CHEM 311 (132) **Final Exam** **3 HOURS**

Sunday, May 18, 2014, 8:00 AM

Building 54 - B

Test Code (000)

(25 Questions)

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Physical constants, conversion factors, and useful equations

Physical Constants

$R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$
$= 0.08206\ \mathrm{L\ atm K^{-1}\ mol^{-1}}$
$= 0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}}$
$N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$
$k_B = 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
$h = 6.626 \times 10^{-34}\ \mathrm{J\ s}$
$F = 96{,}485\ \mathrm{C\ mol^{-1}}$
$c = 2.998 \times 10^{8}\ \mathrm{m\ s^{-1}}$
$g = 9.81\ \mathrm{m\ s^{-2}}$
$e = 1.6022 \times 10^{-19}\ \mathrm{C}$
$\varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{C^2\ J^{-1}\ m^{-1}}$
$B = 0.51\ \mathrm{mol^{-1/2}\ dm^{3/2}}$ (in H_2O, 25°C)

Other Units

$1\ \mathrm{dm^3} = 1\ \mathrm{L}$
$1\ \mathrm{dm^3} = 1000\ \mathrm{cm^3}$
$1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$
$1\ \mathrm{atm} = 1.01325 \times 10^5\ \mathrm{Pa}$
$1\ \mathrm{atm} = 760\ \mathrm{mmHg}$
$1\ \mathrm{Torr} = 1\ \mathrm{mmHg}$
$1\ \mathrm{Torr} = 133.322\ \mathrm{Pa}$
$1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$
$E = h\upsilon$
$c = \upsilon\lambda$
$PV = nRT$
$(RT)/F = 25.6926\ \mathrm{mV}$ at 25°C
$\ln(x)/\log_{10}(x) = 2.30259$ for all x
$\ln(1 - \theta) = -\theta$
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:
$k_{uni} = k_1 k_2 [M](k_{-1}[M] + k_2)^{-1}$
Langmuir isotherm:
$\theta = KP/(1 + KP)$

Important Equations

$$\Lambda = \frac{\kappa}{c}\ ,\ \alpha = \frac{\Lambda}{\Lambda_0}\quad \text{and}\quad I = \frac{1}{2}\sum_i c_i z_i^2$$

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

$\Lambda_m = \Lambda^\circ_m - K(c/c_o)^{1/2}$ (strong)
$1/\Lambda_m = 1/\Lambda^\circ_m + c\Lambda_m/[(\Lambda^\circ_m)^2 K_a]$ (weak)
$\Delta G^\circ_{solvation} = (1/\varepsilon_r - 1)z^2 e^2 N_A/(8\pi\varepsilon_o r)$
$\Delta G = -nFE$ and thus $\Delta G^\circ = -nFE^\circ$

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

$\Delta S = nF(dE/dt)_P$
$a_\pm^{m+n} = a_+^m a_-^n$ for $A_m B_n$
$\kappa = [2e^2 N_A \times (1000\ \mathrm{L\ m^{-3}})/(\varepsilon_o k_B T)]^{1/2} \times [\rho_{solvent}\ I/\varepsilon_r]^{1/2}$
$E^\circ AgCl/Ag = +0.222\ \mathrm{V}$

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

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

$E_a = \Delta^{\ne}H^o - P\Delta^{\ne}V^o + RT$ (sol)
$= \Delta^{\ne}H^o - \Sigma\nu RT + RT$ (gas)
$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$
$t_{1/2} = (\ln 2)/k$ (1st order)
fluorescence lifetime $t_f = (k_f + k_q[Q])^{-1}$
$D = (1/3)\ v_{ave}\ \lambda$
$\kappa = (1/3)\ (C_{V,m}/N_A)\ v_{ave}\ N_p\ \lambda$

$(C_{V,m}/N_A) = (3/2)\ k_B$
$\eta = (1/3)\ v_{ave} N_p \lambda m$
$v_{ave} = (8RT/(\pi M))^{1/2}$
$N_p\lambda = 1/((\sqrt{2})\sigma)$,
$\lambda = RT/(PN_A(\sqrt{2})\sigma)$
$Np = (N/V) = PN_A/(RT)$
$\sigma = \pi d^2$
$x_{rms} = (\sqrt{\langle x^2 \rangle}) = \sqrt{(2Dt)}$

Poisseuille equation: $(\Delta V/\Delta t) = (\pi r^4/(8\eta))\ \Delta P/\Delta L$

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

if r(particle) >> r(solvent molecule)

Ostwald viscosimeter: $\eta = A\rho t$,

Capillary rise: $h = 2\gamma/(dgr)$

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

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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 x 10^{-7} cm^2s^{-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

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

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

$$= 2\,564\,103\,s$$

$$= 2\,564\,103\,s \cdot \cancel{\frac{3600\,s}{h}} \cdot \frac{1h}{3600\,s}$$

$$= 712.3\,h$$

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

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

enter!

2. Upon adding sugar carefully on top of a full cup of water of height 10 cm, sugar will start to diffuse slowly with a diffusion coefficient of ~~id~~ 5.2×10^{-6} cm^2 s^{-1} 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%

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

$$= \sqrt{2 \cdot 5.2 \cdot 10^{-6} \frac{cm^2}{s} \cdot 1\,d \cdot \frac{\overset{24h}{\cancel{3600}}}{d} \cdot \frac{3600s}{h}}$$

$$= \sqrt{0.8986\ cm^2}$$

$$= 0.948\ cm$$

$$\%\ \text{sweet water} = \frac{0.948\ cm}{10\ cm} \cdot 100\% = 9.48\%$$

$$= 9.5\%$$

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 $4.0\text{x}10^{-3}$ kg $\text{m}^{-1}\text{s}^{-1}$, 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 nP e. 55 cPa

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

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

$$= \frac{8 \cdot 4 \cdot 10^{-3} \frac{kg}{ms}}{\pi (6 \cdot 10^{-3} m)^4} 1{,}00\, m \cdot 0{,}66 \cdot 10^{-3} \frac{L}{min}$$

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

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

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

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

$$= 0{,}08645 \frac{kg}{m s^2}$$

$$1\, Pa = 1 \frac{N}{m^2} = 1 \frac{kg\, m}{s^2} \cdot \frac{1}{m^2} = 1 \frac{kg}{m s^2}$$

$$\Delta P = 0{,}08645\, Pa = 86\, m\, Pa$$

enter !

4. The diffusion coefficient of SF_6 in SF_6 gas at 573 K and 1.00 atm is 1.02 x10^{-7} m^2/s.

Calculate the collision cross section of SF_6 at 573 K and 1.00 atm where the average speed of molecules is 288 m/s.

[✓ a. 52 nm^2] b. 25 nm^2 c. 5.2 nm^2 d.0.52 nm^2 e. 0.052 nm^2

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

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

$$\lambda = \frac{3D}{v_{ave}} = \frac{3 \cdot 1{,}02 \cdot 10^{-7} \frac{m^2}{s}}{288 \frac{m}{s}}$$

$$= 1{,}0625 \cdot 10^{-9}\ m$$

$$= 1{,}0625\ nm$$

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

$$= \frac{8{,}314 \frac{J}{K\,mol}\ 573\ K}{1{,}01325 \cdot 10^{5}\ Pa \cdot 6{,}022 \cdot 10^{23}\ mol\ \sqrt{2} \cdot 1{,}0625 \cdot 10^{-7}\ m}$$

$$= 5{,}1959 \cdot 10^{-17}\ \frac{J/\cancel{mol}}{\frac{N}{m^2}\ \cancel{mol} \cdot m}$$

$$= 5{,}1959 \cdot 10^{-17}\ \frac{Nm}{\frac{N}{m}} = 5{,}1959 \cdot 10^{-17}\ m^2$$

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

$$\sigma = 51{,}959 \cdot 10^{-18}\ m^2 = 51{,}959\ nm^2 = 52\ nm^2$$

5. Determine the ratio of the thermal conductivities for Kr ($\sigma = 0.52$ ~~nm2~~ 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

$$\kappa = \cancel{\frac{1}{3}\,\frac{3}{2}k}\ \frac{1}{3}\,\frac{C_{V,m}}{N_A}\,v_{ave}\,\mathcal{N}_p\,\lambda$$

$$= \frac{1}{3}\cdot\frac{3}{2}k_B\,v_{ave}\,\mathcal{N}_p\,\lambda = \frac{1}{2}k_B\,v_{ave}\,\mathcal{N}_p\,\lambda$$

$$\mathcal{N}_p\,\lambda = \frac{1}{\sqrt{2}\,\sigma} \quad \text{for ideal gases}$$

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

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

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

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

$$= \sqrt{\frac{39{,}95}{83{,}80}}\cdot\frac{0{,}36}{0{,}52} = \sqrt{0{,}4767}\cdot 0{,}6923$$

$$= 0{,}478 = 0{,}48$$

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 S m^2 mol^{-1} .

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

[✓ a)] 4.00 × 10^{-3} S m^2 mol^{-1}

b) 5.00 × 10^{-3} S m^2 mol^{-1}

c) 6.00 × 10^{-3} S m^2 mol^{-1}

d) 2.00 × 10^{-3} S m^2 mol^{-1}

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

$$\kappa = \kappa(KCl) + \kappa(XCl)$$

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

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

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

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

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

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

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

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

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

$$= \frac{1}{3} \cdot \cancel{\frac{2}{3}} \frac{3}{2} k_B v_{ave} \cdot \frac{1}{\sqrt{2}\sigma}$$ 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 = $1.256 \times 10^{-4}\ m^2/s$) in 10 minutes is (hint: use x_{rms} again!)

1

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

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

$$= \sqrt{2 \cdot 1,256 \cdot 10^{-4} \frac{m^2}{s} \cdot 10\ min \cdot \frac{60s}{min}}$$

$$= \sqrt{0,1507}\ m$$

$$= 0,3882\ m = 0,39\ m$$

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

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

same T, P, σ

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

enter !

10. The diffusion coefficient for a globular protein molecule in a solvent is 6.48 x 10^{-10} m^2/s at 25 °C. The viscosity of the solution at 25 °C is 9.41 x 10^{-5} 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

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

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

$$= \frac{1{,}381 \cdot 10^{-23} \frac{J}{K} \cdot 298{,}15\,K}{6\pi \cdot 9{,}41 \cdot 10^{-5} \frac{kg}{ms} \, 6{,}48 \cdot 10^{-10} \frac{m^2}{s}}$$

$$= 3{,}582 \cdot 10^{-9}\,m$$

$$V = \frac{4}{3}\pi r^3 = 1{,}925 \cdot 10^{-25}\,m^3$$

$$m = d \cdot V = 7{,}82 \cdot \frac{10^{-3}\,kg}{10^{-6}\,m^3} \cdot 1{,}925 \cdot 10^{-25}\,m^3$$

$$= 1{,}50535\,\cancel{kg} \cdot 10^{-21}\,kg$$

$$M = m N_A = 1{,}50535 \cdot 10^{-21}\,kg \cdot 6{,}022 \cdot 10^{23}\,mol^{-1}$$

= ~~906,34~~ 906,52 kg/mol = ~~906~~ 907 kg/mol

11. The electrolytic conductivity of a 0.0312 M solution of a week base is 1.53 x 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 x 10^{-5}
b) 5.21 x 10^{-3}
c) 2.63 x 10^{-4}
d) 4.51 x 10^{-5}
e) 1.12 x 10^{-5}

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

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

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

$$\alpha = \frac{\Lambda}{\Lambda^0} \qquad \Lambda = \frac{\kappa}{c_0} = \frac{1,53 \cdot 10^{-4}\ S/cm}{0,0312\ mol/L}$$

$$4,904 \cdot 10^{-3}$$

$$= \cancel{4,904}\ \frac{S}{cm} \cdot \frac{dm^3}{mol}$$

$$4,904 \cdot 10^{-3}$$

$$= \cancel{4,904}\ \frac{S}{mol\ cm} \cdot (10\ cm)^3 = 4,904\ \frac{S\,cm^2}{mol}$$

$$\alpha = \frac{\Lambda}{\Lambda^0} = \frac{4,904}{237,0} = 0,02069$$

$$K_b = \frac{\alpha^2}{1-\alpha}\ 0,0312\ M = 1,364 \cdot 10^{-5}\ \frac{M}{c^0}$$

$$c^0 = 1\ M$$

$$\rightarrow K_b = 1,36 \cdot 10^{-5}$$

12. Water is transported upward in trees through channels in the trunk called xylem. An average value of xylem diameter is 2.0 x 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

$$h = \frac{2\gamma}{dgr} = \frac{2 \cdot 71{,}99 \cdot 10^{-3} \frac{N}{m}}{997 \frac{kg}{m^3} \cdot 9{,}81 \frac{m}{s^2} \cdot 1{,}0 \cdot 10^{-7} m}$$

$$= 147{,}2 \; \frac{\frac{kgm}{s^2} \cdot \frac{1}{m}}{\frac{kgm}{s^2} \cdot \frac{1}{m^3} \cdot m}$$

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

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

$Pb(s) | PbSO_4(s) | H_2SO_4$ ($m = 0.100$, $\gamma = 0.265$) | $H_2(g)$ (1 atm)

given that $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$: E°= –0.3505 V?

A) $\overset{0.228}{\cancel{0.288}}$ V

B) 0.814 V

C) 1.25 V

D) 2.21 V

E) 0.604 V

left oxid: $Pb + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-$

right red: $2H^+ + 2e^- \rightarrow H_2$

$$Pb(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2(g)$$

$$\cancel{fo}\ E^{\circ} = -E^{\circ}_{Pb^{2+}/Pb} + E^{\circ}_{H^+/H_2}\ (0.0)$$

(right – left)

E° always for reduction

$\rightarrow$ E° = 0.3505 V

$$E = E^{\circ} - \frac{\cancel{0.0}59.16\ mV}{2} \log_{10} \frac{\overset{\rightarrow \text{ 1 atm, const.}}{P_{H_2}}}{a_{H^+}^2\, a_{SO_4^{2-}}}$$

$$= 0.3505\ V + 29.58\ mV \log_{10} (a_{H^+}^2\, a_{SO_4^{2-}})$$

$$m_{H^+} = 2m_{H_2SO_4}, \quad m_{SO_4^{2-}} = m_{H_2SO_4}$$

$$m_{H^+}^2\, m_{SO_4^{2-}} = 4\, m_{H_2SO_4}^3$$

$$a_{H^+}^2\, a_{SO_4^{2-}} = 4\, m_{H_2SO_4}^3\, \gamma_{\pm}^3$$

$$= 4 \cdot 0.265^3 \cdot 0.1^3 = \overset{7.4439}{\cancel{7.44}} \cdot 10^{-5}$$

turn!

$$E = 0{,}3505\,V + 29{,}58 \cdot 10^{-3}\,V \cdot \log_{10}\left(\underset{7{,}4439}{\cancel{7{,}44}} \cdot 10^{-5}\right)$$

$$= 0{,}2284\,V = 0{,}228\,V$$

1

14. If $\Delta S°$ for the reaction of $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$ ($E°_{rxn} = 1.10V$) at ~~298~~ 298.15 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

$$\Delta S°(298\ K) = -30.9\ J/K$$

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

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

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

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

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

$$E(50°C) = E(25°C) + \left(\frac{\partial E}{\partial T}\right)_p (T_2 - T_1)$$

$$= 1.10\ V - 1.601 \cdot 10^{-4}\ \frac{V}{K}(50°C - 25°C) \cdot \frac{K}{°C}$$

$$= 1.096\ V$$

15. Given that

Pt(s) | H_2 (g, a_{H2} = 1.00) | H^+ (aq, a_{H+} = 1.00) || NaCl(aq, m = 0.300) | AgCl(s) | Ag(s) ~~E°_{cell}~~ E_{cell} = +0.260 V. Determine γ_{Cl^-} assuming $\gamma_\pm = \gamma_{Na+} = \gamma_{Cl^-}$.

[✓ A) 0.760]

B) 0.253

C) 0.596

D) 1.23

E) 3.45

$\frac{1}{2} H_2 \rightarrow H^+ + e^-$ $E^\circ = 0.0$ V left

$AgCl + e^- \rightarrow Ag + Cl^-$ $E^\circ = 0.222$ V right

$AgCl(s) + \frac{1}{2} H_2(g) \rightarrow Ag(s) +$ ~~Cl~~ $HCl(aq)$

$E^\circ = E^\circ(\text{right}) - E^\circ(\text{left}) = 0.222$ V

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

given $a_{H^+} = 1.00$

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

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

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

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

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

$\gamma_{Cl^-} =$ ~~0.759~~ 0.7597 = 0.760

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

[✓ A)] 1.22×10^{-4} mol kg^{-1}

B) 2.44×10^{-4} mol kg^{-1}

C) 3.62×10^{-4} mol kg^{-1}

D) 4.17×10^{-4} mol kg^{-1}

E) 5.21×10^{-4} mol kg^{-1}

$$I = 0.0250 \ m$$

$$\ln \gamma_{\pm} = -1,173 \ \underbrace{z_+ |z_-|}_{2\cdot 2 = 4} \cdot \sqrt{I/1m}$$

$$= -1,173 \cdot 4 \cdot \sqrt{0.025}$$

$$= -0.7419$$

$$\gamma_{\pm} = e^{-0,7419} = 0,4762$$

$$CaCO_3 \xrightarrow{H_2O} Ca^{2+}(aq) + CO_3^{2-}(aq)$$

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

S: solubility = maximum conc. in solution

$$s = \frac{\sqrt{K_{sp}}}{\gamma_I} = \frac{\sqrt{3,4 \cdot 10^{-9}}}{0,4762} \ m = 1,22(4) \cdot 10^{-4} \ m$$

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

(Assume complete dissociation)

[✓ A)] $\gamma_\pm = 0.389$, $a_\pm = 0.0106$, $I = 0.0720\ m$

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

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

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

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

$$Na_3PO_4 \xrightarrow{H_2O} 3\,Na^+(aq) + PO_4^{3-}(aq)$$

$$c_{Na^+} = 3\,c_{Na_3PO_4} = 3c$$

$$c_{PO_4^{3-}} = c_{Na_3PO_4} = c$$

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

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

$$= 6c = 6\cdot 0.0120\ m$$

$$= 0.0720\ m$$

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

$$= -0.9442$$

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

$$= 0.389$$

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

$$= 5.59872\cdot 10^{-7}\ m^4 \qquad m_\pm = 0.02735\ m$$

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

$$m^\circ = 1m \qquad = 0.0106$$

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 $(CH_3)_2NH$ that is in 0.500 *m* $NaNO_3$ if $\gamma\pm$ is 0.428.

$(CH_3)_2NH\,(aq) + H_2O\,(l) \rightarrow (CH_3)_2NH_2^+\,(aq) + OH^-(aq)$

[✓ A)] 10.9%

B) 25.2%

C) 5.4%

D) 34.0%

E) 17.4%

$$[(CH_3)_2NH]_0 = \cancel{x_0}\, c_0 = 0{,}210\ m$$

$$[NaNO_3] = 0{,}5\ m$$

$$\gamma_\pm = 0{,}428$$

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

$$m^0 = 1\ mol/kg$$

$$K = \frac{x^2 \gamma_\pm^2}{\cancel{x_0} \rightarrow c_0 - x}$$

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

$$0{,}183184\, x^2 + 5{,}12 \cdot 10^{-4} \overset{x}{\cancel{x}} - 1{,}0752 \cdot 10^{-4} = 0$$

$$x^2 + 2{,}7950 \cdot 10^{-3} x - 5{,}8695 \cdot 10^{-4} = 0$$

$$x_{1(,2)} = \frac{1}{2}\left[-2{,}7950 \cdot 10^{-3} \underset{(-)}{+} \sqrt{7{,}8120 \cdot 10^{-6} + 2{,}3478 \cdot 10^{-3}}\right]$$

$$= \frac{1}{2}\left[-2{,}7950 \cdot 10^{-3} + \sqrt{2{,}3556 \cdot 10^{-3}}\right]$$

$$= \frac{1}{2}\left[-2{,}7950 \cdot 10^{-3} + 0{,}04853\right]$$

$$= \frac{1}{2}\left[0{,}045735\right] = 0{,}022868$$

turn

$$\% \text{ hydrolysis} = \frac{x}{c^0} \cdot 100\%$$

$$= \frac{0{,}022868}{0{,}210} \cdot 100\%$$

$$= 10{,}89\% = 10{,}9\%$$

19. For the reaction A + B yields 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	1
0.460	0.0620	4.20	2
0.920	0.0620	16.8	3

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) $\alpha = 3/2, \beta = 3/2$

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

$$\frac{R_2}{R_3} = \frac{4,20}{16,8} = 0,25 = \left(\frac{[A]_2}{[A]_3}\right)^{\alpha} = \left(\frac{0,46}{0,92}\right)^{\alpha} = 0,5^{\alpha}$$

$$\ln 0,25 = \alpha \ln 0,5 \quad , \quad \underline{\alpha} = \frac{\ln 0,25}{\ln 0,5} = \underline{2}$$

$$\frac{R_1}{R_2} = \frac{0,525}{4,2} = 0,125 = \left(\frac{0,23}{0,46}\right)^{2}\left(\frac{0,031}{0,062}\right)^{2} = 0,25\cdot(0,5)^{\beta}$$

$$0,5^{\beta} = \frac{0,125}{0,25} = 0,5 \implies \underline{\beta = 1}$$

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

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{2{,}5}\ s^{-1}$$

$$= 0{,}2773\ s^{-1}$$

a_0 decomposed by 40%

$\Rightarrow$ 60% a_0 is left

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

$$t = \frac{-\ln 0.6}{k} = \frac{-\ln 0.6}{0{,}2773\ s^{-1}}$$

$$= 1{,}84(2)\ s$$

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] 3

B) 2x

C) −x

D) −2x

E) 3x

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

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

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

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

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

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

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].

Mechanism: $2A \Longleftrightarrow A^* + A$ forward rate constant k_1

backward rate constant k_{-1}

$A^* \rightarrow P$ rate constant k_2

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

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

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

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

& $k_{-1}[A] \gg k_2$ 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?

$$HBr + h\nu \rightarrow H\bullet + Br\bullet$$
$$H\bullet + HBr \rightarrow H_2 + Br\bullet$$
$$2\,Br\bullet \rightarrow Br_2$$

[✓ 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

1 $h\nu$ ⇒ 2 HBr decomposed $\phi_{HBr} = 2$
1 H_2 formed $\phi_{H_2} = 1$
1 Br_2 formed $\phi_{Br_2} = 1$

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

!

24. For the enzyme catalyzed reaction $CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$ it was measured that

$[CO_2]_o$(mM)	R_o ~~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)] $R_{max} = 1.32 \times 10^{-4}$ M/s, $K_m = 4.69$ mM

B) $R_{max} = 7571$ M/s, $K_m = 4.69$ M

C) $R_{max} = 1.32$ M/s, $K_m = 4.69$ M

D) $R_{max} = 7571$ M/s, $K_m = 4.69$ mM

E) $R_{max} = 1.32$ mM/s, $K_m = 4.69$ M

Lineweaver - Burke equations

$$\frac{1}{R_o} = \frac{1}{R_{max}} + \frac{K_m}{R_{max}} \frac{1}{[C]_o}$$

$$y = b + ax$$

$$y = \frac{1}{R} \mid \quad b = \frac{1}{R_{max}} \mid \quad a = \frac{K_m}{R_{max}} \mid \quad x = \frac{1}{[CO_2]}$$

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

$$\Delta y = \left(\frac{1}{R_o}\right)_2 - \left(\frac{1}{R_o}\right)_1 = \left(\frac{1}{\cancel{2.78 \cdot 10^{-3}}\ 1.07 \cdot 10^{-4}} - \frac{1}{2.78 \cdot 10^{-5}}\right) \frac{s}{M}$$

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

$$\Delta x = \left(\frac{1}{[CO_2]_o}\right)_2 - \left(\frac{1}{[CO_2]_o}\right)_1 = \left(\frac{1}{20 \cdot 10^{-3}} - \frac{1}{1.25 \cdot 10^{-3}}\right) \frac{1}{M}$$

$$= -750 \frac{1}{M}$$

turn

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

$$= 35{,}5\ s$$

$$y_1 = b + a x_1$$

$$b = y_1 - a x_1 = \left(\frac{1}{R_0}\right)_1 - a\left(\frac{1}{[CO_2]_0}\right)_1$$

$$= 35971\ \frac{s}{M} - 35{,}5\ s \cdot 800\ \frac{1}{M}$$

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

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

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

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

$$= 4{,}6888 \cdot 10^{-3}\ M\cancel{/s}$$

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

25. The densities of acetone and water at 20°C are 0.972 g/mL and 0.9982 g/mL, respectively (1 mL = 1 cm^3). The viscosity of water is 1.002 x 10^{-3} kg/ms at this temperature. Water requires 120.$\overset{5}{\cancel{0}}$ s to flow through an Ostwald viscosimeter, while acetone requires 40.5 s. What is the viscosity of acetone?

[✓ A)] 3.28 x 10^{-4} kg/ms
B) 2.90 x 10^{-3} kg/ms
C) 1.03 x 10^{-3} kg/ms
D) 1.00 x 10^{-4} kg/ms
E) 0.56 x 10^{-4} kg/ms

$$\eta = A d t$$

$$\cancel{\frac{\eta_{CH_3OH}}{\eta_{H_2O}} = A\, d_{CH_3OH}\, t_{CH_3}}$$

x = actone = $(CH_3)_2CO$
w = water = H_2O

$$\frac{\eta_x}{\eta_w} = \frac{A d_x t_x}{A d_w t_w} = \frac{d_x}{d_w}\,\frac{t_x}{t_w}$$

$$\eta_x = \eta_w \frac{\cancel{8} d_x t_x}{d_w t_w}$$

$$= 1{,}002 \cdot 10^{-3} \frac{kg}{ms} \cdot \frac{0{,}972}{0{,}9982} \cdot \frac{40{,}5}{120{,}5}$$

$$= 3{,}279 \cdot 10^{-4} \frac{kg}{ms} = 3{,}28 \cdot 10^{-4} \frac{kg}{ms}$$