# Problem 5. Ultrafast reactions

The rate of true neutralization reactions has proved to be immeasurably fast.
Eucken's Lehrbuch der Chemischen Physik, 1949

The main problem with studying ultrafast reactions is mixing the reactants. A smart way to circumvent this problem is the so-called relaxation technique.

Neutralization is a good example of an ultrafast reaction:

$$H^+ + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2O$$
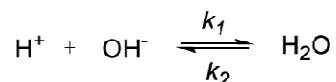
Here, k_1 and k_2 are the rate constants for the forward and backward reaction, respectively. The mean enthalpy for this reaction is −49.65 kJ mol⁻¹ in the temperature range 298–373 K. The density of water is 1.000 g cm⁻³.

5.1 Water has pH = 7.00 at 298 K. Calculate the apparent equilibrium constant $K = \frac{[H_2O]}{[H^+][OH^-]}$ of the neutralization reaction shown above. Calculate also the entropy change for the reaction.

The equilibrium constant is expressed as the dimensionless quantity:

$$K = \frac{\frac{[H_2O]}{1\,M}}{\frac{[H^+]}{1\,M} \cdot \frac{[OH^-]}{1\,M}}$$

as all the terms are activities, for which the reference molar concentration is set to 1 M. We have the molar concentration of H$_2$O given by the density:

$$[H_2O] = \frac{\rho_{H_2O}}{MM_{H_2O}} = \frac{1000\,g/L}{18.016\,g/mol} = 55.50\,M$$

The molar concentration of H$^+$ is given by the pH value, while the molar concentration of OH$^-$ is given by the charge balance:

$$[H^+] = 10^{-pH}\,M = 1 \times 10^{-7}\,M \quad \rightarrow \quad [OH^-] = [H^+] = 1 \times 10^{-7}\,M$$

All the concentrations are known, so the apparent equilibrium constant becomes:

$$K = \frac{\frac{55.50\,M}{1\,M}}{\frac{1\times10^{-7}\,M}{1\,M} \cdot \frac{1\times10^{-7}\,M}{1\,M}} = 5.55 \times 10^{15}$$

The entropy change of the reaction is known from the thermodynamic definition of equilibrium constant and Gibbs' free energy change. We have, from the equilibrium constant definition:

$$\Delta_r g^0(T) = -RT \log K = -8.3144\,J/(mol\,K) \cdot 298\,K \cdot \log(5.55 \times 10^{15}) = -89.82\,kJ/mol$$

and from the definition of the Gibbs' free energy of reaction:

$$\Delta_r g^0(T) = \Delta_r h^0 - T\Delta_r s^0$$

$$\Delta_r s^0 = \frac{\Delta_r h^0 - \Delta_r g^0(T)}{T} = \frac{40.17\,kJ/mol}{298\,K} = 0.135\,kJ/(mol\,K)$$

5.2   Estimate the pH of boiling water (T = 373 K).

The pH is related to the molar concentration of H^+, which can be obtained from the equilibrium constant at 373 K. The Gibbs' free energy change of the reaction at 373 K is obtained from the thermodynamic definition. We know that $\Delta_r h^0$ and $\Delta_r s^0$ are mean values over a temperature range, and since the required temperature is inside such range, we consider both values as constant.

We have, from the Gibbs' free energy change definition:

$$\Delta_r g^0(T) = \Delta_r h^0 - T\Delta_r s^0$$

$$\Delta_r g^0(373 \text{ K}) = -49.65 \text{ kJ/mol} - 373 \text{ K} \cdot 0.135 \text{ kJ/(mol K)} = -99.93 \text{ kJ/mol}$$

and the equilibrium constant:

$$K(373 \text{ K}) = \exp\left(-\frac{-9.993 \times 10^4 \text{J/mol}}{8.3144 \text{J/(mol K)} \cdot 373 \text{ K}}\right) = 9.86 \times 10^{13}$$
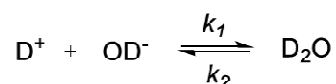
The molar concentration of H^+ is equal to the molar concentration of OH^- from the charge balance, and it is obtained from the equilibrium constant expression in part 5.1 (as the standard concentration of 1 M has been omitted) as follows:

$$K = \frac{[H_2O]}{[H^+] \cdot [H^+]} \quad \rightarrow \quad [H^+]^2 = \frac{[H_2O]}{K} \quad \rightarrow \quad [H^+] = \left(\frac{[H_2O]}{K}\right)^{1/2}$$

and the molar concentration of H_2O is set equal to 55.50 M. Then, the molar concentration of H^+ and the respective pH value is obtained:

$$[H^+] = \left(\frac{55.50}{9.86 \times 10^{13}}\right)^{1/2} = 7.50 \times 10^{-7} \text{M} \quad \rightarrow \quad \text{pH} = -\log_{10}[H^+] = 6.12$$

Heavy water undergoes an analogous neutralization reaction, yet it is less dissociated than light water at the given temperature: $K_w(D_2O)$ = 1.35 × 10^{-15} at 298 K.

$$D^+ + OD^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} D_2O$$

5.3   What is pD of heavy water at 298 K?

From the K_w, which is defined only to include the molar concentrations of D^+ and OD^-, we have:

$$K_W(D_2O) = [D^+][OD^-] = 1.35 \times 10^{-15}$$

The molar concentration of D^+ is equal to the molar concentration of OD^- from the charge balance:

$$[OD^-] = [D^+]$$

thus, the K_W relation is an equation the only unknown $[D^+]$ which is obtained as:

$$K_W(D_2O) = [D^+]^2 \quad \rightarrow \quad [D^+] = \left(K_W(D_2O)\right)^{1/2} = (1.35 \times 10^{-15})^{1/2} = 3.67 \times 10^{-8} \text{M}$$

The pD value is then obtained from the definition:

$$\text{pD} = -\log_{10}[D^+] = 7.43$$

5.4 Write the rate law for the change of the concentration of D_2O in terms of the concentrations of D^+, OD^- and D_2O.

The rate law for the D_2O molar concentration change is expressed as the net of the direct and inverse reaction rates, as follows:

$$\frac{d[D_2O]}{dt} = R_{dir} - R_{inv} = k_1[D^+][OD^-] - k_2[D_2O]$$

The composition of the equilibrium system depends on temperature. If we apply an external stimulus, for example a very fast heat pulse on the system, we disturb the equilibrium and observe a subsequent relaxation to the equilibrium composition. We can describe the relaxation with a new quantity x, a deviation from the equilibrium concentrations:

$$x = [D_2O]_{eq} - [D_2O] = [OD^-] - [OD^-]_{eq} = [D^+] - [D^+]_{eq}$$

5.5 Express the time change $\frac{dx}{dt}$ in terms of x. Give both the exact equation and the equation in which you neglect the small terms of x^2.

From the definition of the equilibrium deviation x, we have a set of relations that link the actual molar concentrations with respect to their equilibrium value:

$$[D_2O] = [D_2O]_{eq} - x$$

$$[D^+] = x + [D^+]_{eq}$$

$$[OD^-] = x + [OD^-]_{eq}$$

and after substituting in the reaction rate expression in 5.4 we obtain:

$$\frac{d([D_2O]_{eq} - x)}{dt} = k_1(x + [D^+]_{eq})(x + [OD^-]_{eq}) - k_2([D_2O]_{eq} - x)$$

Since the equilibrium concentration of any specie does not change with time, we have:

$$\frac{d([D_2O]_{eq} - x)}{dt} = \frac{d[D_2O]_{eq}}{dt} - \frac{dx}{dt} = -\frac{dx}{dt}$$

and we can obtain the exact equation:

$$\frac{dx}{dt} = -k_1(x + [D^+]_{eq})(x + [OD^-]_{eq}) + k_2([D_2O]_{eq} - x)$$

Expanding the first term in the right-hand side, and neglecting the x^2 terms, we have:

$$\frac{dx}{dt} = -x(k_1[D^+]_{eq} + k_1[OD^-]_{eq} + k_2) - k_1[OD^-]_{eq}[D^+]_{eq} + k_2[D_2O]_{eq}$$

From the equilibrium constant definition (as the standard concentration of 1 M has been omitted), we have the following relation:

$$K = \frac{k_1}{k_2} = \frac{[D_2O]_{eq}}{[OD^-]_{eq}[D^+]_{eq}} \quad \rightarrow \quad k_1[OD^-]_{eq}[D^+]_{eq} = k_2[D_2O]_{eq}$$

so, the last two terms cancel out, leaving the following:

$$\frac{dx}{dt} = -x\big(k_1[D^+]_{eq} + k_1[OD^-]_{eq} + k_2\big)$$

Solving the equation derived in 5.5, we get:

$$x = x(0) \times \exp(-t \times (k_1[D^+]_{eq} + k_1[OD^-]_{eq} + k_2))$$

where $x(0)$ is the deviation from equilibrium at the moment of perturbation.

5.6   For heavy water at 298 K, the relaxation time τ (time at which the deviation from equilibrium drops to $\frac{1}{e}$ of the initial value) was measured to be 162 μs. Calculate the rate constant for the forward and backward reaction. The density of heavy water is ρ = 1.107 g cm^{-3} and molar mass is M_r = 20.03.

The definition of relaxation time τ implies that:

$$x(\tau) = \frac{x(0)}{e} = x(0)\exp(-1)$$

so, we substitute the equilibrium change solution and we obtain a direct relation between the rate constants and τ:

$$x(0) \exp\left(-\tau\big(k_1[D^+]_{eq} + k_1[OD^-]_{eq} + k_2\big)\right) = x(0)\exp(-1)$$

$$\tau\big(k_1[D^+]_{eq} + k_1[OD^-]_{eq} + k_2\big) = 1$$

From the charge balance we have $[D^+]_{eq} = [OD^-]_{eq}$, therefore the above expression simplifies into:

$$2k_1[D^+]_{eq} + k_2 = \frac{1}{\tau}$$

also, from the equilibrium constant definition (now as dimensional, without the standard concentration of 1 M) we have $k_1 = k_2 K$, where K is the apparent equilibrium constant. We remark that K must not be confused with the autoionization constant $K_W(D_2O)$, as this relation holds:

$$K = \frac{[D_2O]_{eq}}{[OD^-]_{eq}[D^+]_{eq}} = \frac{[D_2O]_{eq}}{K_W(D_2O)}$$

The equilibrium concentration of D$_2$O is known from the density:

$$[D_2O]_{eq} = \frac{\rho_{D_2O}}{MM_{D_2O}} = \frac{1107\ \text{g/L}}{20.03\ \text{g/mol}} = 55.27\ \text{M}$$

Thus, the dimensional equilibrium constant becomes:

$$K = \frac{[D_2O]_{eq}}{K_W(D_2O)} = \frac{55.27\ \text{M}}{1.35 \times 10^{-15}\text{M}^2} = 4.09 \times 10^{16}\text{M}^{-1}$$

and the main relation between the rate constants reduces to one equation in one unknown, the backward rate constant k_2:

$$2k_1[D^+]_{eq} + k_2 = \frac{1}{\tau} \;\rightarrow\; 2k_2K[D^+]_{eq} + k_2 = \frac{1}{\tau} \;\rightarrow\; k_2 = \frac{1}{\tau \cdot \big(2K[D^+]_{eq} + 1\big)}$$

We know $[D^+]_{eq}$ at 298 K from the pD calculation in 5.3, that is $[D^+]_{eq} = 3.67 \times 10^{-8}\text{M}$. Thus, we have the backward rate constant:

$$k_2 = \frac{1}{1.62 \times 10^{-4}\, s \cdot (2 \cdot 4.09 \times 10^{16}\text{M}^{-1} \cdot 3.67 \times 10^{-8}\text{M} + 1)} = 2.06 \times 10^{-6}\text{s}^{-1}$$

and the forward rate constant is obtained from the dimensional equilibrium constant definition:

$$k_1 = k_2 K = 2.06 \times 10^{-6}\text{s}^{-1} \cdot 4.09 \times 10^{16}\text{M}^{-1} = 8.42 \times 10^{10}\text{M}^{-1}\text{s}^{-1}$$

Ultrafast reactions can also be triggered by a pH jump. Using an ultrafast laser pulse, we can induce a pH jump in a system with so-called photoacids. These compounds have dramatically different acid-base properties in the ground and excited electronic states. For example, the pK_a of 6-hydroxynaphthalene-2-sulfonate is 9.12 in the ground state and 1.66 in the excited state.
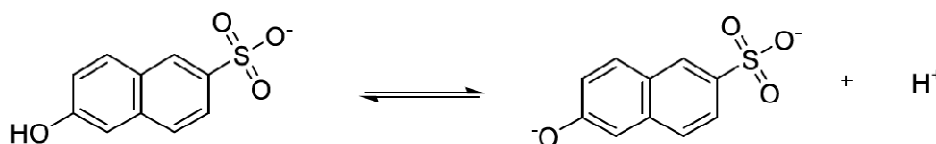
5.7   1 cm³ of 5.0×10^{-3} mol dm⁻³ 6-hydroxynaphthalene-2-sulfonate solution was irradiated by light with the wavelength of 297 nm. The total absorbed energy was 2.228×10^{-3} J. Calculate the pH before and after irradiation. Neglect the autoprotolysis of water in both cases.

Note that the standard state for a solution is defined as c_0 = 1 mol dm⁻³ and assume that the activity coefficient is γ_i = 1 for all species. It may be of advantage to use an online cubic equation solver.

We name the 6-hydroxynaphtalene-2-sulfonate ion as HA, and the dissociation reaction is treated in the standard form HA → H⁺ + A⁻. We may split the problem by evaluating the pH before, during and after irradiation.

• *The pH before irradiation*(BI) is given by the dissociation constant:

$$K_{A,BI} = \frac{[\text{H}^+]_{BI}[\text{A}^-]_{BI}}{[\text{HA}]_{BI}} \quad \rightarrow \quad K_{A,BI} = 10^{-pK_{A,BI}} = 10^{-9.12} = 7.59 \times 10^{-10}$$

From the charge balance, $[\text{A}^-]_{BI} = [\text{H}^+]_{BI} = x$, and the equilibrium concentration of the acid is given as the difference between the initial and reacted amount:

$$[\text{HA}]_{BI} = [\text{HA}]_0 - x = 5.0 \times 10^{-3}\text{M} - x$$

Since $K_{A,BI}$ is very small compared to $[\text{HA}]_0$ we can neglect the x contribution to $[\text{HA}]_{BI}$, or that the equilibrium concentration of HA is approximately equal to its initial value. This leads to a simplified quadratic equation, which gives:

$$K_{A,BI} = \frac{x^2}{[\text{HA}]_0} \quad \rightarrow \quad [\text{H}^+]_{BI} = \left(K_{A,BI}[\text{HA}]_0\right)^{1/2} = (7.59 \times 10^{-10} \cdot 5.0 \times 10^{-3})^{1/2} = 1.95 \times 10^{-6}\text{M}$$

then, from the pH definition we have:

$$\text{pH}_\text{BI} = -\log_{10}[\text{H}^+]_{BI} = 5.71$$

• *The pH during irradiation* (DI) is given not only from the modified dissociation constant, but also from the already existing contribution of $[\text{H}^+]_{BI}$. We have the new constant:

$$K_{A,DI} = \frac{[\text{H}^+]_{DI}[\text{A}^-]_{DI}}{[\text{HA}]_{DI}} \quad \rightarrow \quad K_{A,DI} = 10^{-pK_{A,DI}} = 10^{-1.66} = 2.19 \times 10^{-2}$$

and new values for the molar concentration of involved species, which are now related to the new reacted amount y, as follows:

$$[H^+]_{DI} = [H^+]_{BI} + y$$

$$[A^-]_{DI} = [H^+]_{DI} = [H^+]_{BI} + y$$

$$[HA]_{DI} = [HA]_{BI} - y = [HA]_0 - y$$

We notice that no additional simplifications may be done, since $K_{A,DI}$ is comparable to $[HA]_0$, and thus leading to a quadratic equation:

$$K_{A,DI} = \frac{([H^+]_{BI} + y)^2}{[HA]_0 - y} \quad \rightarrow \quad y^2 + y(K_{A,DI} + 2[H^+]_{BI}) + ([H^+]_{BI}^2 - K_{A,DI}[HA]_0) = 0$$

as the quadratic's coefficients are $a = 1$, $b = 2.19 \times 10^{-2}$ and $c = -1.095 \times 10^{-4}$, which leads to only one positive solution:

$$y = 4.19 \times 10^{-3} \text{M}$$

$$[H^+]_{DI} = [H^+]_{BI} + y = 4.19 \times 10^{-3} \text{M}$$

$$[HA]_{DI} = [HA]_0 - y = 8.10 \times 10^{-4} \text{M}$$

then, from the pH definition we have:

$$\text{pH}_{DI} = -\log_{10}[H^+]_{DI} = 2.38$$

• *The pH after irradiation* (AI) is given from the original dissociation constant $K_{A,AI} = K_{A,BI}$, and the not negligible contribution of $[H^+]_{DI}$. The new values for the molar concentration of involved species, which are now related to the new reacted amount z, are listed as follows:

$$[H^+]_{AI} = [H^+]_{DI} - z$$

$$[A^-]_{AI} = [H^+]_{AI} = [H^+]_{DI} - z$$

$$[HA]_{AI} = [HA]_{DI} + z$$

Since $K_{A,BI}$ is very small compared to $[HA]_{DI}$ we can neglect the z contribution to $[HA]_{AI}$, or that the equilibrium concentration of HA is approximately equal to its value during irradiation. This leads to a simplified quadratic equation, which gives the reacted amount:

$$K_{A,BI} = \frac{([H^+]_{DI} - z)^2}{[HA]_{DI}} \quad \rightarrow \quad z = [H^+]_{DI} - (K_{A,BI}[HA]_{DI})^{1/2}$$

The H^+ molar concentration is then obtained:

$$[H^+]_{AI} = [H^+]_{DI} - z = (K_{A,BI}[HA]_{DI})^{1/2} = (7.59 \times 10^{-10} \cdot 8.10 \times 10^{-4} \text{M})^{1/2} = 7.84 \times 10^{-7} \text{M}$$

then, from the pH definition we have:

$$\text{pH}_{AI} = -\log_{10}[H^+]_{AI} = 6.11$$

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Solution to exercises from 2018 IChO Preparatory Problems