Module 2, Lecture 3
Chemical Thermodynamics
Part 3

Learning Objectives:

- Calculate $\Delta_r G^o$ from $\Delta_f G^o$ values and from $\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o$.
- Understand the concept of coupled reactions.
- Understand the concept that, when $\Delta_r G = 0$, the reaction is at equilibrium.
- Appreciate the difference between $\Delta_r G$ and $\Delta_r G^o$ in relation to equilibrium.
- Carry out calculations relating $\Delta_r G$, $\Delta_r G^o$ and K.
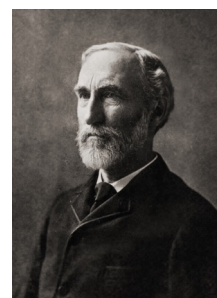
Textbook: Chapter 19

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Gibbs energy

- Gibbs energy (**G**) is defined as follows

$$G = H - TS$$

- **H** is the enthalpy of the system
- **S** is the entropy of the system
- **T** is the temperature in Kelvin (0 °C = 273 K)

Josiah Willard Gibbs

- Can't measure absolute values of *G*, so always talk about the ***change*** in *G* for a process, ΔG

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

- When referring to a chemical reaction (rather than a physical change) we use the usual terminology

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

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ΔG and spontaneity

• The sign of ΔG tells us whether or not a particular process is spontaneous.

If ΔG is negative, the process is spontaneous

If ΔG is zero, the system is at equilibrium

If ΔG is positive, the process is non-spontaneous

• If a process is non-spontaneous, its reverse will be spontaneous.

• The magnitude of ΔG is unimportant with respect to spontaneity, but does tell us **how *far a spontaneous process will proceed towards completion.***

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Spontaneity

		ΔH	
		+	−
ΔS	+	spontaneous at high temperatures / nonspontaneous at low temperatures	spontaneous at all temperatures
	−	nonspontaneous at all temperatures	nonspontaneous at high temperatures / spontaneous at low temperatures

• If ΔH is +ve and ΔS is −ve, the reaction can never be spontaneous at any T

• If ΔH is −ve and ΔS is +ve, the reaction is spontaneous at all T

• If ΔH and ΔS have the same sign, **the spontaneity of the reaction depends on T**

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

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Examples

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

- Melting of ice

$$H_2O(s) \rightarrow H_2O(l)$$

- ΔH is +ve, and ΔS is +ve. We would therefore expect this reaction to be spontaneous only at 'high' temperatures – i.e. above 0 °C
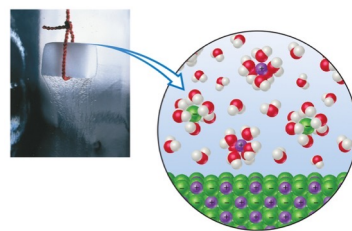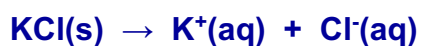
- Freezing of water

$$H_2O(l) \rightarrow H_2O(s)$$

- ΔH is –ve, and ΔS is –ve. We would therefore expect this reaction to be spontaneous only at 'low' temperatures – i.e. below 0 °C

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Entropy of dissolution

$$KCl(s) \rightarrow K^+(aq) + Cl^-(aq)$$

S^o(KCl, s) = 83 J mol^{-1} K^{-1}
S^o(K$^+$, aq) = 103 J mol^{-1} K^{-1}
S^o(Cl$^-$, aq) = 57 J mol^{-1} K^{-1}

ΔS^o = ((103 + 57) – 83) J mol^{-1} K^{-1} = 77 J mol^{-1} K^{-1}

- The entropy change for dissolution of any ionic salt is favourable, as it always involves the formation of a less ordered system

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Enthalpy of dissolution

$$KCl(s) \rightarrow K^+(aq) + Cl^-(aq)$$

$\Delta_f H^o$(KCl, s) = -436 kJ mol^{-1}

$\Delta_f H^o$(K$^+$, aq) = -252 kJ mol^{-1}

$\Delta_f H^o$(Cl$^-$, aq) = -167 kJ mol^{-1}

Be careful that signs don't get lost when subtracting negatives

ΔH^o = [(-252 + -167) – (-436)] kJ mol^{-1} = +17 kJ mol^{-1}

Hence, $\Delta G^o = \Delta H^o – T\Delta S^o$

= 17 × 10^3 J mol^{-1} – (298 K × 77 J mol^{-1} K^{-1})

= -5.9 kJ mol^{-1} Spontaneous

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ΔG^o

- Because most thermodynamic data are tabulated under standard conditions, ΔH^o and ΔS^o values are used to obtain ΔG^o values

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

- However, it is imperative to realise that ΔG^o can **only be used as a criterion of spontaneity _under standard conditions_.**

- As we will see, ΔG^o **is important as a means of determining the position of equilibrium in a chemical system.**

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Calculations involving $\Delta_r G$

• Can generally calculate ΔG for a reaction by one of two methods:

  a) Using $\Delta_r G = \Delta_r H - T\Delta_r S$

*Utilising the fact that G is a **measure of energy including enthalpy and entropy.***

  b) Using $\Delta_f G$ data

*Utilising the fact that the standard Gibbs energy of formation, $\Delta_f G^o$ is **analogous to the standard enthalpy of formation, $\Delta_f H^o$.***
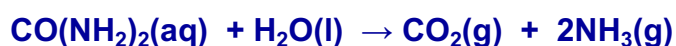
• $\Delta_f G^o$ of any pure element is defined as zero.

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Calculations involving $\Delta_r G$

(a) Calculate $\Delta_r G^o$ for the reaction

$$CO(NH_2)_2(aq) + H_2O(l) \rightarrow CO_2(g) + 2NH_3(g)$$

at 25.0 °C given

$\Delta_r H^o = +119.2$ kJ mol^{-1}

$\Delta_r S^o = +354.8$ J K^{-1} mol^{-1}

Careful Must convert units of either ΔH^o or ΔS^o
Must use temperature in K

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

  $= +119.2$ **× 10^3** J mol^{-1} – (**298** K × 354.8 J K^{-1} mol^{-1})

  $= +13.2 × 10^3$ J mol^{-1}

  $= $ **+13.2 kJ mol^{-1}**

The reaction is non-spontaneous under standard conditions

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Calculations involving $\Delta_r G$

(b) Values of $\Delta_f G^o$ are tabulated and can be used in Hess's Law-type calculations.

$\Delta_r G^o = \sum[\Delta_f G^o \text{ (products)}] - \sum[\Delta_f G^o \text{ (reactants)}]$

(taking account of stoichiometry)

The standard Gibbs energy change for a reaction equals the sum of the Gibbs energies of formation of the products minus the sum of the Gibbs energies of formation of the reactants.

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Calculations involving $\Delta_r G$

(b) Calculate $\Delta_r G^o$ for the reaction

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

at 25.0 ^{o}C given:

$\Delta_f G^o(C_2H_5OH, l) = -174.8$ kJ mol^{-1}

$\Delta_f G^o(CO_2, g) = -394.4$ kJ mol^{-1}

$\Delta_f G^o(H_2O, g) = -228.6$ kJ mol^{-1}

$\Delta_r G^o = [2 \times -394.4$ kJ mol$^{-1} + 3 \times -228.6$ kJ mol$^{-1}]$

$\qquad - [1 \times -174.8$ kJ mol$^{-1} + 3 \times 0$ kJ mol$^{-1}]$

$= -1299.8$ kJ mol^{-1}

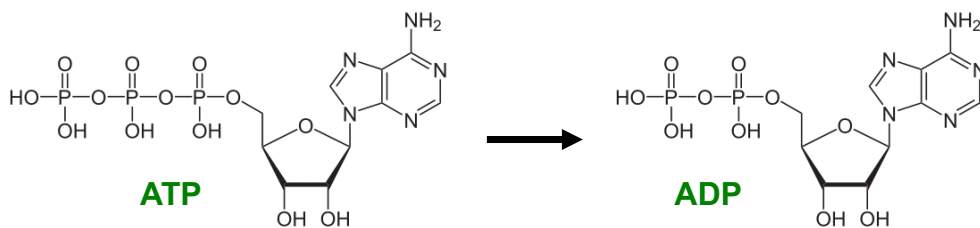**The reaction is spontaneous under standard conditions**

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Coupled reactions

Can use a spontaneous reaction (ΔG -ve) to drive a non-spontaneous reaction (ΔG +ve) by **coupling** them together.

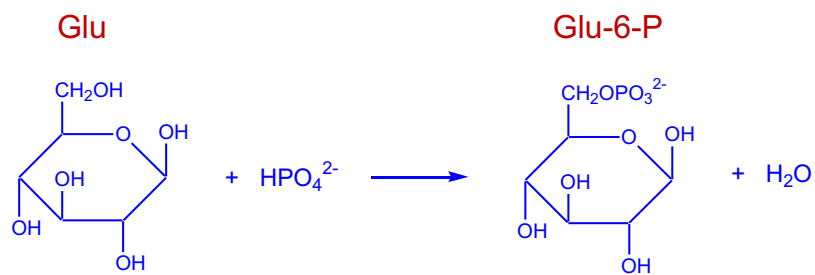In biological systems, the hydrolysis reaction of **adenosine triphosphate**, **ATP**, is often involved.

ATP → **ADP**

$\Delta_r G$ = -30.5 kJ mol^{-1} at pH = 7

NB: Eq. not balanced

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e.g. First step is glucose metabolism is the reaction of glucose with hydrogen phosphate to give glucose-6-phosphate, $\Delta_r G$ = +13.4 kJ mol^{-1} at pH = 7.

Glu   Glu-6-P

$+ HPO_4^{2-}$ → ... $+ H_2O$

Glu → Glu-6-P $\Delta_r G$ = +13.4 kJ mol^{-1}
ATP → ADP $\Delta_r G$ = –30.5 kJ mol^{-1}
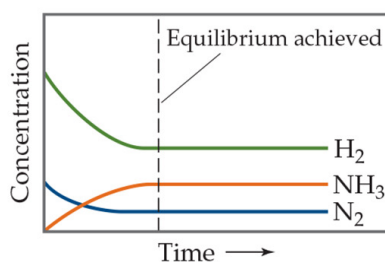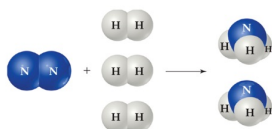
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Glu + ATP → Glu-6-P + ADP $\Delta_r G$ = -17.1 kJ mol^{-1}

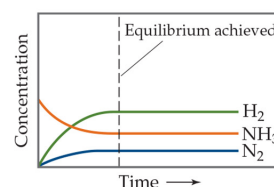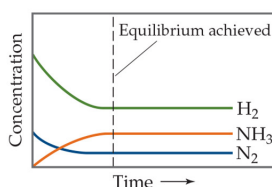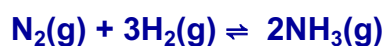**therefore spontaneous at pH = 7**

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$\triangle G = 0$?

- What happens if ΔG is neither +ve or –ve, but zero?

- If $\Delta G = 0$, there is no driving force for chemical or physical change;
   **the system is at equilibrium**

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

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$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
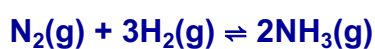
- The equilibrium composition of the N_2,H_2/NH_3 mixture is the same, regardless of whether we start with pure N_2 and H_2, or with pure NH_3.

- The forward and reverse reactions are both occurring at equilibrium. Their rates are identical, so there is **no net change in composition**.

- Why does neither the forward nor reverse reaction proceed to completion? Because **equilibrium is the point where G is minimised.**

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Equilibrium and G

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
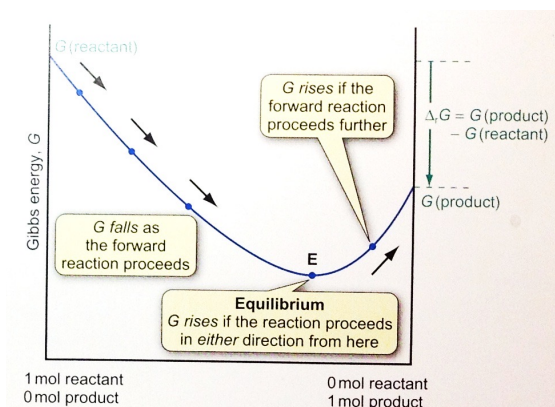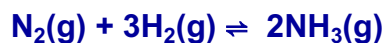
The reaction mixture will reach equilibrium when it reaches the composition corresponding to the minimum G.

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$\Delta_r G$, $\Delta_r G^o$, and K

- $\Delta_r G$ is ***the*** criterion of spontaneity of a process. It is related to $\Delta_r G^o$, which can be obtained from tables, by the equation

$$\boxed{\Delta_r G = \Delta_r G^o + RT \ln Q}$$

- Have already seen that if $\Delta_r G = 0$, the system is at equilibrium. Also, we know that $Q = K$ at equilibrium. Therefore,

$$0 = \Delta_r G^o + RT \ln K$$

and hence

$$\boxed{\Delta_r G^o = -RT \ln K}$$ 🚩 **Careful** Don't forget the negative!

R is the gas constant, 8.314 J mol^{-1} K^{-1}

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Example

Lugol's Iodine is a solution of the triiodide (I_3^-) ion which is used to treat iodine deficiency and as a disinfectant.

I_3^- is prepared by the reaction of I_2 with I^-.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K = 1.26 \times 10^{-3} \text{ at 298 K.}$$

(a)   What is the value of $\Delta_r G^o$ for this reaction?

(b)   If a solution contains $[I_2]$ = 0.65 mol L^{-1}, $[I^-]$ = 1.30 mol L^{-1} and $[I_3^-]$ = 0.02 mol L^{-1}, will the reaction be at equilibrium (ie is $\Delta_r G$ = 0?) and, if not, will the concentration of I_3^- in increase or decrease as equilibrium is established?

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For $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$ $K = 1.26 \times 10^{-3}$ at 298 K.

(a)   What is the value of $\Delta_r G^o$ for this reaction?

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

$= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln(1.26 \times 10^{-3})$

Careful Don't forget the negative!

Answer will be in J mol^{-1} if R is in J K^{-1} mol^{-1}

$= 16542 \text{ J mol}^{-1}$

$= 16.54 \text{ kJ mol}^{-1}$

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For **$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$** K = 1.26x10^{-3} at 298 K.

(b) If a solution contains $[I_2]$ = 0.65 mol L^{-1}, $[I^-]$ = 1.30 mol L^{-1} and $[I_3^-]$ = 0.02 mol L^{-1}, will the reaction be at equilibrium? (i.e. is $\Delta_r G$ = 0?) If not, will the concentration of I_3^- in increase or decrease as equilibrium is established?

$$Q = \frac{[I_3^-]}{[I_2][I^-]} = \frac{(0.02)}{(0.65)(1.30)} = 0.0237$$

$\Delta_r G \quad = \Delta_r G^o + RT \ln Q$

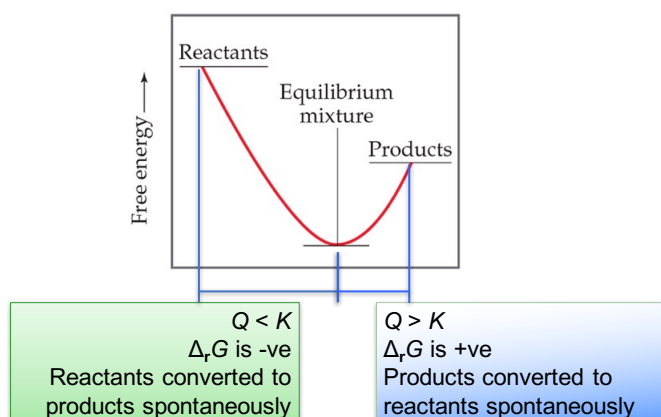**Careful** Make sure $\Delta_r G^o$ is in J mol^{-1} to match R.

$\quad\quad = 16.54 \times 10^3$ J + (8.314 J K^{-1} mol^{-1} x 298 x ln (0.0237)) 🚩

$\quad\quad = 7270$ J mol^{-1}

$\quad\quad = 72.7$ kJ mol^{-1}

$\Delta_r G \neq 0$, therefore the system is not at equilibrium.

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Since the value of $\Delta_r G$ **is +ve**, the **position of equilibrium will move to the left** to achieve equilibrium and, in doing so, the **$[I_3^-]$ will decrease**.

$Q < K$	$Q > K$
$\Delta_r G$ is -ve	$\Delta_r G$ is +ve
Reactants converted to products spontaneously	Products converted to reactants spontaneously

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✳ Homework ✳

Chemistry – the central science 15th Ed

Brown et al.

Problem 19.79

Answers on Blackboard

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