from a negative ΔH° makes ΔG° more positive. The reaction become less spontaneous with increasing temperature.

(30) 3. Carbon monoxide can be converted to carbon dioxide according to the following equation;

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

a) Calculate ΔH° for the reaction above at 25 °C. (6 points)

$$2CO(g) \; + \; O_2(g) \; \rightarrow \; 2CO_2(g)$$

$$\Delta H_f^\circ \left(\frac{kJ}{mol}\right) \quad -110.5 \quad 0 \quad -393.5$$

$$\Delta H_{rxn}^\circ = \Sigma \Delta H_f^\circ \text{ (products)} - \Sigma \Delta H_f^\circ \text{ (reactants)}$$

$$= [2\Delta H_f^\circ (CO_{2}(g))] - [2\Delta H_f^\circ (CO(g)) + \Delta H_f^\circ (O_{2}(g))]$$

$$= [2(-393.5 \text{ kJ mol}^{-1})] - [2(-110.5 \text{ kJ mol}^{-1}) + (0 \text{ kJ mol}^{-1})]$$

$$= -5.66 \times 10^2 \text{ kJ mol}^{-1}$$

b) Calculate ΔS° for the reaction at 25 °C. (6 points)

$$2CO(g) \; + \; O_2(g) \; \rightarrow \; 2CO_2(g)$$

$$S^\circ \left(\frac{J}{K \cdot mol}\right) \quad 198 \quad 205 \quad 214$$

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

$$= 2S^\circ(CO_{2}(g)) - [2S^\circ(CO(g)) + S^\circ(O_{2}(g))]$$

$$= [2(214 \frac{J}{K\ mol})] - [2(198 \frac{J}{K\ mol}) + 205 \frac{J}{K\ mol}] = -173 \text{ J/K mol}$$

c) Calculate ΔG° for the reaction at 25 °C. (6 points)

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

$$= -5.66 \times 10^2 \text{ kJ mol}^{-1} - 298 \text{ K} \cdot (-173 \text{ J/K mol}) \left(\frac{kJ}{1000 \text{ J}}\right)$$

$$= -5.66 \times 10^2 \text{ kJ mol}^{-1} + 51.6 \text{ kJ mol}^{-1}$$

$$= -5.14 \times 10^2 \text{ kJ mol}^{-1}$$

d) Which factor, the change in enthalpy, ΔH°, or the change in entropy, ΔS°, provides the principal driving force for the reaction at 298 K? Explain. (6 points)

e) For the reaction, how is the value of the standard free energy, ΔG°, affected by an increase in temperature? Explain using a mathematical explanation. (6 points)

(10) 6. Short answer

a)

i) Write the formation reaction for $H_2O(l)$ and for $H_2O(g)$ (4 points)

ii) Predict the sign of ΔS for each formation reaction? (2 points)

iii) Is the magnitude of ΔS the same or different (is one value more positive or more negative compared to the other) for the two formation reactions? Explain. (4 points)

(16) 1.

$$Cl_{2(g)} + 3\ F_{2(g)} \rightarrow 2\ ClF_{3(g)}$$

ClF_3 can be prepared by the reaction represented by the equation above. For ClF_3 the standard enthalpy of formation, ΔH_f°, is -163.2 kJ mol^{-1} and the standard free energy of formation, ΔG_f°, is -123.0 kJ mol^{-1}.

(a) Calculate the standard entropy change, ΔS°, for the reaction at 298K.

(b) Does the sign of ΔS° that you calculated in part a) make sense in terms of the balanced chemical equation? Explain.

(c) If ClF_3 were produced as a liquid rather than as a gas, how would the sign and the magnitude of ΔS for the reaction be affected? Explain.

(d) At 298K the absolute entropies of $Cl_{2(g)}$ and $ClF_{3(g)}$ are 222.96 J mol^{-1} K^{-1} and 281.50 J mol^{-1} K^{-1}, respectively.

(i) Account for the larger entropy of $ClF_{3(g)}$ relative to that of $Cl_{2(g)}$.

(ii) Calculate the value of the absolute entropy of $F_{2(g)}$ at 298K.

8. When solid sodium carbonate reacts with aqueous acetic acid bubbles are formed and the container becomes cool to the touch. Which of the following statements best describes what has happened in this system?

(A) ΔG, ΔH and ΔS are all positive;
(B) ΔG and ΔH are negative, but ΔS is positive;

(C) ΔG, ΔH and ΔS are all negative;
(D) ΔS and ΔH are both positive and ΔG is negative;
(E) ΔS and ΔG are both negative and ΔH is positive;

4. Which of the following is an endothermic reaction?

(A) $6CO_2(g) + 6H_2O(g) \rightarrow 2C_3H_6(g) + 9O_2(g)$

(B) $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

(C) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

(D) $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

(E) $H_2O(g) \rightarrow H_2O(l)$

7. Solid mercury(II) oxide must be heated to decompose to elemental mercury and oxygen. Which of the following statements best describes what has happened in this system?

(A) ΔG, ΔH and ΔS are all positive;
(B) ΔG and ΔH are negative, but ΔS is positive;

(C) ΔG, ΔH and ΔS are all negative;
(D) ΔS and ΔH are both positive and ΔG is negative;
(E) ΔS and ΔG are both negative and ΔH is positive;

18. Which of the following reactions is a formation reaction?

(A) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$
(B) $2\ NH_4Cl(s) \rightarrow N_2(g) + 4\ H_2(g) + Cl_2(g)$
(C) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
(D) $Cl_2(g) + 1/2\ O_2(g) \rightarrow Cl_2O(g)$
(E) $Cl_2(g) \rightarrow 2\ Cl(g)$

5. Hydrogen gas reacts with oxygen gas to form liquid water. The container becomes hot to the touch. Which of the following statements best describes what has happened in this system?

(A) ΔG, ΔH and ΔS are all positive;
(B) ΔG and ΔH are negative, but ΔS is positive;

(C) ΔG, ΔH and ΔS are all negative;
(D) ΔS and ΔH are both positive and ΔG is negative;
(E) ΔS and ΔG are both negative and ΔH is positive;

6. ΔG°_{rxn} for the combustion of 1 mol of ethane is

(A) –32.4 kJ mol^{-1}
(B) –598 kJ mol^{-1}
(C) –733 kJ mol^{-1}
(D) –1466 kJ mol^{-1}
(E) –2932 kJ mol^{-1}

Thermodynamic Values (25 ˚C)

Substance and State	ΔH^o_f $\left(\frac{kJ}{mol}\right)$	ΔG^o_f $\left(\frac{kJ}{mol}\right)$	S^o $\left(\frac{J}{K \cdot mol}\right)$
Carbon			
$C(s)$ (graphite)	0	0	6
$C(s)$ (diamond)	2	3	2
$CO(g)$	-110.5		198
$CO_2(g)$	-393.5		214
$CH_4(g)$	?	-51	186
$CH_3OH(g)$	-201	-163	240
$CH_3OH(l)$	-239	-166	127
$CH_3Cl(g)$	-80.8	-57.4	234
$CHCl_3(g)$	-100.8		
$CHCl_3(l)$	-131.8		
$H_2CO(g)$	-116	-110	219
$HCOOH(g)$	-363	-351	249
$HCN(g)$	135.1	125	202
$C_2H_2(g)$	227	209	201
$C_2H_4(g)$	52	68	219
$CH_3CHO(g)$	-166	-129	250
$C_2H_5OH(l)$	-278	-175	161
$C_2H_6(g)$	-84.7	-32.9	229.5
$C_3H_6(g)$	20.9	62.7	266.9
$C_3H_8(g)$	-104	-24	270
$C_4H_{10}(g)$	-125	-16.7	310
$C_4H_8Cl_2(l)$	-229		
Bromine			
$Br_2(l)$	0	0	152.
$BrCl(g)$	14.64	-0.96	240
Chlorine			
$Cl_2(g)$	0	0	223
$Cl_2(aq)$	-23	7	121
$Cl^-(aq)$	-167	-131	57
$HCl(g)$	-92	-95	187
Fluorine			
$F_2(g)$	0	0	
$F^-(aq)$	-333	-279	-14
$HF(g)$	-271	-273	174
Hydrogen			
$H_2(g)$	0	0	131
$H(g)$ 217	203	115	
$H^+(aq)$	0	0	0
$OH^-(aq)$	-230	-157	-11
$H_2O(l)$			
$H_2O(g)$	-242	-229	189
Magnesium			
Mg(s)	0	0	33
Mg(aq)	-492	-456	-118
MgO(s)	-601	-569	26.9

Substance and State	ΔH^o_f $\left(\frac{kJ}{mol}\right)$	ΔG^o_f $\left(\frac{kJ}{mol}\right)$	S^o $\left(\frac{J}{K \cdot mol}\right)$
Oxygen			
$O_2(g)$	0	0	205
$O(g)$ 249	232	161	
$O_3(g)$	143	163	239
Nitrogen			
$N_2(g)$	0	0	192
$NCl_3(g)$	230	271	-137
$NF_3(g)$	-125	-83.6	-139
$NH_3(g)$	?	-17	193
$NH_3(aq)$	?	-27	111
NH_2CONH_2(aq)	?	?	174
$NO(g)$	90	87	211
$NO_2(g)$	32	52	240
$N_2O(g)$	82	104	220
$N_2O_4(g)$	10	98	304
$N_2O_5(g)$	-42	134	178
$HNO_3(aq)$	-207	-111	146
$HNO_3(l)$	-174	-81	156
NH_4Cl(s)	-314	-201	95
$NH_4ClO_4(s)$	-295	-89	186
Silver			
$Ag(s)$	0	0	42.6
$Ag^+(aq)$	105.6	77.1	72.7
$Ag(S_2O_3)^{3-}(aq)$	-1285.7	--	--
AgBr(s)	-100.4	-96.9	107.1
AgCl(s)	-127.1	-109.8	96.2
Sulfur			
S(rhombic)	0	0	31.8
SO_2(g)	-296.8	-300.2	248.8
SO_3(g)	-395.7	-371.1	256.3
H_2S(g)	-20.17	-33.0	205.6
Phosphorus			
$P_4(s)$	0	0	41.1
$PCl_5(g)$	-375	-305	365
Aluminum			
$AlCl_3(s)$	-526	-505	184
Barium			
$BaCl_2(aq)$	-872	-823	123
$Ba(OH)_2 \cdot 8H_2O(s)$	-3342	-2793	427
Iodine			
$I_2(s)$	0	0	116.7
$HI(g)$	25.94	1.30	206.3