2009-J-2

- Most of the lighter elements (at. no. up to 20) are essential elements. They are readily available in nature, so more likely to be utilised by organisms. Similarly most of the lighter *d*-block elements (Sc - Zn) are essential (utilised in redox and electron transport systems in the body) whereas the heavier transition metals are generally toxic.

- The second ionisation of Na will be off the scale as a core electron is ionised. (Actual value > 4500 kJ mol^{-1}) Mg^+ is isoelectronic with Na, Al^+ is isoelectronic with Mg, *etc*., so the second ionisations of the other elements follow the same trends as the first ionisations (for exactly the same reasons), but displaced one atomic number to the right and at a slightly higher energy (as Z_{eff} is greater).

2009-J-3

- $Ca(CH_3CO_2)_2(s) \rightarrow Ca^{2+}(aq) + 2CH_3CO_2^-(aq)$

  9.52

  5.61

2009-J-4

- Water would be a gas. The other hydrides of group 16 elements increase in b.p. as the molar mass increases, due to the increase in dispersion forces. H_2S is a gas. H_2O has an anomalously high b.p. due to H-bonds. Without H-bonds it would have a b.p. below that of H_2S.

- Henry's law states that the higher the pressure of gas above a liquid, the greater the solubility of the gas in that liquid: $c = kP$
  Normal air is 21% O_2. Anaesthetists can ensure a patient receives enough O_2 during surgery by increasing the % (*i.e.* partial pressure) of O_2 in the gas the patient breathes. This is the most practical and easy approach. The alternative would be to get the patient to breathe a mixture of air at a pressure greater than 1 atm, but this would be more difficult to control and could lead to other problems (*e.g.*" the bends").

- 5.5 g

2009-J-5

- Graph B is correct.

  Graphs A and C: As $K_c = 2$, the reaction does not go anywhere near to completion. Graphs A and C can therefore be rejected because at least one reagent in both these graphs has dropped to 0. Also, in Graph C, the rates of change of $[Br_2]$ and $[Cl_2]$ are different, at variance with the stoichiometry of the reaction.

  Graph D: Cl_2 is the limiting reagent, so the maximum [BrCl] that can form is twice the initial $[Cl_2]$. Clearly more than this has formed at equilibrium.

2009-J-6

- 12 hours

- $CO_2(aq)$ and $HCO_3^-(aq)$ constitute a buffer system:

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$
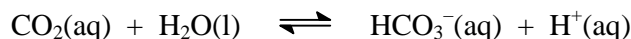
Excess H^+ is removed by: $HCO_3^-(aq) + H^+(aq) \rightarrow CO_2(aq) + H_2O(l)$

Excess OH^- is removed by: $CO_2(aq) + OH^-(aq) \rightarrow HCO_3^-(aq)$

Hyperventilation removes CO_2 from the blood. This shifts the above buffer equilibrium to the left (Le Chatelier's principle), $[H^+(aq)]$ decreases and the blood pH increases.

2009-J-7

- The molecules need to be orientated correctly and they need to have enough energy (above the activation energy, E_a) for a reaction to occur.

The relationships between the activation energy, E_a, the temperature, T, and the rate constant, k, are summarised by the Arrhenius equation, $k = Ae^{-Ea/RT}$. This shows that the higher the activation energy, the lower the rate constant and the lower the reaction rate.

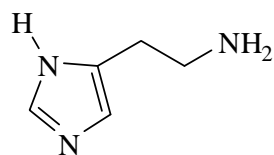- The auto-ionisation of water is an endothermic reaction
$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H > 0.$$
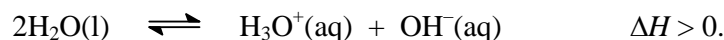
Increasing the temperature will push this reaction to the right, so the $[H_3O^+(aq)]$ will increase and the pH will therefore decrease.

Pure water is neutral as $[H_3O^+(aq)] = [OH^-(aq)]$

2009-J-8

- sp^2 bent

  sp^2 trigonal planar

  sp^3 trigonal pyramidal

N#1 is basic. The "lone pair" on N#2 is part of the aromatic system. The lone pair on N#1 is not, so is available to accept a proton.
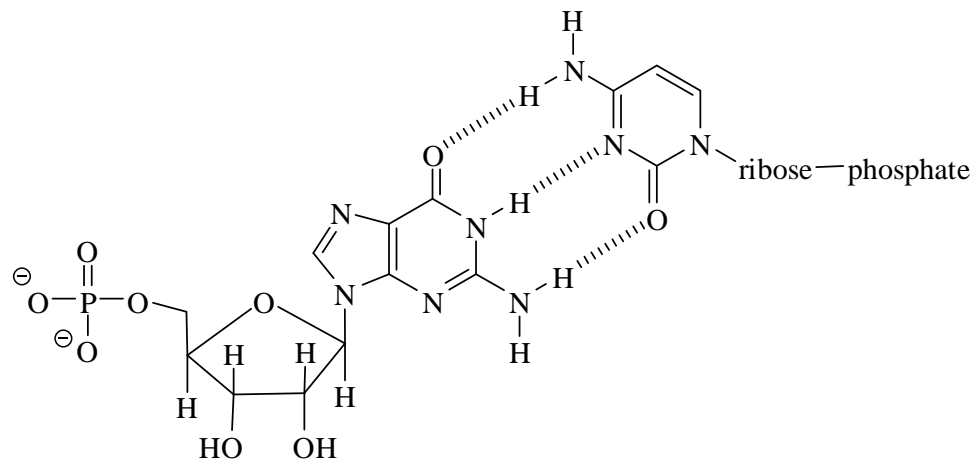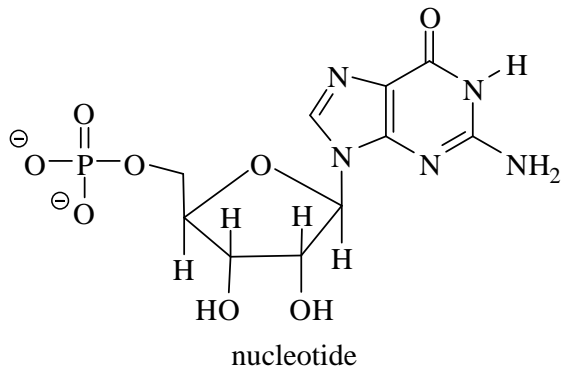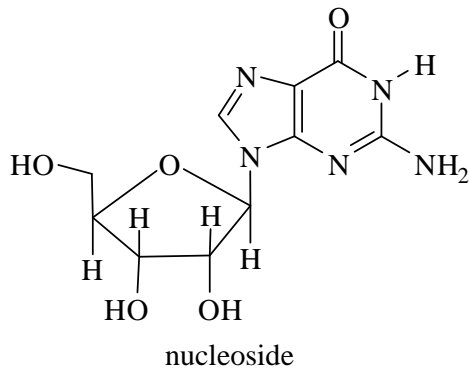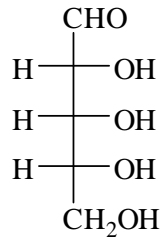
2009-J-9

Polaramine has a basic aromatic N and an aliphatic N separated by 5 bonds, as does histamine. It is therefore likely that it will compete with histamine for the binding sites of certain enzymes in the body and thus block the effects of histamine.

It rotates plane poarised light in a clockwise direction.

- $SOCl_2$

  $NaN(CH_3)_2$ or $HN(CH_3)_2$ followed by OH^-

  excess CH_3OH / H^+ catalyst / heat

2009-J-10

- β

    reducing
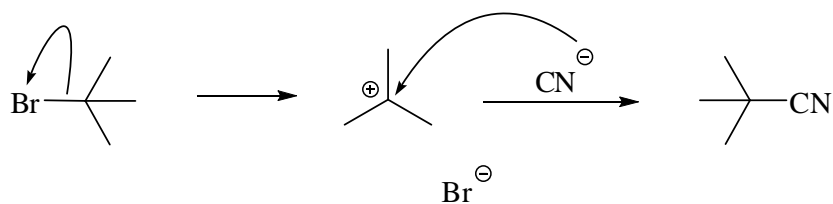

anomeric carbon

nucleoside

nucleotide

ribose—phosphate
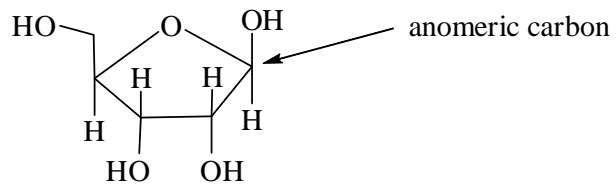
2009-J-11

•

• When HX adds across the double bond of an unsymmetrical alkene, the H goes to the carbon that already has the greater number of H's attached.
This occurs because the relative stabilities of the intermediate carbocations that can form in this reaction have the following order: tertiary > secondary > primary > CH_3^+.
e.g.
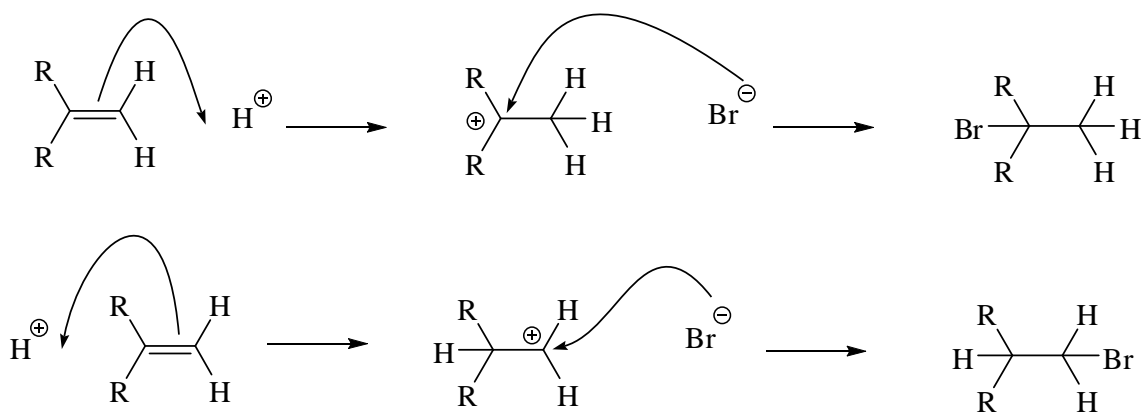
The tertiary carbocation produced in the top reaction is more stable than the primary carbocation produced in the bottom reaction, so the major pathway is the top reaction.

2009-J-12

- Yes. It has a number of charged groups that will be solvated by water molecules due to ion-dipole interactions.

$$\overset{\oplus}{H_3N}-CH-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{}{N}}-CH-\overset{O}{\overset{\|}{C}}-OH$$

with side chains:
CH_2—SH ; CH_2—CH_2—$C{=}O$—OH

$+$

$$HO-\overset{SH}{\underset{}{\overset{|}{C}H_2}}\ \ ;\ \ HO-\overset{}{\underset{O}{\overset{\|}{C}}}-CH-\overset{\oplus}{NH_3}$$

2 x

$$H_2N-CH-CO_2^{\ominus}$$
$$\underset{CH_2}{|}$$
$$\underset{S^{\ominus}}{|}$$

$+$

$$H_2N-CH-CO_2^{\ominus}$$
$$\underset{CH_2}{|}$$
$$\underset{CH_2}{|}$$
$$\underset{CO_2^{\ominus}}{|}$$

$$HO_2CCH_2CH_2\overset{COOH}{\underset{NH_2}{\overset{|}{\underset{}{C}}}}\text{''}H$$

or

$$H_2N\overset{COOH}{\underset{CH_2SH}{\overset{|}{\underset{}{C}}}}\text{''}H$$

2009-J-13

-

$+$ $CH_3\overset{\oplus}{NH_3}$