What quantity of heat is released when 15.2 g of propane (C\textsubscript{3}H\textsubscript{8}) is burnt according to the following equation?

\[
\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \quad \Delta H = -2221 \text{ kJ mol}^{-1}
\]

The molar mass of C\textsubscript{3}H\textsubscript{8} is \((3 \times 12.01 \text{ (C)} + 8 \times 1.008 \text{ (H)}) \text{ g mol}^{-1} = 44.094 \text{ g mol}^{-1}\). Hence, a mass of 15.2 g corresponds to:

\[
\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{15.2 \text{ g}}{44.094 \text{ g mol}^{-1}} = 0.345 \text{ mol}
\]

As 2221 kJ of heat are generated by burning one mole, this quantity generates:

\[
\text{heat} = (0.345 \text{ mol}) \times (2221 \text{ kJ mol}^{-1}) = 766 \text{ kJ}
\]
• Ascorbic acid (Vitamin C) is a monoprotic acid of formula $C_6H_8O_6$. Calculate the pH of a 0.10 M solution of ascorbic acid, given the $K_a$ of ascorbic acid is $8.0 \times 10^{-5}$ M.

As ascorbic acid is a weak acid, $[H_3O^+]$ must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>$C_6H_8O_6$</th>
<th>$H_2O$</th>
<th>$\Rightarrow$</th>
<th>$H_3O^+$</th>
<th>$C_6H_7O_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.1</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>~x</td>
<td>negligible</td>
<td></td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.10 − x</td>
<td>large</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant $K_a$ is given by:

$$K_a = \frac{[H_3O^+(aq)][C_6H_7O_6^-(aq)]}{[C_6H_8O_6(aq)]} = \frac{x^2}{(0.10−x)}$$

As $K_a = 8.0 \times 10^{-5}$ is very small, $0.10−x \sim 0.10$ and hence:

$$x^2 = 0.1 \times (8.0 \times 10^{-5}) \text{ or } x = 2.8 \times 10^{-3} \text{ M} = [H_3O^+(aq)]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+(aq)] = -\log_{10}[0.0028] = 2.5$$

Answer: $pH = 2.5$

• Write equations to show what happens to a buffer solution containing equimolar amounts of $C_6H_5CH_2COOH$ and $C_6H_5CH_2COOK$ when:
  (a) $H_3O^+$ is added, (b) $OH^−$ is added.

(a) $C_6H_5CH_2COO^−(aq) + H_3O^+(aq) \rightarrow C_6H_5CH_2COOH(aq) + H_2O(l)$

(b) $C_6H_5CH_2COOH(aq) + OH^−(aq) \rightarrow C_6H_5CH_2COO^−(aq) + H_2O(l)$
How much heat is evolved when 907 g of ammonia is produced according to the following equation? (Assume the reaction occurs at constant pressure.)

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \quad \Delta H = -91.8 \text{ kJ mol}^{-1} \]

The molar mass of ammonia, \( \text{NH}_3 \), is \( 14.01 \text{ (N)} + 3 \times 1.008 \text{ (H)} = 17.034 \text{ g mol}^{-1} \).

Thus, the number of moles of ammonia is:

\[
\text{number of moles} = \frac{\text{mass (in g)}}{\text{molar mass (in g mol}^{-1})} = \frac{907 \text{ g}}{17.034 \text{ g mol}^{-1}} = 53.2 \text{ mol}
\]

The chemical equation shows that when two moles are produced, \( \Delta H = -91.8 \text{ kJ mol}^{-1} \) and so half this value is evolved when one mole is produced.

Hence, 53.2 mol will produce:

\[
\text{heat produced} = 91.8 \text{ kJ mol}^{-1} \times 0.5 \times 53.2 \text{ mol} = 2440 \text{ kJ} = 2.44 \text{ MJ}
\]

Answer: 2440 kJ or 2.44 MJ
• Calculate the pH of a solution that is 0.010 M in benzoic acid, C₆H₅COOH, and 0.010 M in C₆H₅CO₂Na. The $K_a$ of benzoic acid is $6.4 \times 10^{-5}$ M.

This solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used:

$$\text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

As [acetic acid] = [sodium acetate],

$$\log_{10} \left( \frac{0.010}{0.010} \right) = \log_{10}(1) = 0$$

and so

$$\text{pH} = pK_a = -\log(6.4 \times 10^{-5}) = 4.19$$

Answer: 4.19

Would this solution make a good buffer system? Give reasons for your answer?

Because the concentrations of weak acid and conjugate base are equal, this solution is a good buffer system. (Good buffers require this ratio to be between 0.1 and 10.)

As the concentrations are only 0.010 M, the buffer does not have a very great capacity. It will buffer effectively for small amounts of added $H^+$ or $OH^-$, but large amounts will quickly cause the weak acid/conjugate base ratio to move outside the 0.1-10 range.

• The gases NO₂ and N₂O₄ are in equilibrium according to the following equation.

$$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \quad \Delta H = +57 \text{ kJ mol}^{-1}$$

In which direction will the reaction move when the following changes are made?

The pressure is increased by decreasing the volume.

The reaction involves 1 mol $\rightarrow$ 2 mol so the system will react to an increase in pressure by shifting to lower to the left to reduce it: shift to reactants.

The temperature is increased.

The reaction is endothermic so the system will react to an increase in temperature by shifting to the right to reduce it: shift to products.
Quinine is a natural product that has anti-malarial properties. It was originally extracted for therapeutic use from the bark of the cinchona tree, but is now synthesised by the pharmaceutical industry. Quinine is not very soluble in water and is generally administered as the more soluble hydrochloride salt \((\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2\cdot\text{HCl})\). The \(pK_a\) of this salt is 4.32. What is the pH of a 0.053 M solution of quinine hydrochloride?

As ascorbic acid is a weak acid, \([\text{H}_3\text{O}^+]\) must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>acid</th>
<th>(\text{H}_2\text{O})</th>
<th>(\rightleftharpoons)</th>
<th>(\text{H}_3\text{O}^+)</th>
<th>base</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.053</td>
<td>large</td>
<td>(\rightleftharpoons)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>(-x)</td>
<td>negligible</td>
<td>(+x)</td>
<td>(+x)</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.053 (-x)</td>
<td>large</td>
<td>(x)</td>
<td>(x)</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_a\) is given by:

\[
K_a = \frac{[\text{H}_3\text{O}^+(aq)][\text{base}]}{[\text{acid}]} = \frac{x^2}{(0.053-x)}
\]

As \(pK_a = 4.32\), \(K_a = 10^{-4.32}\) and is very small, \(0.053 - x \sim 0.053\) and hence:

\[
x^2 = 0.053 \times (10^{-4.32}) \text{ or } x = 1.59 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+(aq)]
\]

Hence, the pH is given by:

\[
\text{pH} = -\log_{10}[\text{H}_3\text{O}^+(aq)] = -\log_{10}[0.00159] = 2.80
\]

Answer: \(\text{pH} = 2.80\)

Use chemical equations to illustrate how \(\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-\) can act as a buffer.

The \(\text{HPO}_4^{2-}(aq)\) acts as a base and can take up added \(\text{H}^+(aq)\):

\[
\text{HPO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l)
\]

The \(\text{H}_2\text{PO}_4^-\)(aq) acts as an acid and can take up added \(\text{OH}^-\)(aq):

\[
\text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq) \rightarrow \text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l)
\]

The system thus has the capacity to maintain the pH.
• For the reaction \[ 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \text{ at 25 } ^\circ\text{C} \]

\[ \Delta H^\circ = -198.4 \text{ kJ mol}^{-1} \text{ and } \Delta S^\circ = -187.9 \text{ J K}^{-1} \text{ mol}^{-1} \]

Show that this reaction is spontaneous in the forward direction at 25 °C.

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \]

\[ \Delta G^\circ = ((-198.4 \times 10^3) \text{ J mol}^{-1}) - ((25 + 273) \text{ K}) \times (-187.9 \text{ J K}^{-1} \text{ mol}^{-1}) \]

\[ = -142400 \text{ J mol}^{-1} = -142.4 \text{ kJ mol}^{-1} \]

As \( \Delta G^\circ < 0 \), the reaction is spontaneous.

If the volume of the reaction system is increased at 25 °C, in which direction will the equilibrium move?

In the reaction, 3 mol of gas \( \rightarrow \) 2 mol of gas. In the volume of the reaction system is increased, the pressure will decrease. The reaction will shift to produce more gas: it will shift to the left (reactants).

Calculate the value of the equilibrium constant, \( K_p \), at 25 °C.

Using \( \Delta G^\circ = -RT \ln K_p \):

\[ (-142.4 \times 10^3) \text{ J mol}^{-1} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) \times \ln K_p \]

\[ K_p = 9.3 \times 10^{24} \]

Assuming \( \Delta H^\circ \) and \( \Delta S^\circ \) are independent of temperature, in which temperature range is the reaction non-spontaneous?

The reaction is spontaneous as long as \( \Delta H^\circ - T\Delta S^\circ < 0 \). \( \Delta G^\circ = 0 \) when

\[ T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-198.4 \times 10^3 \text{ J mol}^{-1})}{(-187.9 \text{ J K}^{-1} \text{ mol}^{-1})} = 1056 \text{ K} \]

The reaction is spontaneous below this temperature and non-spontaneous above it.

Answer: \( T > 1056 \text{ K} \)
The balanced equation for the complete oxidation of glucose to carbon dioxide and water is given below.

\[ \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \]

Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of glucose.

The molar mass of glucose is:

\[(6 \times 12.01 (\text{C})) + (12 \times 1.008 (\text{H})) + (6 \times 16.00 (\text{O})) \text{ g mol}^{-1} = 180.156 \text{ g mol}^{-1}\]

1.0 g of glucose corresponds to

\[\frac{\text{mass}}{\text{molar mass}} = \frac{1.00 \text{ g}}{180.156 \text{ g mol}^{-1}} = 0.00555 \text{ mol}\]

From the chemical equation, oxidation of 1 mol of glucose leads 6 mol of CO$_2$. Hence the number of moles of CO$_2$ produced is $6 \times 0.00555 \text{ mol} = 0.0333 \text{ mol}$.

The molar mass of CO$_2$ is $(12.01 (\text{C})) + 2 \times 16.00 (\text{O})) \text{ g mol}^{-1} = 44.01 \text{ g mol}^{-1}$

Therefore, the number of mass of CO$_2$ produced is:

\[\text{mass} = \text{number of moles} \times \text{molar mass} = (0.0333 \text{ mol}) \times (44.01 \text{ g mol}^{-1}) = 1.47 \text{ g}\]

Answer: 1.47 g
Glucose is a common food source. The net reaction for its metabolism in humans is:
\[ \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]

Calculate \( \Delta H^\circ \) for this reaction given the following heats of formation.
\( \Delta H^\circ_f(\text{C}_6\text{H}_{12}\text{O}_6(s)) = -1274 \text{ kJ mol}^{-1} \), \( \Delta H^\circ_f(\text{CO}_2(g)) = -393 \text{ kJ mol}^{-1} \) and \( \Delta H^\circ_f(\text{H}_2\text{O}(l)) = -285 \text{ kJ mol}^{-1} \)

Using \( \Delta_{\text{rxn}}H^\circ = \Sigma m\Delta H^\circ_f(\text{products}) - n\Delta H^\circ_f(\text{reactants}) \) and as \( \Delta H^\circ_f(\text{O}_2(g)) \) for an element in its standard state:
\[
\Delta_{\text{rxn}}H^\circ = [(6 \times -393) + (6 \times -285)] - [-1274] \text{ kJ mol}^{-1} = -2794 \text{ kJ mol}^{-1}
\]

If the combustion of glucose is carried out in air, water is produced as a vapour. Calculate the \( \Delta H^\circ \) for the combustion of glucose in air given that
\[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H = +44 \text{ kJ mol}^{-1} \]

As vaporising liquid water requires energy (+44 kJ mol\(^{-1}\)), the combustion enthalpy is reduced. Six moles of \( \text{H}_2\text{O} \) are produced in the combustion so the enthalpy of combustion is reduced to:
\[ (-2794 + (6 \times +44)) \text{ kJ mol}^{-1} = -2530 \text{ kJ mol}^{-1} \]

Will \( \Delta S \) be different for the two oxidation reactions? If so, how will it differ and why?

As gaseous molecules have higher entropy than liquid phase molecules, oxidation to produce \( \text{H}_2\text{O}(g) \) will lead to a higher value for \( \Delta S \) than oxidation to produce \( \text{H}_2\text{O}(l) \).
Butyric acid, \( \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \), is found in rancid butter and parmesan cheese. The \( K_a \) of butyric acid is 4.83.

(a) What is the pH of a 0.10 M water solution of butyric acid?

As \( pK_a = -\log K_a = 4.83 \), \( K_a = 10^{-4.83} \). Denoting butyric acid as HA, the initial concentration of [HA(aq)] = 0.10 M. The reaction table is then:

<table>
<thead>
<tr>
<th>( t = 0 )</th>
<th>0.10.</th>
<th>( \Leftrightarrow )</th>
<th>[H(_3)O(^+)(aq)]</th>
<th>[A(^-)(aq)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.10-(x)</td>
<td>(x)</td>
<td>(x)</td>
<td></td>
</tr>
</tbody>
</table>

Hence, \( K_a = \frac{[\text{H}_3\text{O}^+(aq)][\text{A}^-\text{(aq)}]}{[\text{AH}(aq)]} = \frac{x^2}{(0.10-x)} \)

As \( K_a \) is small, the amount of dissociation, \( x \), is also small so \( 0.10-x \sim 0.10 \).

Using this approximation, \( K_a = \frac{x^2}{0.10} = 10^{-4.83} \) hence \( x = 1.22 \times 10^{-3} \) M.

As \( x = [\text{H}_3\text{O}^+(aq)] \), \( \text{pH} = -\log[\text{H}_3\text{O}^+(aq)] = -\log(1.22 \times 10^{-3}) = 2.92 \)

Answer: 2.92

(b) Calculate the pH of the solution formed when 0.050 mol of NaOH(s) is added to 1.0 L of 0.10 M butyric acid.

As NaOH is a strong base, it will dissociate completely and each mole of OH\(^-\) will react with butyric acid to form one mole of A\(^-\)(aq).

1.0 L of 0.10 M HA contains 0.10 mol. After addition of 0.050 mol of OH\(^-\), the number of moles of HA = \((0.10 - 0.050) = 0.05 \) mol and the number of moles of A\(^-\) = 0.050 mol.

As 1.0 L of solution is present, [HA(aq)] = 0.05 M and [A\(^-\)(aq)] = 0.05 M. Substituting into the expression for \( K_a \) gives:

\[
K_a = \frac{[\text{H}_3\text{O}^+(aq)][\text{A}^-\text{(aq)}]}{[\text{AH}(aq)]} = \frac{[\text{H}_3\text{O}^+(aq)] \times (0.05)}{0.05} = 10^{-4.83}
\]

so \([\text{H}_3\text{O}^+(aq)] = 1.5 \) M

Hence, \( \text{pH} = -\log[\text{H}_3\text{O}^+(aq)] = 4.83 \)

Answer: 4.83
(c) Using equations, comment on how the final solution in (b) will respond to additions of small amounts of acid or base in comparison to 1 L of water.

Solution (b) consists of a mixture of a weak acid and its conjugate base: it is a buffer system and will resist changes in pH. If acid is added, the system can respond by removing it using $\text{A}^-$:

$$\text{H}^+(\text{aq}) + \text{A}^-(\text{aq}) \rightarrow \text{HA}(\text{aq})$$

If base is added, the system can respond by removing it using HA:

$$\text{OH}^- (\text{aq}) + \text{HA}(\text{aq}) \rightarrow \text{H}_2\text{O}(l) + \text{A}^-(\text{aq})$$
- Consider the reaction of H₂(g) with I₂(g) at 298 K to give HI(g).

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \quad K_p = 2.24 \]

If partial pressures of 0.20 atm of all three gases are mixed, in which direction will the reaction proceed?

The reaction quotient \( Q = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{(0.20)^2}{(0.20)(0.20)} = 1.0 \)

As \( Q < K_p \), the reaction will proceed towards HI, to increase the partial pressure of HI and decrease the partial pressure of H₂ and I₂, until \( Q = K \).

Answer: towards products

Calculate \( \Delta G^\circ \) for this reaction at 298 K.

Using \( \Delta G^\circ = -RT\ln K_p \):

\[ \Delta G^\circ = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(2.24) = -2000 \text{ J mol}^{-1} = -2.00 \text{ kJ mol}^{-1} \]

Answer: -2000 J mol\(^{-1}\) = -2.00 kJ mol\(^{-1}\)