Kinetic Theory of Gases

4 Critical constants :-

For one mole of Vander wall's gas the equation of state is $\begin{pmatrix} P + \frac{a}{V^2} \end{pmatrix} (V - b) = \text{RT} - \dots - (1) \quad [\text{V= Molar volume}] \\
PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = \text{RT} \\
PV^3 - PV^2 b + aV - ab = \text{RTV}^2 \\
V^3 - V^2 b + \frac{aV}{P} - \frac{ab}{P} = \frac{RTV^2}{P} \\
V^3 - (b + \frac{RT}{P}) V^2 - \frac{a}{p} V - \frac{ab}{p} = 0 - \dots - (2)$

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On increasing the temperature 3 roots come closer an ultimately they become identical at critical temperature under this condition $V = V_c$

$$(V - V_c) = 0 - \dots - (3)$$

$$b + \frac{RT_c}{P_c} = 3V_c$$

$$\frac{a}{P_c} = 3V_c^2$$

$$\frac{ab}{P_c} = V_c^3$$

$$V_c = 3b$$

$$T_c = \frac{8a}{27Rb}$$

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Ionic equilibria

Buffer solution:

These are solutions which resist changes in their p^H values when small amount of the acid or bases are added to them.

CH₃COOH+CH₃COONa→ Acidic buffer

NH₄OH+NH₄Cl→alkaline buffer

<u>P^H of Buffer</u>:

Consider a buffer containing a weak acid and its salt A⁻ ionization of weak acid may be represented as-

$$HA + H_2O {\leftrightarrow} H_3O^+ + A$$

$$K_{a} = \frac{[H_{3}O^{+}][A^{-}]}{[HA]}$$
$$[H_{3}O^{+}] = K_{a} \frac{[HA]}{[A^{-}]}$$

Initial concentration of acid C_a and salt C_s. The concentration of unionized acid is C_a - H_3O^+ . The solution is electrically neutral hence $[A^-] = C_s + H_3O^+$.

$$[H_3O^+] = K_a \frac{[C_a - H_3O^+]}{[C_s + H_3O^+]}$$

$$[H_3O^+] = K_a \frac{C_a}{C_s}$$

 $pH = pK_a + \log \frac{[Salt]}{[Acid]}$

This is known as the Henderson equation.

Similarly, for a mixture of a weak base and its salt

$$OH^{-} = K_{b} \frac{[Base]}{[Salt]}$$
$$pOH = pK_{b} + \log \frac{[Sal}{[Bas]}$$

where K_b is the ionization constant of the base

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Electrolytic Conductance

Equivalent conductance and Molar conductance:

Equivalent conductance:

This two terms are important for conductance of solution. Equivalent conductance of an electrolyte is defined as the conductance of volume of solution containing 1gm equivalent of the electrolyte placed between two parallel electrode unit distances apart.

Conductance of all ions produced by 1 gm equivalent of electrolyte in given volume of solution called as equivalent conductance.

Conductance of 1cm^3 solution = k

Conductance of V cm^3 solution = kV

Volume of solution containing N gm equiv = 1000mL

Volume of solution containing 1 gm equiv = $\frac{1000}{N}$ mL



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