CHEM 450 HW 10 Solutions

P 18.46

If the reaction is diffusion controlled, then $k_d < k_{react}$,
So that $k_d \sim 5.0 \times 10^6 \ M^{-1} s^{-1}$,

$$k_d = 4\pi N_A (r_A + r_B) D_{AB}$$

$r_A = 51.2$ Å
$r_B = 2.0$ Å
$D_{AB} = D_A + D_B =$
$6.0 \times 10^{-7} \frac{cm^2}{s} + 1.5 \times 10^{-5} \frac{cm^2}{s}$

$$k_d = (4\pi)(6.02 \times 10^{23} \ mol^{-1})(53.2 \times 10^{-8} \ cm)(1.56 \times 10^{-5} \frac{cm^2}{s})$$

$$= 6.278 \frac{cm^3}{mol \, s} \times \left(\frac{1 \ L}{1000 \ cm^3}\right) = \boxed{6.28 \times 10^{10} \ s^{-1} M^{-1}}$$

This is not a diffusion controlled reaction.

P19.24

Here, we just follow the same path as the derivation of 19.83 but, now, with

$$R_{2(g)} + 2M(\text{surf}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2RM(\text{surface})$$

So, at eqm, $\left(\frac{d\theta}{dt}\right)_{ads} = \left(\frac{d\theta}{dt}\right)_{des}$, so that we need the rates of coverage for each direction.

This time, since the coefficient for <u>each</u> surface component is 2, we must <u>square</u> the θ (or θ-1) term!

$$\frac{d\theta}{dt} = k_a PN(1-\theta)^2 - k_d N\theta^2 = 0$$

Now, solving for θ:

$$k_a PN(1-\theta)^2 = k_d N\theta^2$$

$$\frac{k_a}{k_d} P\frac{\cancel{N}}{\cancel{N}} = \frac{\theta^2}{(1-\theta)^2} \quad \text{or} \quad KP = \frac{\theta^2}{(1-\theta)^2}$$

thus: $\frac{\theta}{1-\theta} = \sqrt{KP} \Rightarrow \sqrt{KP} = \theta(1+\sqrt{KP})$

$$\boxed{\theta = \frac{\sqrt{KP}}{1+\sqrt{KP}}}$$

$\boxed{P19.49}$

a) $\lambda_{sol} = \frac{(\Delta e)^2}{4\pi\varepsilon_0}\left(\frac{1}{d_1} + \frac{1}{d_2} - \frac{1}{r}\right)\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right)$

$n \doteq 1.33 \quad \varepsilon = 80. \quad d_1 = d_2 = 6 \times 10^{-10}\,m \quad r = 15 \times 10^{-10}\,m$

Δe is total charge transferred, that's $(-1 \cdot e) = -1.602 \times 10^{-19}\,C$

So

$\lambda_{sol} = (-1.602 \times 10^{-19}\,C)^2 \cdot 8.99 \times 10^9 \frac{Jm}{C^2}\left(\frac{2}{6 \times 10^{-10}\,m} - \frac{1}{15 \times 10^{-10}\,m}\right)\left(\frac{1}{1.33^2} - \frac{1}{80}\right)$

$\boxed{= 3.401 \times 10^{-19}\,J}$ $\Rightarrow$ it costs energy

b) now, $n = 4$, $\varepsilon = 1.5$, so

$\lambda_{sol} = (-1.602 \times 10^{-19}\,c)^2 \cdot 8.99 \times 10^9 \frac{Jm}{C^2}\left(\frac{2}{6 \times 10^{-10}\,m} - \frac{1}{15 \times 10^{-10}\,m}\right)\left(\frac{1}{1.5^2} - \frac{1}{4}\right)$

$\boxed{= 1.196 \times 10^{-19}\,J}$ less energy expenditure!