



Exam Type Question

In the absence of an adequate supply of oxygen, yeasts obtain metabolic energy by fermentation of glucose to produce ethanol.

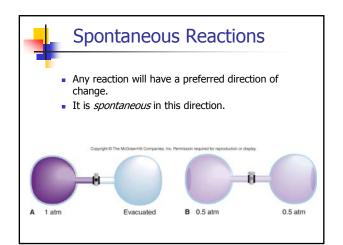
$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(I) + 2CO_2(g)$$

Use the standard enthalpies of formation to calculate $\Delta {\cal H}^{\,\circ}$ for this reaction.

Thermochemical Data at 298 K Substance $\Delta_f H^{\circ}/ \text{ kJ mol}^{-1}$ glucose(s) -1274

 $CO_2(g)$ -393 $C_2H_5OH(I)$ -278

2 marks





Entropy

- While most exothermic reactions ($\Delta H < 0$) are spontaneous, some endothermic ones ($\Delta H > 0$) are also spontaneous.
- Entropy (S) is also important.
- Entropy depends on how random a system is: this disorder can be positional or thermal



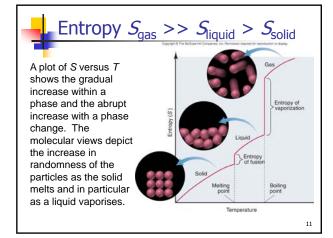




Entropy - 5

- Entropy is a measure of the randomness or disorder.
 - The natural progression of things is from an ordered to a disordered state.
- **Entropy** is a thermodynamic quantity that describes the number of arrangements that are available to the system in a given state.
- The main concept here is the more ways a particular state can be achieved the greater is the likelihood of finding it in that state.







Temperature and Spontaneity

Consider the process: H₂O (I) → H₂O (g)

We could deduce that: ΔH° - endothermic

and ΔS° is positive

Experience shows us:

T>100 °C – vaporisation is spontaneous T<100 °C – condensation is spontaneous

So conclude that: T is important, in the spontaneity of reactions

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Gibbs Free Energy - △G

The effects of enthalpy (ΔH) and entropy (ΔS) on a reaction are combined to give the Gibbs Free Energy

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

(ΔG can not be measured directly but can be calculated from ΔH and ΔS .)

- Note: △G is dependent on temperature
 - $\Delta G > 0$ Reaction is not spontaneous
 - $\Delta G = 0$ System is at equilibrium
 - $\Delta G < 0$ Reaction is spontaneous

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Why is ΔG^o important?



Knowing the ΔG^o values for several reactions allows us to compare the relative tendencies of reactions to occur.

- The more negative the value of ΔG^o the further the reaction will go towards completion.
- (We must use standard free energy for these comparisons since free energy changes with pressure or concentration).

If a reaction is not spontaneous ($\Delta G^o > 0$) we can do two things to get it to work:

- Change the temp until $\Delta G^o < 0$ (in the lab)
- \bullet Couple it with another reaction such that overall $\Delta \textit{G}^{o} < 0$ (living systems)

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Example: $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

At what temperature will the following reaction become spontaneous? $N_2(g) + O_2(g) \rightarrow 2 NO(g)$

$$\Delta S^{\circ} = (2 \times 210.5) - (191.4 + 204.9) = +24.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

 $\Delta H^{\circ} = 2 \times 90.4 = 180.8 \text{ kJ mol}^{-1}$

$$\Delta H^0 = 2 \times 90.4 = 180.8 \text{ kJ mol}^{-1}$$

 $\Delta G^0 = 180.8 - (T \times 24.7 \times 10^{-3}) \text{ kJ mol}^{-1}$

For spontaneity
$$\Delta G < 0$$

 \therefore (T x 24.7 x 10⁻³)> 180.8



Question

Calculate ΔG° (298 K) for the reaction and determine whether it is spontaneous at this temperature.

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

Data:
$$\Delta_1 G^{\circ}$$
 (CO) = -137.2 kJ mol⁻¹, $\Delta_1 G^{\circ}$ (CO₂) = -394.4 kJ mol⁻¹ and, by definition, $\Delta_1 G^{\circ}$ (element) = 0.

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The Role of ATP

The initial step in the metabolic breakdown of glucose is a phosphoralation reaction.

Glucose +
$$HPO_4^{2-}$$
 + $H^+ \rightarrow [glucose phosphate]^- + H_2O
 $\Delta G^\circ = +13.8 \text{ kJ mol}^{-1}$$

But this is not spontaneous so it is coupled with a reaction that is spontaneous. All organisms use the hydrolysis of adenosine triposphate (ATP) to ADP to drive this process.

ATP⁴⁻ +
$$H_2O \rightarrow ADP^{3-} + HPO_4^{2-} + H^+$$

 $\Delta G^{\circ} = -30.5 \text{ kJ mol}^{-1}$



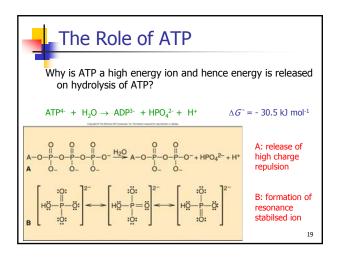
The Role of ATP

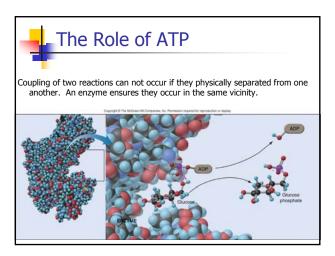
Glucose + HPO₄²⁻ + H⁺
$$\rightarrow$$
 [glucose phosphate]⁻ + H₂O $\triangle G^{\circ}$ = +13.8 kJ mol⁻¹

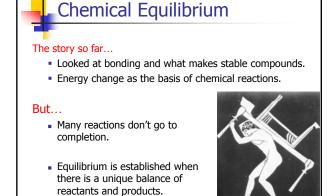
$$ATP^{4-} + H_2O \rightarrow ADP^{3-} + HPO_4^{2-} + H^+$$
 $\Delta G^{\circ} = -30.5 \text{ kJ mol}^{-1}$

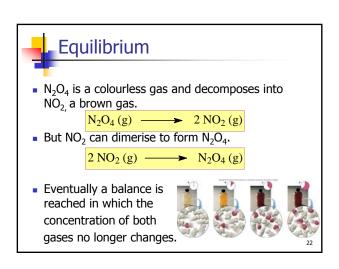
Glucose + ATP⁴⁻
$$\rightarrow$$
 [glucose phosphate]⁻ + ADP³⁻ $\triangle G^{\circ}$ = - 16.7 kJ mol⁻¹

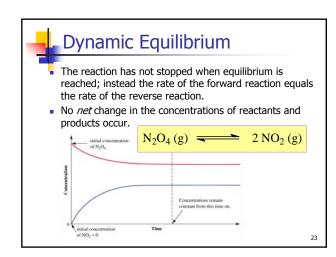
Reactions that release energy convert ADP to ATP and reactions that require energy are coupled with hydrolysis of ATP to ADP.

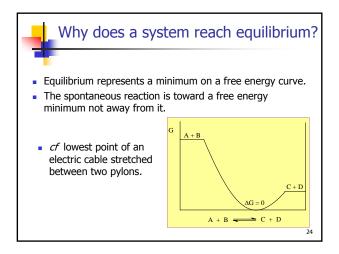


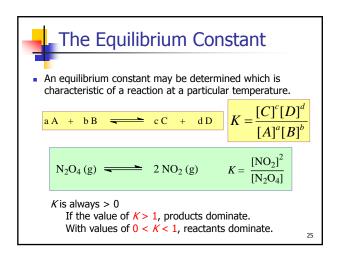


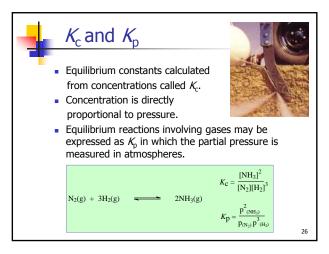


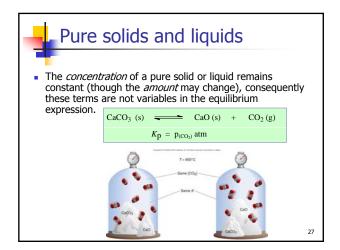


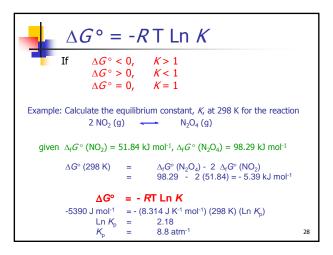


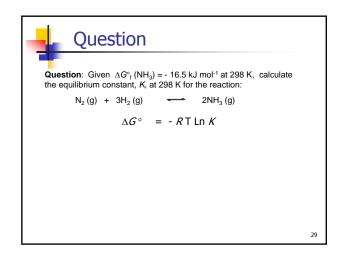


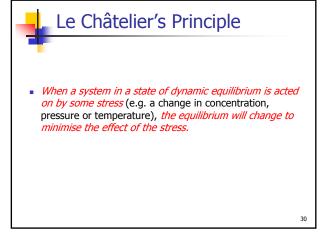














The Effect of Pressure

Add more gaseous reactant or product - conc effect

 The effect will be to shift the reaction in the direction away from the added component.

Add an inert gas at constant volume (one not involved in the reaction)

 This will increase the total pressure but will have no effect on the concentrations or partial pressures of the reactants or products. Thus will have NO effect on the equilibrium.

Increase the volume of the chamber (or add an inert gas at constant pressure)

 Partial pressures (and concentrations) of reactants and products will decrease. The equilibrium shifts to the side of more gas molecules



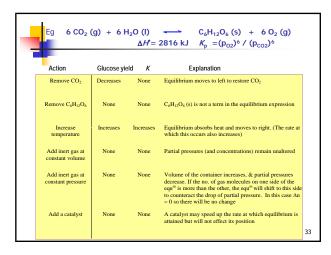
Reduce the volume of the chamber The equilibrium shifts to the left 31

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The Effect of Temperature

- $\, \bullet \,$ The value of K depends on temperature think of enthalpy as a type of product
 - Exothermic reactions: Increase T, decrease K
 N₂ + 3H₂ 2NH₃ and 92 kJ
 - Endothermic reactions: Increase T, increase K 556 kJ and CaCO₃ CaO + CO₂
- A catalyst increases the rate of reaction
 - NO effect on the equilibrium constant (K)

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Question

 The acidity of blood plasma is controlled by the following equilibrium:

$$CO_2$$
 + H_2O \longrightarrow H^+ + HCO_3^-

Normal blood plasma has a pH of 7.4 and ratio of $[HCO_3^-]$ / $[CO_2]$ = 20 / 1.

Hyperventilation (rapid, deep breathing) results in "blow off" of CO₂ which decreases the concentration of dissolved CO₂. What effect will this have on the [H+] of the blood?

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Example

To improve the quality of x-ray photos during the diagnosis of intestinal disorders, a patient drinks a suspension of $BaSO_4$ as Ba^{2+} ions are opaque to x-rays. However Ba^{2+} is also toxic and the suspension is usually administered as a suspension in 0.1 M Na_2SO_4 .

Why?

Note BaSO₄(s)
$$\longrightarrow$$
 Ba²⁺(aq) + SO₄²⁻(aq)
 $K = 1.1 \times 10^{-10} \text{ M}^2$

