

$$\Delta G = [2(-123 \frac{\text{kJ}}{\text{mol}})] - [0 + 0] = -246 \frac{\text{kJ}}{\text{mol}}$$

1992  
 $\text{Cl}_2(\text{g}) + 3 \text{F}_2(\text{g}) \rightarrow 2 \text{ClF}_3(\text{g})$

$\text{ClF}_3$  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  $-163.2$  kilojoules/mole and the standard free energy of formation,  $\Delta G_f^\circ$ , is  $-123.0$  kilojoules/mole.

IN ELEMENTAL STATE.

- (a) Calculate the value of the equilibrium constant for the reaction at 298K.
- (b) Calculate the standard entropy change,  $\Delta S^\circ$ , for the reaction at 298K.
- (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  $\text{Cl}_2(\text{g})$  and  $\text{ClF}_3(\text{g})$  are 222.96 joules per mole · Kelvin and 281.50 joules per mole · Kelvin, respectively.
  - (i) Account for the larger entropy of  $\text{ClF}_3(\text{g})$  relative to that of  $\text{Cl}_2(\text{g})$ .
  - (ii) Calculate the value of the absolute entropy of  $\text{F}_2(\text{g})$  at 298K.

a)  $\Delta G$  FOR  $\text{ClF}_3$  IS  $-\frac{123 \text{ kJ}}{\text{mol}}$

TWO MOLES!

PER MOLE!

$$\Delta G = -RT \ln K$$

$$\ln K = \frac{\Delta G}{-RT} = \frac{2(-123 \frac{\text{kJ}}{\text{mol}})}{(0.00831 \frac{\text{kJ}}{\text{mol} \cdot \text{K}})(298 \text{ K})}$$

$\frac{8.31 \text{ J}}{\text{mol} \cdot \text{K}} \left| \frac{1 \text{ kJ}}{1000 \text{ J}} \right. = 0.00831 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}$

$$K = e^{99.3386} = 1.387 \times 10^{43} = K$$

b)  $\Delta G = \Delta H - T\Delta S$

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

$$\frac{\Delta G - \Delta H}{-T} = \Delta S = \frac{2(-123 \frac{\text{kJ}}{\text{mol}}) - 2(-163.2 \frac{\text{kJ}}{\text{mol}})}{-298 \text{ K}}$$

$$\Delta S = \frac{-0.2698 \text{ kJ}}{\text{mol} \cdot \text{K}} \left| \frac{1000 \text{ J}}{1 \text{ kJ}} \right. = -270 \frac{\text{J}}{\text{mol} \cdot \text{K}} = \Delta S$$

1992 (CON'T) THERMO

c) IF  $\text{ClF}_3$  WERE A LIQUID INSTEAD OF A GAS.

THE VALUE FOR  $\Delta S$  WOULD BE MORE NEGATIVE. GASES HAVE MORE POSITIVE  $\Delta S$ -VALUES THAN LIQUIDS. THE MORE ORDERED THE SUBSTANCE, THE MORE NEGATIVE THE VALUE.

d)  $\text{Cl}_2 = \frac{222.96 \text{ J}}{\text{mol} \cdot \text{K}} = \Delta S$  ;  $\text{ClF}_3 = \frac{281.50 \text{ J}}{\text{mol} \cdot \text{K}} = \Delta S$

i)  $\text{ClF}_3$  HAS A LARGER  $\Delta S$  VALUE THAN  $\text{Cl}_2$  BECAUSE THE  $\text{ClF}_3$  IS MORE COMPLEX, (HAS MORE ATOMS). THE ARRANGEMENT IS A T-SHAPE PLANAR VS  $\text{Cl}_2$  WITH A MORE ORGANIZED LINEAR SHAPE.

ii)  $\Delta S_{\text{RXN}} = \sum \text{PRODUCTS} - \sum \text{REACTANTS}$

$\Delta S_{\text{F}_2} = \Delta S_{\text{RXN}} = -270 \frac{\text{J}}{\text{mol} \cdot \text{K}}$  (FROM PART b)

$-270 \frac{\text{J}}{\text{mol} \cdot \text{K}} = \left[ 2 \left( 281.50 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right]_{\text{PRODUCTS}} - \left[ 222.96 \frac{\text{J}}{\text{mol} \cdot \text{K}} + 3 \Delta S_{\text{F}_2} \right]_{\text{REACTANTS}}$

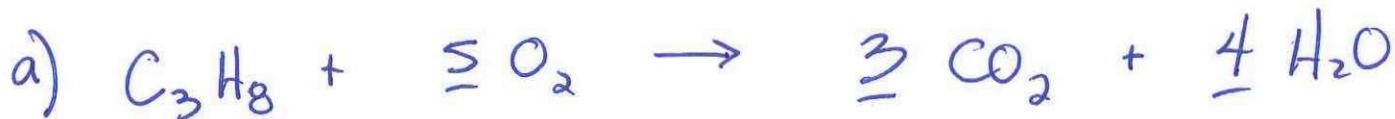
$-270 \frac{\text{J}}{\text{mol} \cdot \text{K}} = \left( 563 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) - \left( 222.96 \frac{\text{J}}{\text{mol} \cdot \text{K}} + 3 \Delta S_{\text{F}_2} \right)$

$-270 \frac{\text{J}}{\text{mol} \cdot \text{K}} = 340.04 \frac{\text{J}}{\text{mol} \cdot \text{K}} - 3 \Delta S_{\text{F}_2}$

$\frac{-610.04 \frac{\text{J}}{\text{mol} \cdot \text{K}}}{-3} = \frac{-3 \Delta S_{\text{F}_2}}{-3} \implies \Delta S_{\text{F}_2} = 203 \frac{\text{J}}{\text{mol} \cdot \text{K}}$

Propane,  $C_3H_8$ , is a hydrocarbon that is commonly used as fuel for cooking.

- (a) Write a balanced equation for the complete combustion of propane gas, which yields  $CO_2(g)$  and  $H_2O(l)$ .  
 (b) Calculate the volume of air at  $30^\circ C$  and 1.00 atmosphere that is needed to burn completely 10.0 grams of propane. Assume that air is 21.0 percent  $O_2$  by volume.  
 (c) The heat of combustion of propane is  $-2,220.1 \text{ kJ/mol}$ . Calculate the heat of formation,  $\Delta H_f^\circ$  of propane given that  $\Delta H_f^\circ$  of  $H_2O(l) = -285.3 \text{ kJ/mol}$  and  $\Delta H_f^\circ$  of  $CO_2(g) = -393.5 \text{ kJ/mol}$ .  
 (d) Assuming that all of the heat evolved in burning 30.0 grams of propane is transferred to 8.00 kilograms of water (specific heat =  $4.18 \text{ J/g}\cdot K$ ), calculate the increase in temperature of water.



$$b) \quad 30^\circ + 273 = 303 K$$

21% OF AIR  
 ↓  
 AIR

$$\frac{10g}{44.094g} \left| \frac{1 \text{ mol } C_3H_8}{1 \text{ mol } C_3H_8} \right| \frac{5 \text{ mol } O_2}{1 \text{ mol } C_3H_8} = 1.13394 \text{ mol } O_2$$

$$V = \frac{nRT}{P} = \frac{(1.13394 \text{ mol})(0.0821 \text{ ATM}\cdot L)(303 K)}{1 \text{ ATM} (\text{mol}\cdot K)} = 28.2 L_{O_2}$$

OXYGEN GAS MAKES UP 21% OF AIR (IN THIS PROBLEM)

$$0.21 = 21\% \quad \frac{28.2 L O_2}{21\% O_2 \text{ IN AIR}} = 134 L$$

$$\text{OR} \quad \frac{28.2 L}{0.21} = 134 L$$

$$c) \quad \Delta H_{RXN} = \sum \Delta H_{PRODUCTS} - \sum \Delta H_{REACTANTS} \quad \Delta H_{RXN} = -2220 \frac{\text{kJ}}{\text{mol}}$$

$$-2220 \frac{\text{kJ}}{\text{mol}} = \left[ \Delta H_{CO_2} + \Delta H_{H_2O} \right] - \left[ \Delta H_{C_3H_8} + \Delta H_{O_2} \right]$$

$$\begin{array}{r} -2220 \frac{\text{kJ}}{\text{mol}} = \left[ 3(-393.5 \frac{\text{kJ}}{\text{mol}}) + 4(-285.3 \frac{\text{kJ}}{\text{mol}}) \right] - \left[ \Delta H_{C_3H_8} + 0 \frac{\text{kJ}}{\text{mol}} \right] \\ + 2321.7 \frac{\text{kJ}}{\text{mol}} \quad \quad \quad - 2321.7 \frac{\text{kJ}}{\text{mol}} \\ + 101.7 \frac{\text{kJ}}{\text{mol}} \quad \quad \quad + 2321.7 \frac{\text{kJ}}{\text{mol}} \end{array}$$

# 1995 (THERMO) CON'T

c) CON'T

$$+ 101.7 \frac{\text{kJ}}{\text{mol}} = -\Delta H_{\text{C}_3\text{H}_8}$$

$$- 101.7 \frac{\text{kJ}}{\text{mol}} = \Delta H_{\text{C}_3\text{H}_8}$$

$\Delta H_{\text{COMBUSTION}}$ !

d)

$$\frac{30 \text{ g C}_3\text{H}_8}{44.094 \text{ g}} \left| \frac{1 \text{ mol C}_3\text{H}_8}{44.094 \text{ g}} \right| \frac{2220.1 \text{ kJ}}{1 \text{ mol C}_3\text{H}_8} = 1510.41 \text{ kJ}$$

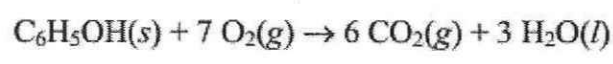
$$\frac{1510.41 \text{ kJ}}{1 \text{ kJ}} \left| \frac{1000 \text{ J}}{1 \text{ kJ}} \right| = 1.51 \times 10^6 \text{ J}$$

$$q = mc\Delta T$$

$$\frac{8.00 \text{ kg H}_2\text{O}}{1 \text{ kg}} \left| \frac{1000 \text{ g}}{1 \text{ kg}} \right| =$$

$$\Delta T = \frac{q}{mc} = \frac{1.51 \times 10^6 \text{ J (g}^\circ\text{C)}}{(8000 \text{ g})(4.18 \text{ J})} = 45.2^\circ\text{C}$$

$$\Delta T = 45.2^\circ\text{C} \quad \text{INCREASE}$$



When a 2.000-gram sample of pure phenol,  $C_6H_5OH(s)$ , is completely burned according to the equation above, 64.98 kilojoules of heat is released. Use the information in the table below to answer the questions that follow.

$\Delta H_{rxn} = -64.98 \text{ kJ}$   
 For 2.00 g

Substance	Standard Heat of Formation, $\Delta H_f^\circ$ , at 25°C (kJ/mol)	Absolute Entropy, $S^\circ$ , at 25°C (J/mol-K)
$C_{(graphite)}$	0.00	5.69
$CO_2(g)$	-393.5	213.6
$H_2(g)$	0.00	130.6
$H_2O(l)$	-285.85	69.91
$O_2(g)$	0.00	205.0
$C_6H_5OH(s)$	?	144.0

- (a) Calculate the molar heat of combustion of phenol in kilojoules per mole at 25°C.
- (b) Calculate the standard heat of formation,  $\Delta H_f^\circ$ , of phenol in kilojoules per mole at 25°C.
- (c) Calculate the value of the standard free-energy change,  $\Delta G^\circ$  for the combustion of phenol at 25°C.
- (d) If the volume of the combustion container is 10.0 liters, calculate the final pressure in the container when the temperature is changed to 110°C. (Assume no oxygen remains unreacted and that all products are gaseous.)

a)

$$\frac{2.00 \text{ g } C_6H_5OH}{94.108 \text{ g}} \times 1 \text{ mol } C_6H_5OH = 0.021252 \text{ mol}$$

$$\Delta H_{rxn} = \frac{\text{kJ}}{\text{mol}} = \frac{-64.98 \text{ kJ}}{0.021252 \text{ mol}} = -3057.57 \frac{\text{kJ}}{\text{mol}} = \Delta H_{rxn}$$

b)

$$\Delta H_{rxn} = \sum \text{PRODUCTS} - \sum \text{REACTANTS}$$

$$\Delta H_{rxn} = [\Delta H_{CO_2} + \Delta H_{H_2O}] - [\Delta H_{C_6H_5OH} + \Delta H_{O_2}]$$

$$-3057.57 \frac{\text{kJ}}{\text{mol}} + 3218.55 \frac{\text{kJ}}{\text{mol}} = [6(-393.5 \frac{\text{kJ}}{\text{mol}}) + 3(-285.85 \frac{\text{kJ}}{\text{mol}})] - [\Delta H_{C_6H_5OH} + 0]$$

$$+160.98 \frac{\text{kJ}}{\text{mol}} = -3218.55 \frac{\text{kJ}}{\text{mol}} + 3218.55 \frac{\text{kJ}}{\text{mol}} - \Delta H_{C_6H_5OH}$$

$$+160.98 \frac{\text{kJ}}{\text{mol}} = -\Delta H_{C_6H_5OH} \Rightarrow \Delta H_{C_6H_5OH} = -160.98 \frac{\text{kJ}}{\text{mol}}$$

## 1998 (THERMO) CONT

$$c) \Delta G = \Delta H - T\Delta S$$

$$\Delta S = \sum_{\text{PRODUCTS}} - \sum_{\text{REACTANTS}}$$

$$\Delta S = \left[ 6 \left( 213.6 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + 3 \left( 69.91 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right] -$$

$$\left[ 144 \frac{\text{J}}{\text{mol}\cdot\text{K}} + 7 \left( 205 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right]$$

$$\Delta S = 1491.33 \frac{\text{J}}{\text{mol}\cdot\text{K}} - 1579 \frac{\text{J}}{\text{mol}\cdot\text{K}} = -87.67 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\frac{87.67 \text{ J}}{\text{mol}\cdot\text{K}} \bigg| \frac{1 \text{ kJ}}{1000 \text{ J}} = -0.08767 \frac{\text{kJ}}{\text{mol}\cdot\text{K}}$$

$$\Delta G = -3057.57 \frac{\text{kJ}}{\text{mol}} - \left( 298 \text{ K} \left( -0.08767 \frac{\text{kJ}}{\text{mol}\cdot\text{K}} \right) \right) =$$

$$\boxed{\Delta G = -3031 \frac{\text{kJ}}{\text{mol}}}$$

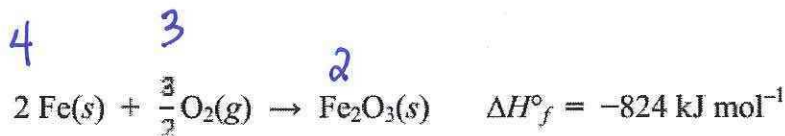
d) " Assume No OXYGEN GAS REMAINS - AND ALL PRODUCTS ARE GASES! "

$$\frac{2.00 \text{ g } C_6H_5OH}{94.108 \text{ g}} \bigg| \frac{1 \text{ mol } C_6H_5OH}{94.108 \text{ g}} \bigg| \frac{9 \text{ mol GASES}}{1 \text{ mol } C_6H_5OH} = 0.19127 \frac{\text{mol}}{\text{GAS}}$$

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{(0.19127 \text{ mol})(0.0821 \text{ ATM}\cdot\text{L})(110^\circ + 273)}{(10 \text{ L}) \text{ mol}\cdot\text{K}} = \boxed{0.601 \text{ ATM}}$$

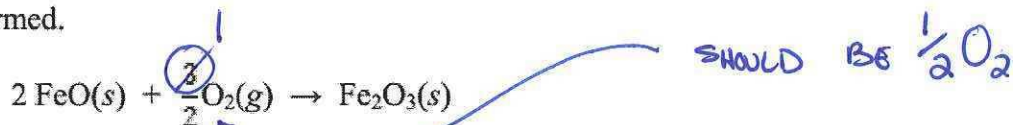
2004



Iron reacts with oxygen to produce iron(III) oxide, as represented by the equation above. A 75.0 g sample of Fe(s) is mixed with 11.5 L of O<sub>2</sub>(g) at 2.66 atm and 298 K.

- (a) Calculate the number of moles of each of the following before the reaction begins.
- Fe(s)
  - O<sub>2</sub>(g)
- (b) Identify the limiting reactant when the mixture is heated to produce Fe<sub>2</sub>O<sub>3</sub>(s). Support your answer with calculations.
- (c) Calculate the number of moles of Fe<sub>2</sub>O<sub>3</sub>(s) produced when the reaction proceeds to completion.
- (d) The standard free energy of formation, ΔG<sup>∘</sup><sub>f</sub>, of Fe<sub>2</sub>O<sub>3</sub>(s) is -740. kJ mol at 298 K.
- Calculate the standard entropy of formation, ΔS<sup>∘</sup><sub>f</sub>, of Fe<sub>2</sub>O<sub>3</sub>(s) at 298 K. Include units with your answer.
  - Which is more responsible for the spontaneity of the formation reaction at 298 K, the standard enthalpy of formation, ΔH<sup>∘</sup><sub>f</sub>, or the standard entropy of formation, ΔS<sup>∘</sup><sub>f</sub>? Justify your answer.

The reaction represented below also produces iron(III) oxide. The value of ΔH<sup>∘</sup> for the reaction is -280. kJ per mole of Fe<sub>2</sub>O<sub>3</sub>(s) formed.



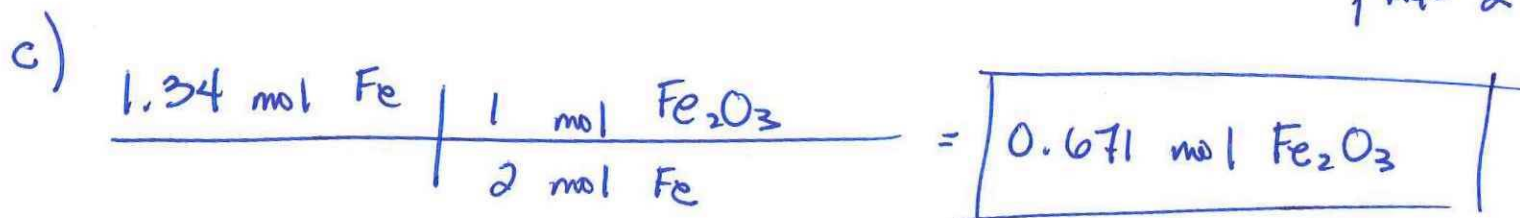
Calculate the standard enthalpy of formation, ΔH<sup>∘</sup><sub>f</sub>, of FeO(s).

a) i)  $\frac{75 \text{ g Fe}}{55.85 \text{ g}} \times \frac{1 \text{ mol Fe}}{1} = 1.34 \text{ mol Fe}$  PV = nRT

ii)  $n = \frac{PV}{RT} = \frac{(2.66 \text{ atm})(11.5 \text{ L})}{(0.0821 \text{ atm}\cdot\text{L})(298 \text{ K})} = 1.25 \text{ mol O}_2$

b)  $\frac{1.34 \text{ mol Fe}}{4 \text{ mol Fe}} \times \frac{3 \text{ mol O}_2}{2 \text{ mol Fe}} = 1.007 \text{ mol O}_2 \text{ NEEDED TO REACT WITH ALL } 1.34 \text{ mol Fe. HAVE } 1.25 \text{ mol O}_2 \dots \text{O}_2 \text{ IS IN EXCESS.}$

IRON IS LIMITING REACTANT



d) i)  $\Delta H = -824 \frac{\text{kJ}}{\text{mol}}$  (GIVEN NEXT TO EQUATION @ TOP OF SHEET).

$$\begin{array}{l} \Delta G = \Delta H - T\Delta S \\ -\Delta H \quad -\Delta H \end{array} \quad \rightsquigarrow \quad \Delta G - \Delta H = \textcircled{-T\Delta S}$$

$$\Delta S = \frac{\Delta G - \Delta H}{-T} = \frac{(-740 \frac{\text{kJ}}{\text{mol}}) - (-824 \frac{\text{kJ}}{\text{mol}})}{-298 \text{ K}}$$

$$\Delta S = -0.282 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}$$

$$\frac{-0.282 \text{ kJ}}{\text{mol} \cdot \text{K}} \quad | \quad \frac{1000 \text{ J}}{1 \text{ kJ}} =$$

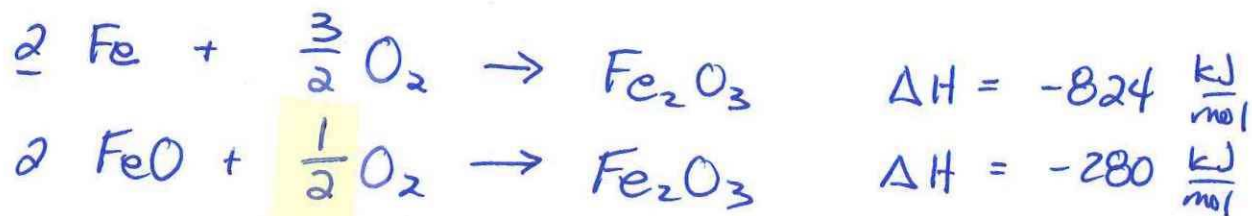
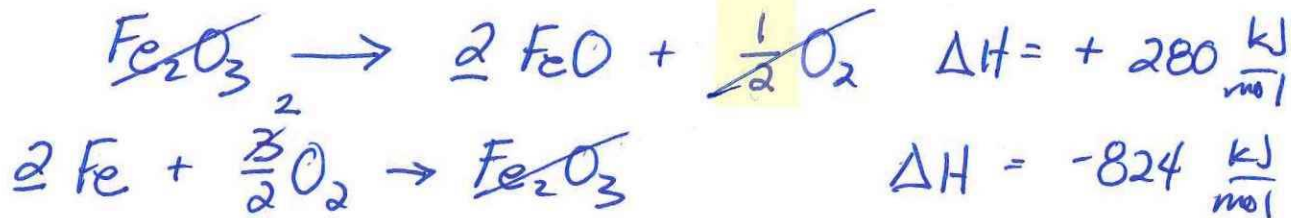
$$\boxed{\Delta S = \frac{-282 \text{ J}}{\text{mol} \cdot \text{K}}}$$

ii)  $\Delta H$  IS THE IMPORTANT FACTOR IN THIS REACTION.  $\Delta H$  HAS A NEGATIVE (LARGE NEGATIVE) VALUE THAT FAVORS THE OVERALL SIGN FOR  $\Delta G$ .  $\Delta S$  HAS A NEGATIVE VALUE (MORE ORDERED) AND IS NOT RESPONSIBLE THE "FAVOR" FOR THE REACTION TO BE SPONTANEOUS.



HESS !!!

REACTIONS GIVEN:

CALCULATE FORMATION OF FeO, ?  $\Delta H$  VALUES

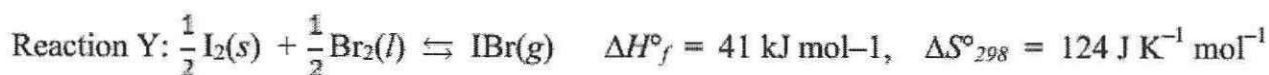
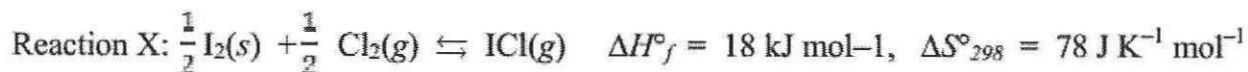
↑  
2 MOLES!

$$\Delta H = \frac{-544 \frac{\text{kJ}}{\text{mol}}}{2} =$$

↑  
PER MOLE!

$$\boxed{-272 \frac{\text{kJ}}{\text{mol}} = \Delta H}$$

Answer the following questions about the thermodynamics of the reactions represented below.



- (a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.
- (b) Calculate the value of the equilibrium constant,  $K_{eq}$ , for reaction X at 25°C.
- (c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.
- (d) Explain why the standard entropy change is greater for reaction Y than for reaction X.
- (e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0? Justify your answer with calculations.
- (f) For the vaporization of solid iodine,  $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$ , the value of  $\Delta H^\circ_{298}$  is  $62 \text{ kJ mol}^{-1}$ . Using this information, calculate the value of  $\Delta H^\circ_{298}$  for the reaction represented below.



a)  $\Delta G = \Delta H - T\Delta S = \left(18 \frac{\text{kJ}}{\text{mol}}\right) - \left(\left(298 \text{ K}\right)\left(\frac{78 \text{ J}}{\text{mol} \cdot \text{K}} \left| \frac{1 \text{ kJ}}{1000 \text{ J}}\right.\right)\right) = -5.2 \frac{\text{kJ}}{\text{mol}}$

$\Delta G = -5.2 \frac{\text{kJ}}{\text{mol}}$ , REACTION IS SPONTANEOUS SINCE  $\Delta G$  HAS A NEGATIVE VALUE.

b)  $\Delta G = -RT \ln K$  ;  $\ln K = \frac{\Delta G}{-RT} = \frac{-5.2 \frac{\text{kJ}}{\text{mol}}}{-\left(\left(0.00831 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}\right)\left(298\right)\right)}$

$\ln K = 2.117$  ;  $K = e^{2.117} = \boxed{8.31 = K}$   $\frac{8.31 \text{ J}}{\text{mol} \cdot \text{K}} \left| \frac{1 \text{ kJ}}{1000 \text{ J}}\right.$

c) INCREASE IN TEMPERATURE WILL CAUSE A SHIFT TOWARD THE PRODUCTS, CAUSING  $K$  TO INCREASE. REASON: ENDOTHERMIC REACTION AT EQUILIBRIUM, ADDING ENERGY WILL CAUSE A SHIFT AWAY FROM THE ADDITION (LECHATLIER).

d)  $\Delta S$  VALUE IS GREATER FOR THE REACTION Y BECAUSE "Y" STARTS AS A SOLID AND A LIQUID (AS REACTANTS) AND THEN CHANGES INTO A GAS. "X" STARTS AS A SOLID AND A GAS AND THEN CHANGES INTO A GAS. THE GREATER STATE CHANGE OCCURS WITH REACTION "Y" IN ENTROPY

e)  $\Delta G = 0$  @ EQUILIBRIUM

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

REACTION Y:  $\Delta H = 41 \frac{\text{kJ}}{\text{mol}}$

$$\Delta S = 124 \frac{\text{J}}{\text{mol}} \left| \frac{1 \text{kJ}}{1000 \text{J}} \right| =$$

$$0.124 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}$$

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

$$\frac{\Delta G - \Delta H}{-\Delta S} = \frac{0 - (41 \frac{\text{kJ}}{\text{mol}}) (\text{mol} \cdot \text{K})}{-0.124 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}} = 331 \text{ K}$$

TEMPERATURE NEEDS TO BE GREATER THAN 331 K

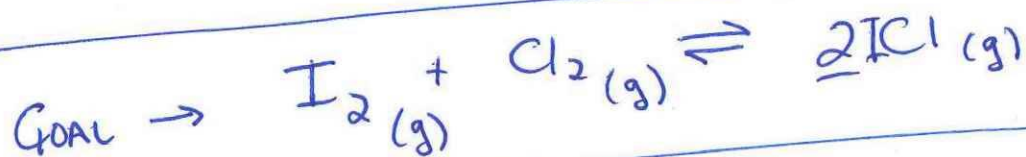
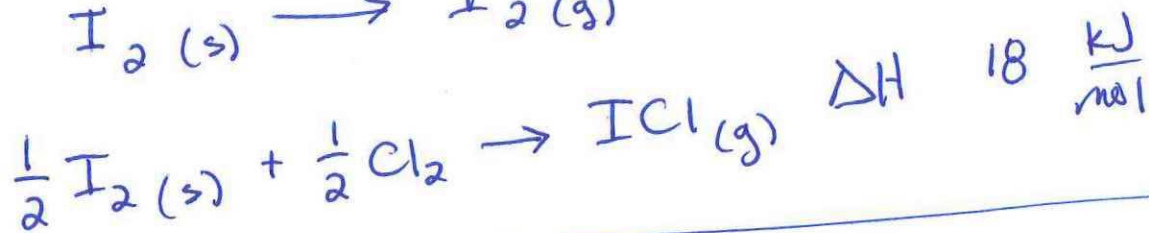
→ NEXT PAGE!

006 B (THERMO) CON'T

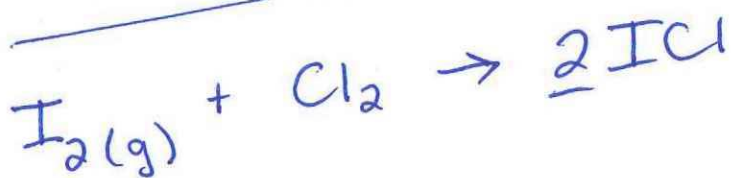
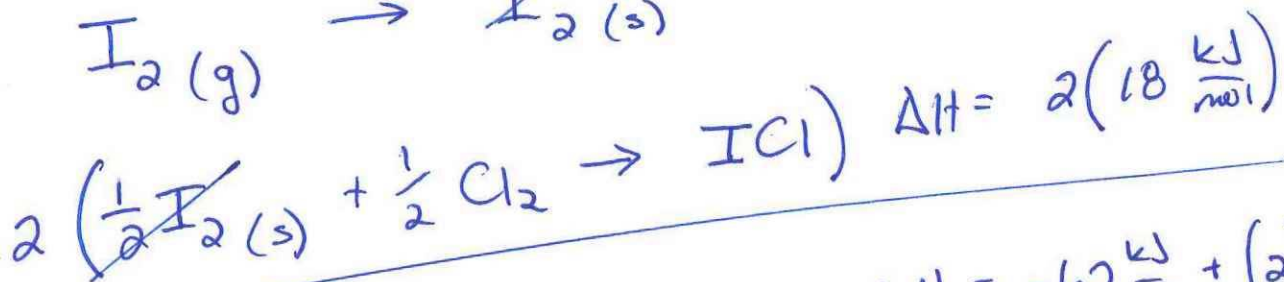
f) HESS !!!



$$\Delta H = 62 \frac{\text{kJ}}{\text{mol}}$$



$$\Delta H = -62 \frac{\text{kJ}}{\text{mol}}$$



$$\Delta H = -62 \frac{\text{kJ}}{\text{mol}} + (2) 18 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H = -26 \frac{\text{kJ}}{\text{mol}}$$