

## Chapter 19 – Chemical Thermodynamics

### • Thermochemistry Review

- Enthalpy,  $\Delta H = q_p$

-- for a chemical reaction,  $\Delta H_{rxn}^{\circ} = \sum n\Delta H_f^{\circ} \text{ products} - m\Delta H_f^{\circ} \text{ reactants}$

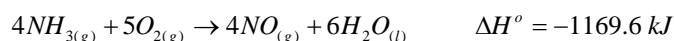
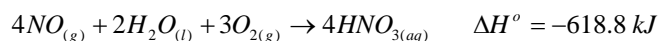
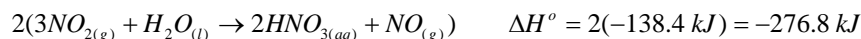
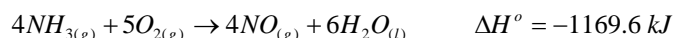
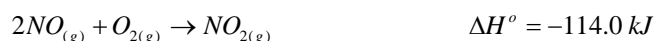
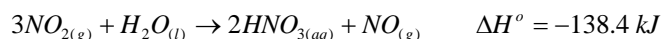
- Hess's Law: for a set of reactants going to a set of products the enthalpy of the reaction is constant

-- this is true regardless of whether the reaction takes place in a single step or multiple steps

-- this is where you add up the chemical equations and their corresponding enthalpies to obtain the enthalpy of reaction

Ex: Calculate  $\Delta H_f^{\circ}(\text{HNO}_{3(aq)})$  given the following information:

$$\Delta H_f^{\circ}(\text{NH}_{3(g)}) = -46.1 \text{ kJ/mol}, \Delta H_f^{\circ}(\text{H}_2\text{O}_{(l)}) = -285.5 \text{ kJ/mol}$$



$$\Delta H_{rxn}^{\circ} = 4\Delta H_f^{\circ}(\text{HNO}_{3(aq)}) + 4\Delta H_f^{\circ}(\text{H}_2\text{O}_{(l)}) - [4\Delta H_f^{\circ}(\text{NH}_{3(g)}) + 5\Delta H_f^{\circ}(\text{O}_{2(g)})]$$

$$-1788.4 \text{ kJ} = 4\Delta H_f^{\circ}(\text{HNO}_{3(aq)}) + 4(-285.5 \text{ kJ}) - 4(-46.1 \text{ kJ}) - 8(0.0 \text{ kJ})$$

$$\Delta H_f^{\circ}(\text{HNO}_{3(aq)}) = -207.7 \text{ kJ}$$

### • 19.1 Spontaneous Processes

- spontaneous vs. nonspontaneous process

-- spontaneous: occurs without outside intervention like heat

-- nonspontaneous: requires outside intervention like heat

- experimental conditions may impact spontaneity (T & P)

-- for example ice will spontaneously form at 0°C or below (see Figure 19.3)

### • 19.2 Entropy & the Second Law of Thermodynamics

- entropy

-- defn: system disorder, randomness, motion

-- e.g. a messy room has more entropy than a neat one

-- takes energy to keep maintain a neat room

- entropy changes in the surroundings occurs as a consequence of heat flow

- if a process occurs at lower temperatures than impact of heat flow is greater

-  $\Delta S_{surr}$

--the sign is dependent on the direction of our heat flow

-- the magnitude is dependent on T

- the dependency of  $\Delta S_{surr}$  on T is

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

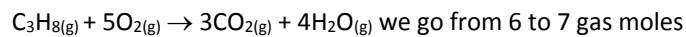
-- if the reaction is exothermic then  $\Delta H < 0$  and  $\Delta S_{surr} > 0$  which makes sense since heat is flowing into the surroundings from the system

-- the opposite is true for an endothermic reaction

- second law of thermodynamics: a process is spontaneous if

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

-- when the number of moles of gas are increased from the reactants to products the system is spontaneous



-- the opposite is also true if we reduce the number of gas moles we loose disorder,  $\Delta S_{univ} < 0$

### • 19.3 The Molecular Interpretation of Entropy & the Third Law of Thermodynamics

- we are skipping the molecular interpretation of thermos

- third law of thermodynamics: the entropy of a perfect crystal at absolute 0 is 0

### • 19.4 Entropy Changes in Chemical Reactions

-- standard molar entropy: entropy of a substance at 1 bar of pressure (1 bar = 0.9872 atm) and 298K

$$\Delta S_{rxn}^{\circ} = \sum n S_{products}^{\circ} - \sum m S_{reactants}^{\circ}$$

-- very similar to  $\Delta H_{rxn}^{\circ}$

-- Ex: Compute the  $\Delta S_{rxn}^{\circ}$  for  $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$  using the data in Appendix C

Compound	$S^{\circ}$ (J/mol K)
$\text{C}_3\text{H}_8(\text{g})$	269.9
$\text{O}_2(\text{g})$	205.0
$\text{CO}_2(\text{g})$	213.6
$\text{H}_2\text{O}(\text{g})$	188.7

$$\Delta S_{rxn}^{\circ} = 3(213.6) + 4(188.7) - [269.9 + 5(205.0)] = 100.7 \text{ J / K}$$

### • 19.5 Gibbs Free Energy & 19.6 Free Energy and Temperature

- two driving forces which make chemical rxns happen:

-- formation of low-energy products from high-energy reactants,  $\Delta H < 0$

-- formation of high-entropy products from low-entropy reactants,  $\Delta S > 0$

- not practical to measure disorder or entropy directly

- free energy

-- called the Gibb's "free energy" because it is the maximum amount of energy available to do work  
--- anymore E than this will have to be put into the system

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

-- exergonic ( $\Delta G < 0$ , spontaneous)

-- endergonic ( $\Delta G > 0$ , nonspontaneous)

$\Delta H$	$\Delta S$	$\Delta G$	Spontaneity
<0	>0	always <0	always spontaneous
<0	<0	<0 at low T	spontaneous at low T
>0	>0	<0 at high T	spontaneous at high T
>0	<0	always >0	nonspontaneous

- Ex: The standard enthalpy and entropy changes for the combustion of methane are -801 kJ and -5 J/K, respectively. Is the reaction spontaneous under standard conditions?

$$\Delta G = -801 \text{ kJ} - 298\text{K} * (-5 \text{ J/K} \times 1\text{kJ}/1000\text{J}) = -803 \text{ kJ}$$

yes it is spontaneous and it is also exergonic

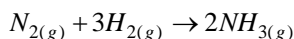
- when  $\Delta G = 0$  then the reaction is in chemical equilibrium - we will discuss this later

-- just like  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$  is also zero for elements in their natural states, e.g.  $O_2$

$$\Delta G_{\text{rxn}}^\circ = \sum nG_{f,\text{products}}^\circ - \sum mG_{f,\text{reactants}}^\circ$$

-- Ex: Is the reaction below exothermic or endothermic? Is the reaction spontaneous at all temperature?

Determine the Gibbs free energy from  $\Delta G_{\text{rxn}}^\circ$  and from  $\Delta H - T\Delta S$  at STP



Compound	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol*K)	$\Delta G_f^\circ$ (kJ/mol)
$N_{2(g)}$	0.0	191.5	0.0
$H_{2(g)}$	0.0	130.6	0.0
$NH_{3(g)}$	-46.1	192.3	-16.5

$$\Delta H_{\text{rxn}}^\circ = 2(-46.1) - [0.0 + 3*0.0] = -92.2 \text{ kJ}$$

therefore it's exothermic

$$\Delta S_{\text{rxn}}^\circ = 2(192.3) - [191.5 + 3(130.6)] = -198.7 \text{ J / K}$$

therefore at STP the reaction is spontaneous

$$\Delta G_{\text{rxn}}^\circ = 2(-16.5) - [0.0 + 3(0.0)] = -33 \text{ kJ}$$

Alternatively, we can use  $\Delta G = \Delta H - T\Delta S$

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ = -92.2 \text{ kJ / mol} - 298\text{K}(-198.7 \text{ J / mol}\cdot\text{K}) \times \frac{1\text{kJ}}{1000\text{J}} = -32.99 \text{ kJ / mol}$$

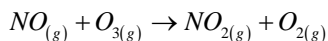
Since both  $\Delta H$  &  $\Delta S < 0$  the reaction will be spontaneous only at low temperatures

## • 19.7 Free Energy & the Equilibrium Constant

- it turns out the relationship btwn P and  $\Delta G$  is based on the law of mass action:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- Ex: Using the data below calculate  $\Delta G$  for the reaction at 25°C.



	$NO_{(g)}$	$O_{3(g)}$	$NO_{2(g)}$	$O_{2(g)}$
$\Delta G^\circ$ (kJ/mol)	87	163	52	0
Pressure (atm)	$1.00 \times 10^{-6}$	$2.00 \times 10^{-6}$	$1.00 \times 10^{-7}$	$1.00 \times 10^{-3}$

$$\Delta G_{rxn}^{\circ} = [(52 + 0) - (87 + 163)] \frac{\text{kJ}}{\text{mol}} = -198 \frac{\text{kJ}}{\text{mol}}$$

$$Q = \frac{P_{\text{NO}_2} P_{\text{O}_2}}{P_{\text{NO}} P_{\text{O}_3}} = \frac{(1.00 \times 10^{-7})(1.00 \times 10^{-3})}{(1.00 \times 10^{-6})(2.00 \times 10^{-6})} = 50.$$

$$\Delta G = \Delta G^{\circ} + RT \ln Q = -198 \frac{\text{kJ}}{\text{mol}} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \frac{\text{kJ}}{1000 \text{ J}} \times 298.15 \text{ K} \ln 50.$$

$$\Delta G = -188 \frac{\text{kJ}}{\text{mol}}$$

- as I mentioned previously when eq is reached  $\Delta G = 0$  therefore,

$$0 = \Delta G^{\circ} + RT \ln K \rightarrow -\frac{\Delta G^{\circ}}{RT} = \ln K \rightarrow K = e^{-\Delta G^{\circ} / RT}$$

- we develop the following qualitative relationships based on the aforementioned mathematical one

-- when  $\Delta G^{\circ} = 0$ , then  $K = 1$  and so all the gases are at 1 atm or 1 mol/L

-- when  $\Delta G^{\circ} < 0$ , then  $K > 1$  and so  $\Delta G_{\text{reactants}}^{\circ} > \Delta G_{\text{products}}^{\circ}$

-- when  $\Delta G^{\circ} > 0$ , then  $K < 1$  and so  $\Delta G_{\text{reactants}}^{\circ} < \Delta G_{\text{products}}^{\circ}$

- T & K

$$\ln K = -\frac{\Delta G^{\circ}}{RT} = -\frac{\Delta H^{\circ} - T \Delta S^{\circ}}{RT} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

-- hence we could plot the eq constant at different T to determine  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  by using a linear relationship