Chemistry 132 NT

I wish I would have a real tragic love affair and get so bummed out that I'd just quit my job and become a bum for a few years, because I was thinking about doing that anyway.

Jack Handey

1

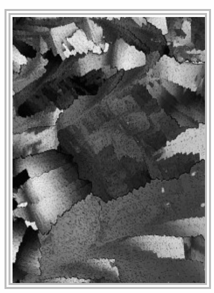
Chem 132 NT

Thermodynamics and Equilibrium

Module 2

Free Energy and Equilibrium Constants

- **Free Energy and Spontaneity**
- **Interpretation of Free Energy**
- **Relating DG to the Equilibrium Constant**
- **Changes of Free Energy with Temperature**



Photomicrograph of urea crystals under polarized light.

2

Review

- Calculating the entropy change for a phase transition
- Predicting the sign of the entropy change of a reaction
- Calculating ΔS^o for a reaction

3

Free Energy Concept

- The American physicist J. Willard Gibbs introduced the concept of **free energy** (sometimes called the **Gibbs free energy**), **G,** which is a thermodynamic quantity defined by the equation **G=H-TS**.
  - This quantity gives a direct criterion for spontaneity of reaction.

Free Energy and Spontaneity

- Changes in **H** an **S** during a reaction result in a **change in free energy,** ΔG , given by the equation

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

  - Thus, if you can show that ΔG **is negative** at a given temperature and pressure, you can predict that **the reaction will be spontaneous**.

Standard Free-Energy Change

- The **standard free energy change,** ΔG^o, is the free energy change that occurs when reactants and products are in their standard states.
  - The next example illustrates the calculation of the standard free energy change, ΔG^o, from ΔH^o and ΔS^o.

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

A Problem To Consider

- What is the standard free energy change, ΔG^o, for the following reaction at 25 ^oC? Use values of ΔH_f^o and S^o, from the appendix in your text.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

	$N_2(g)$	$3H_2(g)$	$2NH_3(g)$
ΔH_f^o:	0	0	2 x (-45.9) kJ
S^o:	191.5	3 x 130.6	2 x 193 J/K

  - Place below each formula the values of ΔH_f^o and S^o multiplied by stoichiometric coefficients.

7

A Problem To Consider

- What is the standard free energy change, ΔG^o, for the following reaction at 25 ^oC? Use values of ΔH_f^o and S^o, from the appendix in your text.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

  - You can calculate ΔH^o and ΔS^o using their respective summation laws.

$$\Delta H^o = \sum n\Delta H_f^o(\text{products}) - \sum m\Delta H_f^o(\text{reactants})$$
$$= [2 \times (-45.9) - 0]\ kJ = -91.8\ kJ$$

8

A Problem To Consider

- What is the standard free energy change, ΔG^o, for the following reaction at 25 ^oC? Use values of ΔH_f^o and S^o, from the appendix in your text.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

  - You can calculate ΔH^o and ΔS^o using their respective summation laws.

$$\Delta S^o = \sum n\Delta S^o(\text{products}) - \sum m\Delta S^o(\text{reactants})$$
$$= [2 \times 193 - (191.5 + 3 \times 130.6)]\ J/K = -197\ J/K$$

9

A Problem To Consider

- What is the standard free energy change, ΔG^o, for the following reaction at 25 °C? Use values of ΔH_f^o and S^o, from the appendix in your text.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

  - Now substitute into our equation for ΔG^o. Note that ΔS^o is converted to kJ/K.

$$\Delta G^o = \Delta H^o - T\Delta S^o$$
$$= -91.8\,kJ - (298\,K)(-0.197\,kJ/K)$$
$$= -33.1\,kJ$$

10

Standard Free Energies of Formation

- The **standard free energy of formation, ΔG_f^o,** of a substance is the free energy change that occurs when 1 mol of a substance is formed from its elements in their most stable states at 1 atm pressure and 25 °C.
  - By tabulating ΔG_f^o for substances, as in the appendix in your text, **you can calculate the ΔG^o** for a reaction by using a summation law.

$$\Delta G^o = \sum n\Delta G_f^o(\text{products}) - \sum m\Delta G_f^o(\text{reactants})$$

11

A Problem To Consider

- Calculate ΔG^o for the combustion of 1 mol of ethanol, C_2H_5OH, at 25 °C. Use the standard free energies of formation given in your appendix.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

ΔG_f^o: -174.8 0 2(-394.4) 3(-228.6)kJ

  - Place below each formula the values of ΔG_f^o multiplied by stoichiometric coefficients.

12

A Problem To Consider

- Calculate ΔG^o for the combustion of 1 mol of ethanol, C_2H_5OH, at 25 °C. Use the standard free energies of formation given in your appendix.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

ΔG_f^o: -174.8   0   2(-394.4)   3(-228.6)kJ

- You can calculate ΔG^o using the summation law.

$$\Delta G^o = \sum n\Delta G_f^o(\text{products}) - \sum m\Delta G_f^o(\text{reactants})$$

$$\Delta G^o = [2(-394.4) + 3(-228.6) - (-174.8)]\,kJ$$

13

A Problem To Consider

- Calculate ΔG^o for the combustion of 1 mol of ethanol, C_2H_5OH, at 25 °C. Use the standard free energies of formation given in your appendix.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

ΔG_f^o: -174.8   0   2(-394.4)   3(-228.6)kJ

- You can calculate ΔG^o using the summation law.

$$\Delta G^o = \sum n\Delta G_f^o(\text{products}) - \sum m\Delta G_f^o(\text{reactants})$$

$$\Delta G^o = -1299.8\,kJ$$

14

ΔG^o as a Criteria for Spontaneity

- The following rules are useful in judging the spontaneity of a reaction.

1. When ΔG^o is a large negative number (more negative than about –10 kJ), **the reaction is spontaneous as written**, and the reactants transform almost entirely to products when equilibrium is reached.

15

ΔG° as a Criteria for Spontaneity

- The following rules are useful in judging the spontaneity of a reaction.

2. When ΔG° is a large positive number (more positive than about +10 kJ), **the reaction is nonspontaneous as written**, and reactants do not give significant amounts of product at equilibrium.

16

ΔG° as a Criteria for Spontaneity

- The following rules are useful in judging the spontaneity of a reaction.

3. When ΔG° is a small negative or positive value (less than about 10 kJ), the reaction gives **an equilibrium mixture with significant amounts of both reactants and products**.

17

Maximum Work

- Often reactions are not carried out in a way that does useful **work**.
  - As a spontaneous precipitation reaction occurs, the free energy of the system decreases and entropy is produced, but **no useful work is obtained**
  - In principle, if a reaction is carried out to obtain the maximum useful work, no entropy is produced.

18

Maximum Work

- Often reactions are not carried out in a way that does useful **work**.
  - It can be shown that the maximum useful work, w_{max} , for a spontaneous reaction is ΔG.

$$w_{max} = \Delta G$$

  - The term ***free energy*** comes from this result.

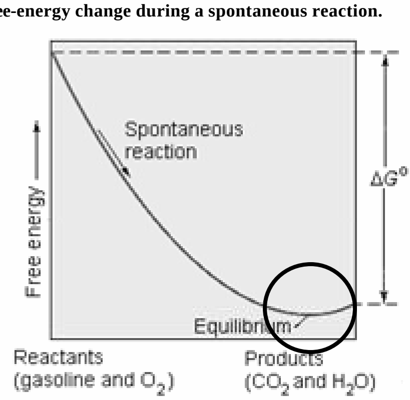
19

Free Energy Change During Reaction

- As a system approaches equilibrium, the **instantaneous change in free energy approaches zero**.
  - The next slide illustrates the change in free energy during a spontaneous reaction.
  - As the reaction proceeds, the free energy eventually reaches its minimum value.
  - At that point, Δ**G = 0**, and the net reaction stops; it comes to **equilibrium**.

20

Free-energy change during a spontaneous reaction.

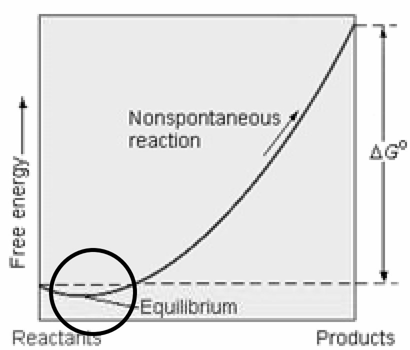


Free Energy Change During Reaction

- As a system approaches equilibrium, the **instantaneous change in free energy approaches zero**.
  - The next slide illustrates the change in free energy during a **nonspontaneous** reaction.
  - Note that there is a small decrease in free energy as the system goes to equilibrium.

22

Free-energy change during a nonspontaneous reaction.



Relating ΔG^o to the Equilibrium Constant

- The free energy change when reactants are **in non-standard states** (other than 1 atm pressure or 1 M) is related to the standard free energy change, ΔG^o, by the following equation.

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

  - Here Q is the thermodynamic form of the reaction quotient.

24

Relating DG° to the Equilibrium Constant

- The free energy change when reactants are **in non-standard states** (other than 1 atm pressure or 1 M) is related to the standard free energy change, ΔG°, by the following equation.

$$\text{D}\mathbf{G} = \text{D}\mathbf{G}^{\mathbf{o}} + \mathbf{RT}\ \mathbf{ln}\mathbf{Q}$$

  - ΔG represents an instantaneous change in free energy at some point in the reaction approaching equilibrium.

25

Relating DG° to the Equilibrium Constant

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$$\text{D}\mathbf{G} = \text{D}\mathbf{G}^{\mathbf{o}} + \mathbf{RT}\ \mathbf{ln}\mathbf{Q}$$

  - At equilibrium, ΔG=0 and the reaction quotient Q becomes the equilibrium constant K.

26

Relating DG° to the Equilibrium Constant

- The free energy change when reactants are **in non-standard states** (other than 1 atm pressure or 1 M) is related to the standard free energy change, ΔG°, by the following equation.

$$\mathbf{0} = \text{D}\mathbf{G}^{\mathbf{o}} + \mathbf{RT}\mathbf{ln}\,\mathbf{K}$$

  - At equilibrium, ΔG=0 and the reaction quotient Q becomes the equilibrium constant K.

27

Relating ΔG^o to the Equilibrium Constant

- This result easily rearranges to give the basic equation **relating the standard free-energy change to the equilibrium constant**.

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

  - When K > 1 , the ln K is positive and ΔG^o is negative.
  - When K < 1 , the ln K is negative and ΔG^o is positive.

28

A Problem To Consider

- Find the value for the equilibrium constant, K, at 25 °C (298 K) for the following reaction. The standard free-energy change, ΔG^o, at 25 °C equals –13.6 kJ.

$$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$$

  - Rearrange the equation ΔG^o=-RTlnK to give

$$\ln K = \frac{\Delta G^o}{-RT}$$

29

A Problem To Consider

- Find the value for the equilibrium constant, K, at 25 °C (298 K) for the following reaction. The standard free-energy change, ΔG^o, at 25 °C equals –13.6 kJ.

$$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$$

  - Substituting numerical values into the equation,

$$\ln K = \frac{-13.6 \times 10^3 \, J}{-8.31 \, J/(mol \cdot K) \times 298 \, K} = 5.49$$

30

A Problem To Consider

- Find the value for the equilibrium constant, K, at 25 °C (298 K) for the following reaction. The standard free-energy change, ΔG^o, at 25 °C equals –13.6 kJ.

$$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$$

  - Hence,

$$K = e^{5.49} = 2.42 \times 10^2$$

31

Spontaneity and Temperature Change

- All of the four possible choices of signs for ΔH^o and ΔS^o give different temperature behaviors for ΔG^o.

ΔH^o	ΔS^o	ΔG^o	Description
–	+	–	Spontaneous at all T
+	–	+	Nonspontaneous at all T
–	–	+ or –	Spontaneous at low T; Nonspontaneous at high T
+	+	+ or –	Nonspontaneous at low T; Spontaneous at high T

32

Calculation of ΔG^o at Various Temperatures

- In this method you **assume that ΔH^o and ΔS^o are essentially constant** with respect to temperature.
  - You get the value of ΔG_T^o at any temperature T by substituting values of ΔH^o and ΔS^o at 25 °C into the following equation.

$$\Delta G_T^o = \Delta H^o - T\Delta S^o$$

33

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 ^oC and 1000 ^oC. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- Place below each formula the values of ΔH_f^o and S^o multiplied by stoichiometric coefficients.

34

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 ^oC and 1000 ^oC. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- You can calculate ΔH^o and ΔS^o using their respective summation laws.

35

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 ^oC and 1000 ^oC. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

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ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

$$\Delta H^o = \sum n\Delta H_f^o(\text{products}) - \sum m\Delta H_f^o(\text{reactants})$$

$$= [(-635.1 - 393.5) - (-1206.9)]\,kJ = 178.3\,kJ$$

36

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 ^{o}C and 1000 ^{o}C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

$$\Delta S^o = \sum n\Delta S^o(\text{products}) - \sum m\Delta S^o(\text{reactants})$$

$$= [(38.2 + 213.7) - (92.9)] = 159.0\ J/K$$

37

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 ^{o}C and 1000 ^{o}C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- Now you substitute ΔH^o, ΔS^o (=0.1590 kJ/K), and T (=298K) into the equation for ΔG_f^o.

$$\Delta G_T^o = \Delta H^o - T\Delta S^o$$

38

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 ^{o}C and 1000 ^{o}C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- Now you substitute ΔH^o, ΔS^o (=0.1590 kJ/K), and T (=298K) into the equation for ΔG_f^o.

$$\Delta G_T^o = 178.3\ kJ - (298\ K)(0.1590\ kJ/K)$$

39

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- Now you substitute ΔH^o, ΔS^o (=0.1590 kJ/K), and T (=298K) into the equation for ΔG_f^o.

$$\Delta G_T^o = 130.9\ kJ$$

So the reaction is **nonspontaneous** at 25 °C.

40

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- Now we'll use 1000 °C (1273 K) along with our previous values for ΔH^o and ΔS^o.

$$\Delta G_T^o = 178.3\ kJ - (1273\ K)(0.1590\ kJ/K)$$

41

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- Now we'll use 1000 °C (1273 K) along with our previous values for ΔH^o and ΔS^o.

$$\Delta G_T^o = -24.1\ kJ$$

So the reaction is **spontaneous** at 1000 °C.

42

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- To determine the minimum temperature for spontaneity, we can set $\Delta G_f^o = 0$ and solve for T.

$$T = \frac{\Delta H^o}{\Delta S^o}$$

43

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- To determine the minimum temperature for spontaneity, we can set $\Delta G_f^o = 0$ and solve for T.

$$T = \frac{178.3\,kJ}{0.1590\,kJ/K} = 1121\,K\ \ (848\ ^oC)$$

44

A Problem To Consider

- Find the ΔG^o for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

ΔH_f^o:	-1206.9	-635.1	-393.5 kJ
S^o:	92.9	38.2	213.7 J/K

- Thus, $CaCO_3$ should be thermally stable until its heated to approximately 848 °C.

45

Operational Skills

- Calculating ΔG^o from ΔH^o and ΔS^o
- Calculating ΔG^o from standard free energies of formation
- Interpreting the sign of ΔG^o
- Writing the expression for a thermodynamic equilibrium constant
- Calculating K from the standard free energy change
- Calculating ΔG^o and K at various temperatures

46

Key Equations

$$\Delta U = q + w$$

$$w = -P\Delta V$$

$$\Delta S > \frac{q}{T}$$ **(For a spontaneous process)**

$$\Delta S = \frac{q}{T}$$ **(For an equilibrium process)**

$$\Delta S^o = \sum n\Delta S^o(\text{products}) - \sum m\Delta S^o(\text{reactants})$$

47

Key Equations

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

$$\Delta G^o = \sum n\Delta G_f^o(\text{products}) - \sum m\Delta G_f^o(\text{reactants})$$

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

$$\Delta G^o = -RT\ln K \quad \textbf{or} \quad \Delta G^o = -2.303\,RT\log K$$

$$\Delta G_T^o = \Delta H^o - T\Delta S^o$$

Time for a few review questions

48


TEACH
Peace
49