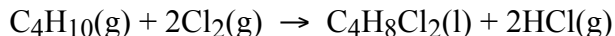


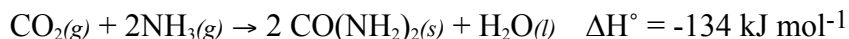
Spring 2009

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.)



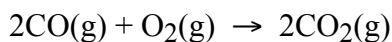
- a) Calculate  $\Delta H^\circ_{\text{rxn}}$  for the reaction above. (8 points)
- b) Predict the sign of  $\Delta S^\circ_{\text{rxn}}$  for the reaction above. Provide an explanation to support the sign of  $\Delta S^\circ_{\text{rxn}}$ . (5 points)
- c) Which factor, the change in enthalpy,  $\Delta H^\circ$ , or the change in entropy,  $\Delta S^\circ$ , provides the principal driving force for the reaction at 298 K? Explain. (6 points)
- d) For the reaction, how is the value of the standard free energy,  $\Delta G^\circ$ , 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)

(15) 1. Given the reaction



- a) For the reaction, indicate whether the standard entropy change,  $\Delta S^\circ$ , is positive, negative or zero. Support your response with a brief explanation. (5)
- b) Which factor, the change in enthalpy,  $\Delta H^\circ$ , or the change in entropy,  $\Delta S^\circ$ , provides the principal driving force for the reaction at 298 K. Explain. (5)
- c) For the reaction, how is the value of the standard free energy change,  $\Delta G^\circ$  affected by an increase in temperature? Explain. (5)

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



- a) Calculate  $\Delta H^\circ$  for the reaction above at 25 °C. (6 points)

b) Calculate  $\Delta S^\circ$  for the reaction at 25 °C. (6 points)

c) Calculate  $\Delta G^\circ$  for the reaction at 25 °C. (6 points)

d) Which factor, the change in enthalpy,  $\Delta H^\circ$ , or the change in entropy,  $\Delta S^\circ$ , 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,  $\Delta G^\circ$ , affected by an increase in temperature? Explain using a mathematical explanation. (6 points)

(10) 6. Short answer

a)

i) Write the formation reaction for  $\text{H}_2\text{O}(\text{l})$  and for  $\text{H}_2\text{O}(\text{g})$  (4 points)

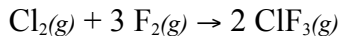
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ii) Predict the sign of  $\Delta S$  for each formation reaction? (2 points)

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iii) Is the magnitude of  $\Delta S$  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.



$\text{ClF}_3$  can be prepared by the reaction represented by the equation above. For  $\text{ClF}_3$  the standard enthalpy of formation,  $\Delta H_f^\circ$ , is  $-163.2 \text{ kJ mol}^{-1}$  and the standard free energy of formation,  $\Delta G_f^\circ$ , is  $-123.0 \text{ kJ mol}^{-1}$ .

(a) Calculate the standard entropy change,  $\Delta S^\circ$ , for the reaction at 298K.

(b) Does the sign of  $\Delta S^\circ$  that you calculated in part a) make sense in terms of the balanced chemical equation? Explain.

- (c) If  $\text{ClF}_3$  were produced as a liquid rather than as a gas, how would the sign and the magnitude of  $\Delta S$  for the reaction be affected? Explain.
- (d) At 298K the absolute entropies of  $\text{Cl}_2(g)$  and  $\text{ClF}_3(g)$  are  $222.96 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $281.50 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively.
- (i) Account for the larger entropy of  $\text{ClF}_3(g)$  relative to that of  $\text{Cl}_2(g)$ .
- (ii) Calculate the value of the absolute entropy of  $\text{F}_2(g)$  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)  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are all positive;
- (B)  $\Delta G$  and  $\Delta H$  are negative, but  $\Delta S$  is positive;
- (C)  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are all negative;
- (D)  $\Delta S$  and  $\Delta H$  are both positive and  $\Delta G$  is negative;
- (E)  $\Delta S$  and  $\Delta G$  are both negative and  $\Delta H$  is positive;

4. Which of the following is an endothermic reaction?

- (A)  $6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{C}_3\text{H}_6(\text{g}) + 9\text{O}_2(\text{g})$
- (B)  $4\text{Al}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Al}_2\text{O}_3(\text{s})$
- (C)  $\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$
- (D)  $\text{H}_2\text{SO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
- (E)  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$

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)  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are all positive;
- (B)  $\Delta G$  and  $\Delta H$  are negative, but  $\Delta S$  is positive;
- (C)  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are all negative;
- (D)  $\Delta S$  and  $\Delta H$  are both positive and  $\Delta G$  is negative;
- (E)  $\Delta S$  and  $\Delta G$  are both negative and  $\Delta H$  is positive;

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

- (A)  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
- (B)  $2\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{N}_2(\text{g}) + 4\text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$
- (C)  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
- (D)  $\text{Cl}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Cl}_2\text{O}(\text{g})$
- (E)  $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$

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)  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are all positive;
- (B)  $\Delta G$  and  $\Delta H$  are negative, but  $\Delta S$  is positive;
- (C)  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are all negative;
- (D)  $\Delta S$  and  $\Delta H$  are both positive and  $\Delta G$  is negative;
- (E)  $\Delta S$  and  $\Delta G$  are both negative and  $\Delta H$  is positive;

6.  $\Delta G^\circ_{\text{rxn}}$  for the combustion of 1 mol of ethane is

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

## Thermodynamic Values (25 °C)

Substance and State	$\Delta H_f^\circ$ ( $\frac{\text{kJ}}{\text{mol}}$ )	$\Delta G_f^\circ$ ( $\frac{\text{kJ}}{\text{mol}}$ )	$S^\circ$ ( $\frac{\text{J}}{\text{K}\cdot\text{mol}}$ )	Substance and State	$\Delta H_f^\circ$ ( $\frac{\text{kJ}}{\text{mol}}$ )	$\Delta G_f^\circ$ ( $\frac{\text{kJ}}{\text{mol}}$ )	$S^\circ$ ( $\frac{\text{J}}{\text{K}\cdot\text{mol}}$ )
<b>Carbon</b>				<b>Oxygen</b>			
C(s) (graphite)	0	0	6	O <sub>2</sub> (g)	0	0	205
C(s) (diamond)	2	3	2	O(g) 249	232	161	
CO(g)	-110.5		198	O <sub>3</sub> (g)	143	163	239
CO <sub>2</sub> (g)	-393.5		214	<b>Nitrogen</b>			
CH <sub>4</sub> (g)	?	-51	186	N <sub>2</sub> (g)	0	0	192
CH <sub>3</sub> OH(g)	-201	-163	240	NCl <sub>3</sub> (g)	230	271	-137
CH <sub>3</sub> OH(l)	-239	-166	127	NF <sub>3</sub> (g)	-125	-83.6	-139
CH <sub>3</sub> Cl(g)	-80.8	-57.4	234	NH <sub>3</sub> (g)	?	-17	193
CHCl <sub>3</sub> (g)	-100.8			NH <sub>3</sub> (aq)	?	-27	111
CHCl <sub>3</sub> (l)	-131.8			NH <sub>2</sub> CONH <sub>2</sub> (aq)	?	?	174
H <sub>2</sub> CO(g)	-116	-110	219	NO(g)	90	87	211
HCOOH(g)	-363	-351	249	NO <sub>2</sub> (g)	32	52	240
HCN(g)	135.1	125	202	N <sub>2</sub> O(g)	82	104	220
C <sub>2</sub> H <sub>2</sub> (g)	227	209	201	N <sub>2</sub> O <sub>4</sub> (g)	10	98	304
C <sub>2</sub> H <sub>4</sub> (g)	52	68	219	N <sub>2</sub> O <sub>5</sub> (g)	-42	134	178
CH <sub>3</sub> CHO(g)	-166	-129	250	HNO <sub>3</sub> (aq)	-207	-111	146
C <sub>2</sub> H <sub>5</sub> OH(l)	-278	-175	161	HNO <sub>3</sub> (l)	-174	-81	156
C <sub>2</sub> H <sub>6</sub> (g)	-84.7	-32.9	229.5	NH <sub>4</sub> Cl(s)	-314	-201	95
C <sub>3</sub> H <sub>6</sub> (g)	20.9	62.7	266.9	NH <sub>4</sub> ClO <sub>4</sub> (s)	-295	-89	186
C <sub>3</sub> H <sub>8</sub> (g)	-104	-24	270	<b>Silver</b>			
C <sub>4</sub> H <sub>10</sub> (g)	-125	-16.7	310	Ag(s)	0	0	42.6
C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> (l)	-229			Ag <sup>+</sup> (aq)	105.6	77.1	72.7
<b>Bromine</b>				Ag(S <sub>2</sub> O <sub>3</sub> ) <sup>3-</sup> (aq)	-1285.7	--	--
Br <sub>2</sub> (l)	0	0	152.	AgBr(s)	-100.4	-96.9	107.1
BrCl(g)	14.64	-0.96	240	AgCl(s)	-127.1	-109.8	96.2
<b>Chlorine</b>				<b>Sulfur</b>			
Cl <sub>2</sub> (g)	0	0	223	S(rhombic)	0	0	31.8
Cl <sub>2</sub> (aq)	-23	7	121	SO <sub>2</sub> (g)	-296.8	-300.2	248.8
Cl <sup>-</sup> (aq)	-167	-131	57	SO <sub>3</sub> (g)	-395.7	-371.1	256.3
HCl(g)	-92	-95	187	H <sub>2</sub> S(g)	-20.17	-33.0	205.6
<b>Fluorine</b>				<b>Phosphorus</b>			
F <sub>2</sub> (g)	0	0		P <sub>4</sub> (s)	0	0	41.1
F <sup>-</sup> (aq)	-333	-279	-14	PCl <sub>5</sub> (g)	-375	-305	365
HF(g)	-271	-273	174	<b>Aluminum</b>			
<b>Hydrogen</b>				AlCl <sub>3</sub> (s)	-526	-505	184
H <sub>2</sub> (g)	0	0	131	<b>Barium</b>			
H(g) 217	203	115		BaCl <sub>2</sub> (aq)	-872	-823	123
H <sup>+</sup> (aq)	0	0	0	Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O(s)	-3342	-2793	427
OH <sup>-</sup> (aq)	-230	-157	-11	<b>Iodine</b>			
H <sub>2</sub> O(l)				I <sub>2</sub> (s)	0	0	116.7
H <sub>2</sub> O(g)	-242	-229	189	HI(g)	25.94	1.30	206.3
<b>Magnesium</b>							
Mg(s)	0	0	33				
Mg(aq)	-492	-456	-118				
MgO(s)	-601	-569	26.9				

