

KEY

CHGM-141

General and Analytical Chemistry I

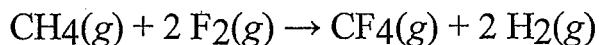
With Dr. Bailey

Recitation Week 12

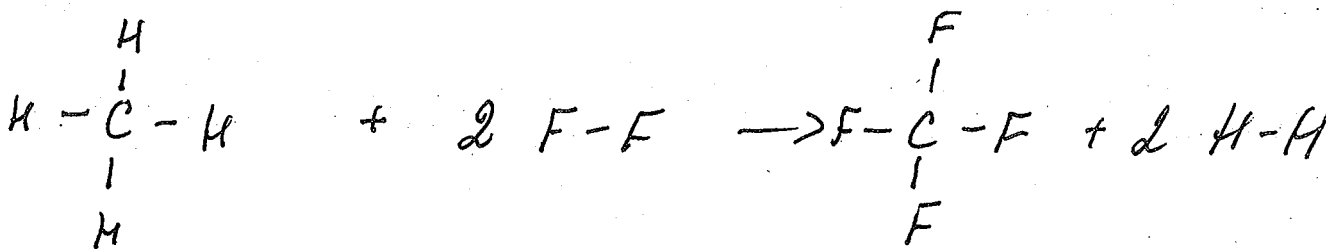
(Bond Dissociation Energies, Entropy, Free Energy)

Part A:

1) Use the given average bond dissociation energies, D , to estimate ΔH for the reaction of methane, $\text{CH}_4(\text{g})$, with fluorine according to the equation:



Bond	D , kJ/mol
C-F	450
C-H	410
F-F	158
H-H	436



$$\Delta H^\circ = D(\text{Reactant bonds}) - D(\text{Product bonds})$$

$$\Delta H^\circ = [4 D_{\text{C-H}} + 2 D_{\text{F-F}}] - [4 D_{\text{C-F}} + 2 D_{\text{H-H}}] =$$

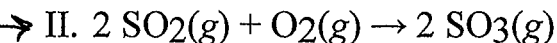
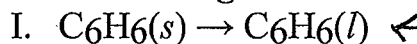
$$= \left[(4 \text{ mol}) \cdot \left(410 \frac{\text{kJ}}{\text{mol}} \right) + (2 \text{ mol}) \cdot \left(158 \frac{\text{kJ}}{\text{mol}} \right) \right] -$$

$$- \left[(4 \text{ mol}) \cdot \left(450 \frac{\text{kJ}}{\text{mol}} \right) + (2 \text{ mol}) \cdot \left(436 \frac{\text{kJ}}{\text{mol}} \right) \right] =$$

$$= 1956 \text{ kJ} - 2672 \text{ kJ} = \boxed{-716 \text{ kJ}}$$

Part B:

1) Determine the sign of ΔS° for each of the following:



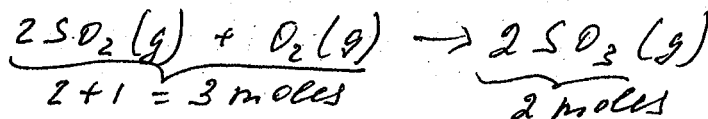
A) ΔS° should be negative for I and negative for II.

B) ΔS° should be negative for I and positive for II.

C) ΔS° should be positive for I and negative for II.

D) ΔS° should be positive for I and positive for II.

Liquids have more randomness and higher entropy than solids so $\Delta S^\circ > 0$



= fewer moles of product so $\Delta S^\circ < 0$

2) The reaction of gaseous H_2 and liquid Br_2 to give gaseous HBr has

$\Delta H = -17.4 \text{ kcal/mol}$ and $\Delta S = 27.2 \text{ cal / (mol} \times \text{K)}$

- Write the balanced equation for this reaction
- Does entropy increase or decrease in this process?
- Is this process spontaneous at all temperature? Explain.
- What is the value of ΔG for the reaction at 300 K?



(b) Entropy increases because the number of gaseous product molecules is greater than the number of gaseous reactant molecules.

(c) The process is spontaneous at all temperatures because ΔH is negative and ΔS is positive.

(d) $\Delta G = \Delta H - T\Delta S$; $\Delta H = -17.4 \text{ kcal/mol}$; $\Delta S = 27.2 \text{ cal/(mol} \cdot \text{K)}$; $T = 300 \text{ K}$

$$T\Delta S = 300 \text{ K} \times \frac{27.2 \text{ cal}}{\text{mol K}} \times \frac{1 \text{ kcal}}{10^3 \text{ cal}} = \frac{8.16 \text{ kcal}}{\text{mol}}$$

$$\Delta G = -17.4 \text{ kcal/mol} - 8.16 \text{ kcal/mol} = \boxed{-25.6 \text{ kcal/mol}}$$

Reaction is "product-favored"

= spontaneous

→ see add. →
sample problems

Part C:

Given:

Specific heat of water ice, $2.09 \text{ J/g}^\circ\text{C}$

Heat of fusion of water, 334 J/g

Specific heat of water, $4.18 \text{ J/g}^\circ\text{C}$

Heat of vaporization of water, 2260 J/g

Specific heat of water steam, $2.03 \text{ J/g}^\circ\text{C}$

Specific heat capacity of copper is $0.382 \text{ J/g}^\circ\text{C}$.

Heat of fusion for copper is 205 J/g

1) How much heat energy, in joules, is required to melt following:

a) 1.25 kg of copper at its melting point of 1083°C ?

b) One mole of copper?

$$a) \quad 1.25 \text{ kg Cu} \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{205 \text{ J}}{1 \text{ g Cu}} = \boxed{2.56 \times 10^5 \text{ J}}$$

$$b) \quad \text{MM}_{\text{Cu}} = 63.55 \text{ g/mol} \quad 63.55 \frac{\text{g}}{\text{mol}} \times \frac{205 \text{ J}}{\text{g}} = 13028 = \boxed{1.30 \times 10^4 \frac{\text{J}}{\text{mol}}}$$

2) Calculate the amount of heat required, in joules, to convert 125.0 g of ice at -15.0°C to steam at 110.0°C

(Hint: calculate the amount of heat required in each of the steps, and then add these amounts together to get your final answer).

$$\begin{aligned} & \underline{\text{5 Steps: heating ice} \rightarrow \text{melting} \rightarrow \text{heating water} \rightarrow \text{evaporation} \rightarrow \text{heating steam}} \\ & 125.0 \text{ g} \times \frac{2.1 \text{ J}}{\text{g}^\circ\text{C}} \times [0.0 - (-15.0)]^\circ\text{C} + 125.0 \text{ g} \times \frac{334 \text{ J}}{\text{g}} + \\ & + 125.0 \text{ g} \times \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} (100.0 - 0.0)^\circ\text{C} + 125.0 \text{ g} \times \frac{2260 \text{ J}}{\text{g}} + \\ & + 125.0 \text{ g} \times \frac{2.0 \text{ J}}{\text{g}^\circ\text{C}} \times (110.0 - 100.0)^\circ\text{C} = \\ & = 2937.5 \text{ J} + 41750.0 \text{ J} + 52250.0 \text{ J} + 282500.0 \text{ J} + 2500.0 \text{ J} = \\ & = 382937.5 \text{ J} = \boxed{3.83 \times 10^5 \text{ J}} \end{aligned}$$

See add. sample problems

Gibbs Free Energy, G

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

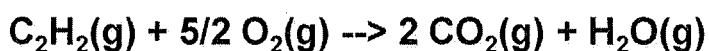
ΔH°	ΔS°	ΔG° Reaction
exo(-)	increase(+)	Prod-favored
endo(+)	decrease(-)+	React-favored
exo(-)	decrease(-)?	T dependent
endo(+)	increase(+)?	T dependent

Sample Problems

Calculating $\Delta G^\circ_{\text{rxn}}$

Example

Combustion of acetylene



$$\Delta H^\circ_{\text{rxn}} = -1238 \text{ kJ}$$

$$\Delta S^\circ_{\text{rxn}} = -97.4 \text{ J/K or } -0.0974 \text{ kJ/K}$$

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= -1238 \text{ kJ} - (298 \text{ K})(-0.0974 \text{ kJ/K}) \\ &= -1209 \text{ kJ}\end{aligned}$$

Reaction is product-favored in spite of negative

$$\Delta S^\circ_{\text{rxn}}$$

Reaction is "enthalpy driven"

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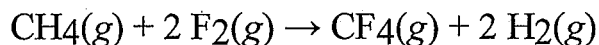
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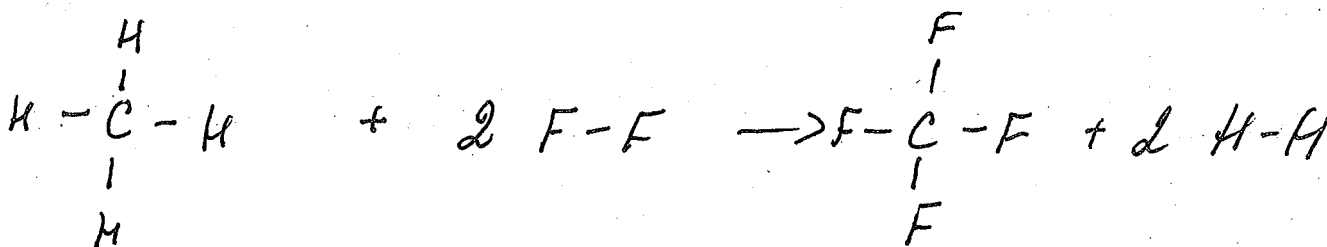
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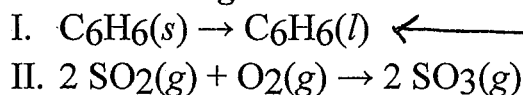
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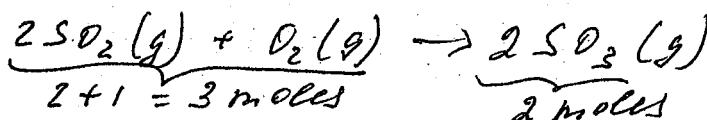
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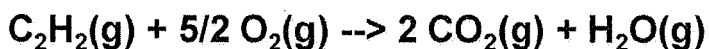
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$$\Delta S^\circ_{\text{rxn}}$$

Reaction is "enthalpy driven"

Calculating $\Delta G^\circ_{\text{rxn}}$

Example



$$\Delta H^\circ_{\text{rxn}} = +25.7 \text{ kJ}$$

$$\Delta S^\circ_{\text{rxn}} = +108.7 \text{ J/K or } +0.1087 \text{ kJ/K}$$

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= +25.7 \text{ kJ} - (298 \text{ K})(+0.1087 \text{ kJ/K}) \\ &= -6.7 \text{ kJ}\end{aligned}$$

Reaction is **product-favored** in spite of positive $\Delta H^\circ_{\text{rxn}}$.

Reaction is "entropy driven"