

CHEM 311 (132)

Final Exam

3 HOURS

Sunday, May 18, 2014, 8:00 AM

Building 54 - B

Test Code (000)

(25 Questions)

Dr. Mazen Khaled	Section 1
Dr. Mohamed Morsy	Section 2
Dr. Foerner	Section 3
Dr. Maung	Section 4

Physical constants, conversion factors, and useful equations

Physical Constants

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$= 0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$F = 96,485 \text{ C mol}^{-1}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$g = 9.81 \text{ m s}^{-2}$$

$$e = 1.6022 \times 10^{-19} \text{ C}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

$$B = 0.51 \text{ mol}^{-1/2} \text{ dm}^{3/2} \text{ (in H}_2\text{O, 25}^\circ\text{C)}$$

Other Units

$$1 \text{ dm}^3 = 1 \text{ L}$$

$$1 \text{ dm}^3 = 1000 \text{ cm}^3$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$1 \text{ atm} = 760 \text{ mmHg}$$

$$1 \text{ Torr} = 1 \text{ mmHg}$$

$$1 \text{ Torr} = 133.322 \text{ Pa}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$E = h\nu$$

$$c = \nu\lambda$$

$$PV = nRT$$

$$(RT)/F = 25.6926 \text{ mV at } 25^\circ\text{C}$$

$$\ln(x)/\log_{10}(x) = 2.30259 \text{ for all } x$$

$$\ln(1 - \theta) = -\theta$$

$$\text{if } \theta \ll 1$$

Sequential reactions:

$$[B] = (k_1/(k_2 - k_{-1})) f(t)[A]_0$$

$$f(t) = \exp(-k_1 t) - \exp(-k_2 t)$$

Michaelis - Menten equation:

$$(1/R_0) = (1/R_{\max}) + (K_m/R_{\max}) \times (1/[S]_0)$$

Lindemann mechanism:

$$k_{\text{uni}} = k_1 k_2 [M] / (k_{-1} [M] + k_2)^{-1}$$

Langmuir isotherm:

$$\theta = KP / (1 + KP)$$

Note:

Quantum yield/efficiency = Φ = moles of product formed / moles of photons absorbed

Important Equations

$$\Lambda = \frac{\kappa}{c}, \quad \alpha = \frac{\Lambda}{\Lambda_0} \quad \text{and} \quad I = \frac{I}{2} \sum_i c_i z_i^2$$

$$\log_{10} \gamma_i = -z_i^2 B \sqrt{I} \quad \text{and} \quad \log_{10} \gamma_{\pm} = -z_{\pm} |z_{\pm}| B \sqrt{I}$$

$$\Lambda_m = \Lambda_m^\circ - K (c/c_0)^{1/2} \text{ (strong)}$$

$$1/\Lambda_m = 1/\Lambda_m^\circ + c\Lambda_m / [(\Lambda_m^\circ)^2 K_a] \text{ (weak)}$$

$$\Delta G^\circ_{\text{solvation}} = (1/\epsilon_r - 1) z^2 e^2 N_A / (8\pi\epsilon_0 r)$$

$$\Delta G = -nFE \quad \text{and thus} \quad \Delta G^\circ = -nFE^\circ$$

$$E = E^\circ - \frac{RT}{zF} \ln \left(\frac{[Y]^y [Z]^z}{[A]^a [B]^b} \right)^u$$

$$\Delta S = nF(dE/dT)_P$$

$$a_{\pm}^{m+n} = a_+^m a_-^n \text{ for } A_m B_n$$

$$\kappa = [2e^2 N_A \times (1000 \text{ L m}^{-3}) / (\epsilon_0 k_B T)]^{1/2} \times [\rho_{\text{solvent}} / \epsilon_r]^{1/2}$$

$$E^\circ_{\text{AgCl/Ag}} = +0.222 \text{ V}$$

$$k = A e^{-E_a / RT}$$

$$k = \frac{k_B T}{h} e^{-\Delta^\ddagger G^\ddagger / RT}$$

$$E_a = \Delta^\ddagger H^\circ - P \Delta^\ddagger V^\circ + RT \text{ (sol)}$$

$$= \Delta^\ddagger H^\circ - \Sigma \nu RT + RT \text{ (gas)}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

$$t_{1/2} = (\ln 2) / k \text{ (1}^\text{st} \text{ order)}$$

$$\text{fluorescence lifetime } t_f = (k_f + k_q[Q])^{-1}$$

$$D = (1/3) v_{\text{ave}} \lambda$$

$$\kappa = (1/3) (C_{V,m} / N_A) v_{\text{ave}} N_p \lambda$$

$$(C_{V,m} / N_A) = (3/2) k_B$$

$$\eta = (1/3) v_{\text{ave}} N_p \lambda m$$

$$v_{\text{ave}} = (8RT / (\pi M))^{1/2}$$

$$N_p \lambda = 1 / ((\sqrt{2}) \sigma)$$

$$\lambda = RT / (P N_A (\sqrt{2}) \sigma)$$

$$N_p = (N/V) = P N_A / (RT)$$

$$\sigma = \pi d^2$$

$$x_{\text{rms}} = (\sqrt{\langle x^2 \rangle}) = \sqrt{2Dt}$$

$$\text{Poisuille equation: } (\Delta V / \Delta t) = (\pi r^4 / (8\eta)) \Delta P / \Delta L$$

$$\text{Stokes-Einstein equation: } D = k_B T / (6\pi \eta r)$$

$$\text{if } r(\text{particle}) \gg r(\text{solvent molecule})$$

$$\text{Ostwald viscosimeter: } \eta = A \rho t$$

$$\text{Capillary rise: } h = 2\gamma / (d \rho g)$$

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Sec # 01: Dr. Morsy SEC# 02: Dr. Khaled Sec # 03: Dr. Foerner
Sec# 04: Dr. Maung

Please give your section number below

STUDENT NAME : _____

STUDENT ID NUMBER: _____

STUDENT SECTION NUMBER: _____

Number of Correct Answers	Your Score out of 100%

1. Investigations of high power cables showed that copper atoms were assembled beyond the insulator of thickness 20 mm which created a short-circuit. Taking the diffusion coefficient of copper as $7.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, estimate the time required for a copper atom to cross the insulator. (Hint: use the root mean square displacement x_{rms} as traveled distance)

a. 1 month b. 25 days c. 5 days d. 10 hours e. 67 s

$$x_{\text{rms}} = \sqrt{2Dt}$$

$$\rightarrow t = \frac{x_{\text{rms}}^2}{2D} = \frac{(20 \cdot 10^{-1} \text{ cm})^2}{2 \cdot 7.8 \cdot 10^{-7} \text{ cm}^2/\text{s}}$$

$$= 2564103 \text{ s}$$

$$= 2564103 \text{ s} \cdot \frac{3600 \text{ h}}{1 \text{ d}} \cdot \frac{1 \text{ d}}{3600 \text{ s}}$$

$$= 712.3 \text{ h}$$

$$= 712.3 \text{ h} \frac{1 \text{ d}}{24 \text{ h}}$$

$$= 29.68 \text{ d} \approx 30 \text{ d} \approx 1 \text{ month}$$

2. Upon adding sugar carefully on top of a full cup of water of height 10 cm, ^{enter!} sugar will start to diffuse slowly with a diffusion coefficient of $2.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25°C . Determine the percent of sweet water vs unsweet water after 1 day. (Hint: as above in problem 1)

a. 9.5%

b. 35%

c. 27.3%

d. 50.5%

e. 89.4%

$$\begin{aligned}
 x_{\text{rms}} &= \sqrt{2Dt} \\
 &= \sqrt{2.5 \cdot 2 \cdot 10^{-6} \frac{\text{cm}^2}{\text{s}} \cdot 1 \text{ d} \cdot \frac{24 \text{ h}}{24 \text{ h}} \cdot \frac{3600 \text{ s}}{1 \text{ h}}} \\
 &= \sqrt{0.8986 \text{ cm}^2} \\
 &= 0.948 \text{ cm}
 \end{aligned}$$

$$\begin{aligned}
 \% \text{ sweet water} &= \frac{0.948 \text{ cm}}{10 \text{ cm}} \cdot 100\% = 9.48\% \\
 &= 9.5\%
 \end{aligned}$$

3. Liquids undergo a pressure drop when flowing through pipes. Assume a liquid flowing in a 6.00 mm radius tube for 1.00 m length at an average rate of 0.66 mL min⁻¹ with a viscosity of 4.0 × 10⁻³ kg m⁻¹s⁻¹, then determine the pressure that should be applied to correct for the pressure drop.

- (a) 86 mPa b. 21 Pa c. 25 mPa d. 68 nPa e. 55 cPa

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{8 \eta} \frac{\Delta P}{\Delta L}$$

$$\Delta P = \frac{8 \eta}{\pi r^4} \Delta L \cdot \frac{\Delta V}{\Delta t}$$

$$= \frac{8 \cdot 4 \cdot 10^{-3} \frac{\text{kg}}{\text{m s}}}{\pi (6 \cdot 10^{-3} \text{ m})^4} 1.00 \text{ m} \cdot 0.66 \cdot 10^{-3} \frac{\text{L}}{\text{min}}$$

$$= 5187 \frac{\text{kg}}{\text{m s}} \frac{1}{\text{m}^4} \cdot \text{m} \cdot \frac{\text{L}}{\text{min}}$$

$$= 5187 \frac{\text{kg}}{\text{m}^4 \text{ s}} \cdot \frac{\text{L}}{\text{min}}$$

$$= 5187 \frac{\text{kg}}{\text{m}^4 \text{ s}} \cdot \frac{\text{dm}^3}{\text{min}}$$

$$= 5187 \frac{\text{kg}}{\text{m}^4 \text{ s}} \cdot \frac{(10^{-1} \text{ m})^3}{60 \text{ s}}$$

$$= 0.08645 \frac{\text{kg}}{\text{m s}^2}$$

$$1 \text{ Pa} = 1 \frac{\text{N}}{\text{m}^2} = 1 \frac{\text{kg m s}^{-2}}{\text{m}^2} = 1 \frac{\text{kg}}{\text{m s}^2}$$

$$\Delta P = 0.08645 \text{ Pa} = 86 \text{ mPa}$$

4. The diffusion coefficient of SF₆ in SF₆ gas at 573 K and 1.00 atm is $1.02 \times 10^{-7} \text{ m}^2/\text{s}$. enter !

Calculate the collision cross section of SF₆ at 573 K and 1.00 atm where the average speed of molecules is 288 m/s.

- a. 52 nm² b. 25 nm² c. 5.2 nm² d. 0.52 nm² e. 0.052 nm²

$$D = \frac{1}{3} v_{\text{ave}} \lambda$$

~~$$= \frac{1}{3} \sqrt{\frac{8RT}{\pi M}} \lambda$$~~

$$\lambda = \frac{3D}{v_{\text{ave}}} = \frac{3 \cdot 1.02 \cdot 10^{-7} \frac{\text{m}^2}{\text{s}}}{288 \frac{\text{m}}{\text{s}}}$$

$$= 1.0625 \cdot 10^{-9} \text{ m}$$

$$= 1.0625 \text{ nm}$$

$$\sigma = \frac{RT}{P N_A \sqrt{2} \lambda}$$

$$= \frac{8.314 \frac{\text{J}}{\text{K mol}} \cdot 573 \text{ K}}{1.01325 \cdot 10^5 \text{ Pa} \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1} \sqrt{2} \cdot 1.0625 \cdot 10^{-9} \text{ m}}$$

$$= 5.1959 \cdot 10^{-17} \frac{\text{J/mol}}{\frac{\text{N}}{\text{m}^2} \text{ mol} \cdot \text{m}}$$

$$= 5.1959 \cdot 10^{-17} \frac{\text{Nm}}{\frac{\text{N}}{\text{m}}} = 5.1959 \cdot 10^{-17} \text{ m}^2$$

$$1 \text{ nm}^2 = (1 \cdot 10^{-9})^2 \text{ m}^2 = 1 \cdot 10^{-18} \text{ m}^2$$

$$\sigma = 51.959 \cdot 10^{-18} \text{ m}^2 = 51.959 \text{ nm}^2 = 52 \text{ nm}^2$$

5. Determine the ratio of the thermal conductivities for Kr ($\sigma = 0.52 \text{ nm}^2$) versus Ar ($\sigma = 0.36 \text{ nm}^2$). Molar masses: 39.95 g/mol for Ar and 83.80 g/mol for Kr.

a. 0.48 b. 2 c. 10 d. 1.5 e. 100

$$\kappa = \frac{1}{3} \cdot \frac{3}{2} k_B \cdot \frac{c_{v,m}}{N_A} \cdot v_{ave} \cdot N_p \cdot \lambda$$

$$= \frac{1}{3} \cdot \frac{3}{2} k_B v_{ave} N_p \lambda = \frac{1}{2} k_B v_{ave} N_p \lambda$$

$$N_p \lambda = \frac{1}{\sqrt{2} \sigma} \text{ for ideal gases}$$

$$\kappa = \frac{1}{2} k_B v_{ave} \cdot \frac{1}{\sqrt{2} \sigma}$$

$$\frac{\kappa_{Kr}}{\kappa_{Ar}} = \frac{v_{ave}(Kr)}{v_{ave}(Ar)} \cdot \frac{\sigma_{Ar}}{\sigma_{Kr}}$$

$$v_{ave} = \sqrt{\frac{8RT}{\pi M}}$$

$$= \sqrt{\frac{M_{Ar}}{M_{Kr}}} \cdot \frac{\sigma_{Ar}}{\sigma_{Kr}}$$

$$= \sqrt{\frac{39.95}{83.80}} \cdot \frac{0.36}{0.52} = \sqrt{0.4767} \cdot 0.6923$$

$$= 0.478 = 0.48$$

6. The electrolytic conductivity of a solution mixture of 0.1 M KCl and 0.2 M

XCl (both of which are strong electrolytes) is 3.82 S m^{-1} . Calculate λ for X^+ in $\text{S m}^2 \text{ mol}^{-1}$.

[Note: $\lambda_{\text{K}^+} = 7.4 \times 10^{-3}$; $\lambda_{\text{Cl}^-} = 7.6 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ and $\lambda_i = \kappa_i / c_i$]

a) $4.00 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

b) $5.00 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

c) $6.00 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

d) $2.00 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

e) $19.1 \text{ S m}^2 \text{ mol}^{-1}$

$$\kappa = \kappa(\text{KCl}) + \kappa(\text{XCl})$$

$$= (\lambda_{\text{K}^+} + \lambda_{\text{Cl}^-}) \cdot 0.1 \text{ M}$$

$$+ (\lambda_{\text{X}^+} + \lambda_{\text{Cl}^-}) \cdot 0.2 \text{ M}$$

$$= \lambda_{\text{K}^+} \cdot 0.1 \text{ M} + \lambda_{\text{Cl}^-} \cdot 0.3 \text{ M} + \lambda_{\text{X}^+} \cdot 0.2 \text{ M}$$

$$\lambda_{\text{X}^+} = \frac{\kappa - \lambda_{\text{K}^+} \cdot 0.1 \text{ M} - \lambda_{\text{Cl}^-} \cdot 0.3 \text{ M}}{0.2 \text{ M}}$$

$$1 \text{ M} = 1 \frac{\text{mol}}{\text{L}} = 1 \frac{\text{mol}}{\text{dm}^3} = 1 \frac{\text{mol}}{(10^{-1} \text{ m})^3} = 10^3 \frac{\text{mol}}{\text{m}^3}$$

$$\lambda_{\text{X}^+} = \frac{3.82 \frac{\text{S}}{\text{m}} - 7.4 \cdot 10^{-3} \frac{\text{S m}^2}{\text{mol}} \cdot 0.1 \cdot 10^3 \frac{\text{mol}}{\text{m}^3} - 7.6 \cdot 10^{-3} \frac{\text{S m}^2}{\text{mol}} \cdot 0.3 \cdot 10^3 \frac{\text{mol}}{\text{m}^3}}{0.2 \cdot 10^3 \frac{\text{mol}}{\text{m}^3}}$$

$$= \frac{0.800 \text{ S/m}}{0.200 \cdot 10^3 \frac{\text{mol}}{\text{m}^3}} = 4.00 \cdot 10^{-3} \frac{\text{S m}^2}{\text{mol}}$$

7. The thermal conductivity of an ideal gas

- a) is proportional to $T^{1/2}$
- b) is independent of T
- c) decreases with increasing temperature
- d) is inversely proportional to T
- e) is proportional to T

$$\kappa = \frac{1}{3} \frac{C_{V,m}}{N_A} v_{ave} N_P \cdot \lambda$$

$$= \frac{1}{3} \cdot \frac{2}{2} \cdot \frac{3}{2} k_B v_{ave} \cdot \frac{1}{\sqrt{2} \sigma} \quad \text{ideal gas}$$

k_B, σ do not depend on T

$$v_{ave} = \sqrt{\frac{8RT}{\pi M}}$$

$$\rightarrow \kappa = \frac{1}{2} k_2 \sqrt{\frac{8RT}{\pi M}} \frac{1}{\sqrt{2} \sigma}$$

$$\Rightarrow \kappa \sim T^{1/2}$$

8. The mean root square distance travelled by a He atom (molar mass 4.0 g/mol) at 25 °C and 101.324 kPa pressure through air ($D = 1.256 \times 10^{-4} \text{ m}^2/\text{s}$) in 10 minutes is (hint: use x_{rms} again!) |

- a. 0.39 m
- b. 0.075 m²
- b. 0.15 m²
- c. $2.5 \times 10^{-3} \text{ m}^2$
- e. 0.27 m

$$x_{\text{rms}} = \sqrt{2Dt}$$

$$= \sqrt{2 \cdot 1.256 \cdot 10^{-4} \frac{\text{m}^2}{\text{s}} \cdot 10 \text{ min} \cdot \frac{60 \text{ s}}{\text{min}}}$$

$$= \sqrt{0.1507} \text{ m}$$

$$= 0.3882 \text{ m} = 0.39 \text{ m}$$

9. The ratio of diffusion coefficients of hydrogen gas (H_2) relative to deuterium gas (D_2), assuming they have the same size, is

- a. more than one at the same and constant temperature and pressure
- b. less than one at the same and constant temperature and pressure
- c. equal to one at constant temperature and pressure
- d. not affected by varying the temperature or pressure
- e. equal to one if collision cross section ratio of H_2/D_2 is equal to half

$$\frac{D_{H_2}}{D_{D_2}} = \frac{\left(\sqrt{\frac{8RT}{\pi M}} \cdot \frac{RT}{P N_A \sqrt{2} \sigma} \right)_{H_2}}{\left(\sqrt{\frac{8RT}{\pi M}} \cdot \frac{RT}{P N_A \sqrt{2} \sigma} \right)_{D_2}}$$

same T, P, σ

$$\rightarrow \frac{D_{H_2}}{D_{D_2}} = \sqrt{\frac{M_{D_2}}{M_{H_2}}} = \sqrt{\frac{4 \text{ amu}}{2 \text{ amu}}} = \sqrt{2} = 1.4 > 1$$

10. The diffusion coefficient for a globular protein molecule in a solvent is $6.48 \times 10^{-10} \text{ m}^2/\text{s}$ at 25°C . The viscosity of the solution at 25°C is $9.41 \times 10^{-5} \text{ kg/ms}$ and the density of the protein (pure solid compound) is 7.82 g/cm^3 . Assuming the protein molecules to be of spherical shape (globular protein) and much larger than the solvent molecules, what is the molar mass of the protein?

- a) 907 kg/mol
 b) 174 kg/mol
 c) 90.6 g/mol
 d) 17.4 g/mol
 e) 0.906 g/mol

Stokes-Einstein equations

$$D = \frac{k_B T}{6\pi\eta r} \quad \text{protein} \gg \text{solvent}$$

$$r = \frac{k_B T}{6\pi\eta D}$$

$$= \frac{1.381 \cdot 10^{-23} \frac{\text{J}}{\text{K}} \cdot 298.15 \text{ K}}{6\pi \cdot 9.41 \cdot 10^{-5} \frac{\text{kg}}{\text{ms}} \cdot 6.48 \cdot 10^{-10} \frac{\text{m}^2}{\text{s}}}$$

$$= 3.582 \cdot 10^{-9} \text{ m}$$

$$V = \frac{4}{3} \pi r^3 = 1.925 \cdot 10^{-25} \text{ m}^3$$

$$m = d \cdot V = 7.82 \cdot \frac{10^{-3} \text{ kg}}{10^{-6} \text{ m}^3} \cdot 1.925 \cdot 10^{-25} \text{ m}^3$$

$$= 1.50535 \cdot 10^{-21} \text{ kg}$$

$$M = m N_A = 1.50535 \cdot 10^{-21} \text{ kg} \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1}$$

$$= \frac{906.34}{906.52} \text{ kg/mol} = \frac{906}{907} \text{ kg/mol}$$

11. The electrolytic conductivity of a 0.0312 M solution of a weak base is 1.53×10^{-4} S/cm. If the sum of the limiting molar ionic conductance for BH^+ and OH^- is 237.0 S cm^2/mol , what is the value of the base constant K_b ?

- a) 1.36×10^{-5}
 b) 5.21×10^{-3}
 c) 2.63×10^{-4}
 d) 4.51×10^{-5}
 e) 1.12×10^{-5}



$$K_b = \frac{[BH^+][OH^-]}{(B)}$$

$$K_b = \frac{\alpha^2}{1-\alpha} c_0 \quad \text{Ostwald's dilution law}$$

$$\alpha = \frac{\Lambda}{\Lambda^0}$$

$$\Lambda = \frac{\kappa}{c_0} = \frac{1.53 \cdot 10^{-4} \text{ S/cm}}{0.0312 \text{ mol/L}} = 4.904 \cdot 10^{-3} \frac{\text{S}}{\text{cm}} \cdot \frac{\text{dm}^3}{\text{mol}}$$

$$4.904 \cdot 10^{-3}$$

$$= 4.904 \frac{\text{S}}{\text{mol cm}} \cdot (10 \text{ cm})^3 = 4.904 \frac{\text{S cm}^2}{\text{mol}}$$

$$\alpha = \frac{\Lambda}{\Lambda^0} = \frac{4.904}{237.0} = 0.02069$$

$$K_b = \frac{\alpha^2}{1-\alpha} 0.0312 \text{ M} = 1.364 \cdot 10^{-5} \frac{\text{M}}{c^0}$$

$$c^0 = 1 \text{ M}$$

$$\rightarrow K_b = 1.36 \cdot 10^{-5}$$

12. Water is transported upward in trees through channels in the trunk called xylem. An average value of xylem diameter is 2.0×10^{-7} m. What will be the maximum rise of water in the capillary xylem channels, assuming complete wetting and the water surface tension and density are 71.99 mN m^{-1} and 997 kg m^{-3} , respectively?

a. 147 m

b. 0.74 m

c. 25 m

d. 0.25 m

e. 54 m

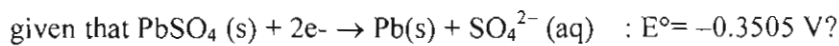
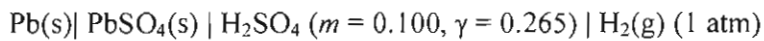
capillary rise h for complete wetting

$$h = \frac{2\gamma}{\rho g r} = \frac{2 \cdot 71.99 \cdot 10^{-3} \frac{\text{N}}{\text{m}}}{997 \frac{\text{kg}}{\text{m}^3} \cdot 9.81 \frac{\text{m}}{\text{s}^2} \cdot 1.0 \cdot 10^{-7} \text{ m}}$$

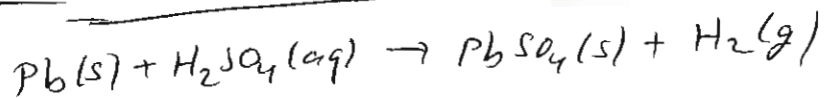
$$= 147.2 \frac{\frac{\text{kg m}}{\text{s}^2} \cdot \frac{1}{\text{m}}}{\frac{\text{kg m}}{\text{s}^2} \cdot \frac{1}{\text{m}^3} \cdot \text{m}}$$

$$= 147 \frac{1/\text{m}}{1/\text{m}^2} = 147 \text{ m}$$

13. What is the cell potential at 25°C of the cell,



- A) ~~0.288~~ ^{0.228} V left oxid: $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$
 B) 0.814 V right red: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
 C) 1.25 V
 D) 2.21 V
 E) 0.604 V ~~for~~ $E^\circ = -E^\circ_{\text{Pb}^{2+}/\text{Pb}} + E^\circ_{\text{H}^+/\text{H}_2} (0.0)$



(right - left)

E° always for reduction

$$\rightarrow E^\circ = 0.3505 \text{ V}$$

$$E = E^\circ - \frac{0.05916 \text{ mV}}{2} \log_{10} \frac{P_{\text{H}_2}}{a_{\text{H}^+}^2 a_{\text{SO}_4^{2-}}}$$

$\rightarrow 1 \text{ atm, const.}$

$$= 0.3505 \text{ V} + 29.58 \text{ mV} \log_{10} (a_{\text{H}^+}^2 a_{\text{SO}_4^{2-}})$$

$$m_{\text{H}^+} = 2m_{\text{H}_2\text{SO}_4}, \quad m_{\text{SO}_4^{2-}} = m_{\text{H}_2\text{SO}_4}$$

$$m_{\text{H}^+}^2 m_{\text{SO}_4^{2-}} = 4m_{\text{H}_2\text{SO}_4}^3$$

$$a_{\text{H}^+}^2 a_{\text{SO}_4^{2-}} = 4m_{\text{H}_2\text{SO}_4}^3 \gamma_{\pm}^3$$

$$= 4 \cdot 0.265^3 \cdot 0.1^3 = 7.4439 \cdot 10^{-5}$$

turn h

$$E = 0.3505 \text{ V} + 29.58 \cdot 10^{-3} \text{ V} \cdot \log_{10} \left(\frac{7.44 \cdot 10^{-5}}{7.4439} \right)$$

$$= 0.2284 \text{ V} = 0.228 \text{ V}$$

14. If ΔS° for the reaction of $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Cu}$ ($E^\circ_{\text{rxn}} = 1.10\text{V}$) at ^{298.15}~~298~~ K is -30.9 J K^{-1} . What is E°_{rxn} at 50°C for this reaction?

- (A) 1.096 V
- B) 3.512 V
- C) 2.230 V
- D) 0.213 V
- E) 0.762 V

$$\Delta S^\circ(298 \text{ K}) = -30.9 \text{ J/K}$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P$$

$$E_{T_2} = E_{T_1} + \left(\frac{\partial E}{\partial T} \right)_P (T_2 - T_1)$$

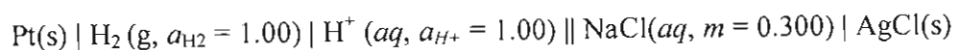
$$\left(\frac{\partial E}{\partial T} \right)_P = \frac{\Delta S}{nF} = \frac{-30.9 \text{ J/K}}{2 \text{ mol} \cdot 96485 \text{ C/mol}}$$

$$= -1.601 \cdot 10^{-4} \frac{\text{VAs/K}}{\text{As}}$$

$$= -1.601 \cdot 10^{-4} \text{ V/K}$$

$$\begin{aligned} E(50^\circ\text{C}) &= E(25^\circ\text{C}) + \left(\frac{\partial E}{\partial T} \right)_P (T_2 - T_1) \\ &= 1.10 \text{ V} - 1.601 \cdot 10^{-4} \frac{\text{V}}{\text{K}} (50^\circ\text{C} - 25^\circ\text{C}) \cdot \frac{\text{K}}{^\circ\text{C}} \\ &= 1.096 \text{ V} \end{aligned}$$

15. Given that



| Ag(s) $E_{\text{cell}}^{\circ} = +0.260 \text{ V}$. Determine γ_{Cl^-} assuming $\gamma_{\pm} = \gamma_{\text{Na}^+} = \gamma_{\text{Cl}^-}$.

E_{cell}

- (A) 0.760 $\frac{1}{2} \text{H}_2 \rightarrow \text{H}^+ + \text{e}^- \quad E^{\circ} = 0.0 \text{ V} \quad \text{left}$
- B) 0.253 $\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^- \quad E^{\circ} = 0.222 \text{ V} \quad \text{right}$
- C) 0.596 $\text{AgCl(s)} + \frac{1}{2} \text{H}_2(\text{g}) \rightarrow \text{Ag(s)} + \text{HCl(aq)}$
- D) 1.23
- E) 3.45 $E^{\circ} = E^{\circ}(\text{right}) - E^{\circ}(\text{left}) = 0.222 \text{ V}$

$$E_{\text{cell}} = E^{\circ} - 0.05916 \text{ V} \log_{10} (a_{\text{H}^+} a_{\text{Cl}^-})$$

$$\text{given } a_{\text{H}^+} = 1.00$$

$$a_{\text{Cl}^-} = m_{\text{NaCl}} \cdot \gamma_{\text{Cl}^-}$$

$$0.260 \text{ V} = 0.222 \text{ V} - 0.05916 \text{ V} \log_{10} (1.0 \cdot 0.3 \cdot \gamma_{\text{Cl}^-})$$

$$0.038 \text{ V} = -0.05916 \text{ V} \log_{10} (0.3 \gamma_{\text{Cl}^-})$$

$$\log_{10} (0.3 \gamma_{\text{Cl}^-}) = -0.6423$$

$$0.3 \gamma_{\text{Cl}^-} = 10^{-0.6423} = 0.2279$$

$$\gamma_{\text{Cl}^-} = \frac{0.2279}{0.3} = 0.7597 = 0.760$$

16. What is the solubility of CaCO_3 ($K_{sp} = 3.4 \times 10^{-9}$) in an aqueous solution with $I = 0.0250 \text{ mol kg}^{-1}$.

A) $1.22 \times 10^{-4} \text{ mol kg}^{-1}$

B) $2.44 \times 10^{-4} \text{ mol kg}^{-1}$

C) $3.62 \times 10^{-4} \text{ mol kg}^{-1}$

D) $4.17 \times 10^{-4} \text{ mol kg}^{-1}$

E) $5.21 \times 10^{-4} \text{ mol kg}^{-1}$

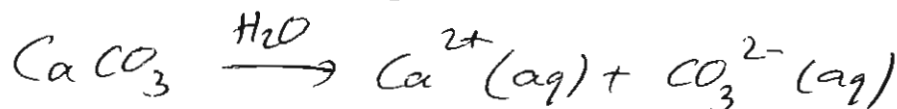
$$I = 0.0250 \text{ m}$$

$$\ln \gamma_{\pm} = -1.173 \underbrace{z_+ |z_-|}_{2 \cdot 2 = 4} \sqrt{I / 1 \text{ m}}$$

$$= -1.173 \cdot 4 \cdot \sqrt{0.025}$$

$$= -0.7419$$

$$\gamma_{\pm} = e^{-0.7419} = 0.4762$$



$$\rightarrow K_{sp} = s^2 \gamma_{\pm}^2$$

s : solubility = maximum conc. in solution

$$s = \frac{\sqrt{K_{sp}}}{\gamma_{\pm}} = \frac{\sqrt{3.4 \cdot 10^{-9}}}{0.4762} \text{ m} = 1.22(4) \cdot 10^{-4} \text{ m}$$

17. Which of the following is **true** for a 0.0120 m solution of Na_3PO_4 at 298 K?

(Assume complete dissociation)

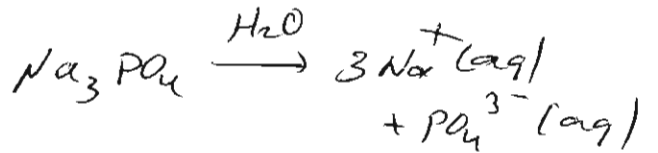
A) $\gamma_{\pm} = 0.389$, $a_{\pm} = 0.0106$, $I = 0.0720 \text{ m}$

B) $\gamma_{\pm} = 0.580$, $a_{\pm} = 0.0204$, $I = 0.0820 \text{ m}$

C) $\gamma_{\pm} = 0.645$, $a_{\pm} = 0.1063$, $I = 0.1420 \text{ m}$

D) $\gamma_{\pm} = 0.789$, $a_{\pm} = 0.5106$, $I = 0.3720 \text{ m}$

E) $\gamma_{\pm} = 0.623$, $a_{\pm} = 0.0106$, $I = 0.0720 \text{ m}$



$$c_{\text{Na}^+} = 3 c_{\text{Na}_3\text{PO}_4} = 3c$$

$$c_{\text{PO}_4^{3-}} = c_{\text{Na}_3\text{PO}_4} = c$$

$$I = \frac{1}{2} \sum_i c_i (z_i)^2 = \frac{1}{2} (3c (+1)^2 + c (-3)^2)$$

$$= \frac{1}{2} c (3 + 9)$$

$$= 6c = 6 \cdot 0.0120 \text{ m}$$

$$= 0.0720 \text{ m}$$

$$\ln \gamma_{\pm} = -1.173 \cdot (+1) \cdot (-3) \cdot \sqrt{0.072}$$

$$= -0.9442$$

$$\gamma_{\pm} = e^{-0.9442} = 0.38899$$

$$= 0.389$$

$$m_{\pm}^4 = (0.036)^3 \cdot 0.012 \text{ m}^4$$

$$= 5.59872 \cdot 10^{-7} \text{ m}^4$$

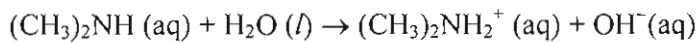
$$m_{\pm} = 0.02735 \text{ m}$$

$$a_{\pm} = \frac{m_{\pm} \cdot \gamma_{\pm}}{m^{\circ}} = 0.02735 \cdot 0.38899 = 0.01064$$

$$= 0.0106$$

$$m^{\circ} = 1 \text{ m}$$

18. The equilibrium constant for the following reaction is 5.12×10^{-4} . Calculate the extent of hydrolysis for a 0.210 m solution of $(\text{CH}_3)_2\text{NH}$ that is in 0.500 m NaNO_3 if γ_{\pm} is 0.428 .



- (A) 10.9%
 B) 25.2%
 C) 5.4%
 D) 34.0%
 E) 17.4%

$$[(\text{CH}_3)_2\text{NH}]_0 = c_0 = 0.210 \text{ m}$$

$$[\text{NaNO}_3] = 0.5 \text{ m}$$

$$\gamma_{\pm} = 0.428$$

hydrolyzed amount: $x = \frac{m}{m^0}$

$$m^0 = 1 \text{ mol/kg}$$

$$K = \frac{x^2 \gamma_{\pm}^2}{c_0 - x}$$

$$Kc_0 - Kx = x^2 \gamma_{\pm}^2$$

$$0.183184 x^2 + 5.12 \cdot 10^{-4} x - 1.0752 \cdot 10^{-4} = 0$$

$$x^2 + 2.7950 \cdot 10^{-3} x - 5.8695 \cdot 10^{-4} = 0$$

$$x_{1(2)} = \frac{1}{2} \left[-2.7950 \cdot 10^{-3} \pm \sqrt{7.8120 \cdot 10^{-6} + 2.3478 \cdot 10^{-3}} \right]$$

$$= \frac{1}{2} \left[-2.7950 \cdot 10^{-3} + \sqrt{2.3556 \cdot 10^{-3}} \right]$$

$$= \frac{1}{2} \left[-2.7950 \cdot 10^{-3} + 0.04853 \right]$$

24

$$= \frac{1}{2} [0.045735] = 0.022868$$

turn

$$\begin{aligned}\% \text{ hydrolysis} &= \frac{x}{c^0} \cdot 100\% \\ &= \frac{0.022868}{0.210} \cdot 100\% \\ &= 10.89\% = 10.9\%\end{aligned}$$

19. For the reaction $A + B \rightarrow \text{product P}$ for different sets of initial A and B concentrations the following initial rates R_0 were found:

$[A]_0$ (mM)	$[B]_0$ (mM)	R_0 (mM/s)
0.230	0.0310	0.525
0.460	0.0620	4.20
0.920	0.0620	16.8

Determine the rate of reaction with respect to A, α , and with respect to B, β .

- A) $\alpha = 1, \beta = 2$
 B) $\alpha = 2, \beta = 1$
 C) $\alpha = 0, \beta = 3$
 D) $\alpha = 3, \beta = 0$
 E) $\alpha = 3/2, \beta = 3/2$

$$\frac{d[P]}{dt} = k [A]^\alpha [B]^\beta = R_0$$

$$\frac{R_2}{R_3} = \frac{4.20}{16.8} = 0.25 = \left(\frac{[A]_2}{[A]_3}\right)^\alpha = \left(\frac{0.46}{0.92}\right)^\alpha = 0.5^\alpha$$

$$\ln 0.25 = \alpha \ln 0.5, \quad \alpha = \frac{\ln 0.25}{\ln 0.5} = \underline{2}$$

$$\frac{R_1}{R_2} = \frac{0.525}{4.2} = 0.125 = \left(\frac{0.23}{0.46}\right)^2 \left(\frac{0.031}{0.062}\right)^\beta = 0.25 \cdot (0.5)^\beta$$

$$0.5^\beta = \frac{0.125}{0.25} = 0.5 \Rightarrow \underline{\beta = 1}$$

20. Substance A decomposes in the atmosphere in a first order reaction A yields P.
The half-life of A is 2.5 s. After what time will the initial amount of A be decomposed by 40%?

A) 1.84 s

B) 0.54 s

C) 0.303 s

D) -1.845 s

E) 3.30 s

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{2.5} \text{ s}^{-1}$$
$$= 0.2773 \text{ s}^{-1}$$

a_0 decomposed by 40%

$\Rightarrow 60\% a_0$ is left

$$\Rightarrow a = 0.6 a_0 = a_0 e^{-kt}$$

$$t = \frac{-\ln 0.6}{k} = \frac{-\ln 0.6}{0.2773 \text{ s}^{-1}}$$
$$= 1.84(2) \text{ s}$$

21. When the activation energy of a reaction 2 ($2E_a$), rate constant k_2 , is double that of a reaction 1 (E_a), rate constant k_1 , what is $\ln(k_1/k_2)$ in terms of $x=E_a/RT$ when both reactions have the same pre-exponential factor A ? *at the same temperature for both?*

A) x

B) $2x$

C) $-x$

D) $-2x$

E) $3x$

$$k_1 = A e^{-E_a/RT}$$

$$k_2 = A e^{-2E_a/RT}$$

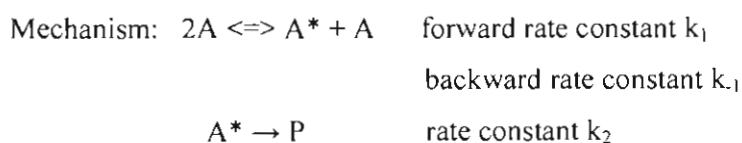
$$\frac{k_1}{k_2} = e^{-E_a/RT + 2E_a/RT}$$

$$= e^{(-1+2)E_a/RT}$$

$$= e^x, \quad x = E_a/RT$$

$$\rightarrow \ln \frac{k_1}{k_2} = x$$

22. For the Lindemann mechanism, when only reactant A is initially present in the reaction mixture (no buffer gas M), derive an expression for the concentration of the activated reactant molecules, $[A^*]$, using the steady state approximation (SSA) in case of very high reactant concentration, $[A]$.



- A) $[A^*] = (k_1/k_{-1})[A]$
- B) $[A^*] = k_1[A]^2 / (k_{-1}[A] + k_2)$
- C) $[A^*] = (k_1/k_2)[A]^2$
- D) $[A^*] = k_1[A]^2$
- E) $[A^*] = k_1[A]$

SSA

$$\frac{d[A^*]}{dt} = 0 = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$$

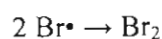
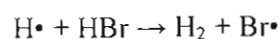
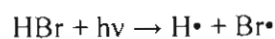
$$0 = k_1[A]^2 - (k_{-1}[A] + k_2)[A^*]$$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

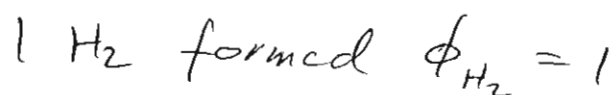
$\hookrightarrow k_{-1}[A] \gg k_2$ when $[A]$ is very high

$$\rightarrow [A^*] = \frac{k_1[A]^2}{k_{-1}[A]} = \frac{k_1}{k_{-1}}[A]$$

23. Is a quantum yield of $\Phi = 2$ for the formation of H_2 consistent with the following mechanism?



- A) No, because $\Phi = 1$ for the formation of H_2 *decomposition*
- B) Yes, because $\Phi = 2$ for the formation of HBr
- C) Yes, because $\Phi = 2$ for the formation of Br_2 *no, $\Phi = 1$*
- D) No, because there is no quantum yield involved in this mechanism
- E) It is not possible to know



Thus, if $\Phi_{H_2} = 2$ then the mechanism cannot be correct!

24. For the enzyme catalyzed reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ it was measured that

$[\text{CO}_2]$ (mM)	R_0 Rate (M/s)
1.25	2.78×10^{-5}
20	1.07×10^{-4}

Determine the maximum rate R_{max} and the Michaelis constant K_m , assuming a Michaelis-Menten mechanism.

- A) $R_{\text{max}} = 1.32 \times 10^{-4}$ M/s, $K_m = 4.69$ mM
- B) $R_{\text{max}} = 7571$ M/s, $K_m = 4.69$ M
- C) $R_{\text{max}} = 1.32$ M/s, $K_m = 4.69$ M
- D) $R_{\text{max}} = 7571$ M/s, $K_m = 4.69$ mM
- E) $R_{\text{max}} = 1.32$ mM/s, $K_m = 4.69$ M

Lineweaver - Burk equations

$$\frac{1}{R_0} = \frac{1}{R_{\text{max}}} + \frac{K_m}{R_{\text{max}}} \frac{1}{[\text{CO}_2]}$$

$$y = b + ax$$

$$y = \frac{1}{R} \quad b = \frac{1}{R_{\text{max}}} \quad a = \frac{K_m}{R_{\text{max}}} \quad x = \frac{1}{[\text{CO}_2]}$$

$$a = \frac{\Delta y}{\Delta x}$$

$$\Delta y = \left(\frac{1}{R_0} \right)_2 - \left(\frac{1}{R_0} \right)_1 = \left(\frac{1}{1.07 \cdot 10^{-4}} - \frac{1}{2.78 \cdot 10^{-5}} \right) \frac{\text{s}}{\text{M}}$$

$$= -2.6625 \cdot 10^4 \frac{\text{s}}{\text{M}}$$

$$\Delta x = \left(\frac{1}{[\text{CO}_2]} \right)_2 - \left(\frac{1}{[\text{CO}_2]} \right)_1 = \left(\frac{1}{20 \cdot 10^{-3}} - \frac{1}{1.25 \cdot 10^{-3}} \right) \frac{1}{\text{M}}$$

$$= -750 \frac{1}{\text{M}} \quad \text{turn}$$

$$a = \frac{\Delta y}{\Delta x} = \frac{-2,6625 \cdot 10^4 \frac{\text{s}}{\text{M}}}{-750 \frac{1}{\text{M}}}$$
$$= 35,5 \text{ s}$$

$$y_i = b + ax_i$$

$$b = y_i - ax_i = \left(\frac{1}{R_0}\right)_i - a \left(\frac{1}{[CO]_0}\right)_i$$
$$= 35971 \frac{\text{s}}{\text{M}} - 35,5 \text{ s} \cdot 800 \frac{1}{\text{M}}$$

$$= 7571 \frac{\text{s}}{\text{M}}$$

$$R_{\max} = \frac{1}{b} = 1,32(1) \cdot 10^{-4} \text{ M/s}$$

$$K_m = a \cdot R_{\max}$$

$$= 35,5 \text{ s} \cdot 1,3208 \cdot 10^{-4} \text{ M/s}$$

$$= 4,6888 \cdot 10^{-3} \text{ M}$$

$$= 4,69 \text{ mM}$$

25. The densities of acetone and water at 20°C are 0.972 g/mL and 0.9982 g/mL, respectively (1 mL = 1 cm³). The viscosity of water is 1.002 × 10⁻³ kg/ms at this temperature. Water requires 120.5 s to flow through an Ostwald viscosimeter, while acetone requires 40.5 s. What is the viscosity of acetone?

- A) 3.28 × 10⁻⁴ kg/ms
- B) 2.90 × 10⁻³ kg/ms
- C) 1.03 × 10⁻³ kg/ms
- D) 1.00 × 10⁻⁴ kg/ms
- E) 0.56 × 10⁻⁴ kg/ms

$$\eta = A d t$$

$$\frac{\eta_{\text{CH}_3\text{OH}}}{\eta_{\text{H}_2\text{O}}} = A \frac{d_{\text{CH}_3\text{OH}} t_{\text{CH}_3\text{OH}}}{d_{\text{H}_2\text{O}} t_{\text{H}_2\text{O}}}$$

$$X = \text{acetone} = (\text{CH}_3)_2\text{CO}$$

$$W = \text{water} = \text{H}_2\text{O}$$

$$\frac{\eta_X}{\eta_W} = \frac{A d_X t_X}{A d_W t_W} = \frac{d_X t_X}{d_W t_W}$$

$$\eta_X = \eta_W \frac{d_X t_X}{d_W t_W}$$

$$= 1.002 \cdot 10^{-3} \frac{\text{kg}}{\text{ms}} \cdot \frac{0.972}{0.9982} \cdot \frac{40.5}{120.5}$$

$$= 3.279 \cdot 10^{-4} \frac{\text{kg}}{\text{ms}} = 3.28 \cdot 10^{-4} \frac{\text{kg}}{\text{ms}}$$