CHEM 3523 001 Spring 2023 — **Name:** KEY

ID:

Final Exam

Answer Sheet: (The conceptual questions are multiple choice. List the letter that corresponds to the correct answer. For the calculation problems list under ***a) the final equation*** that gives the solution. Use only symbols, not intermediate numerical results. List under ***b) the final numerical result***. Make no mistakes when transferring the answers! Put your names on **both** answer sheets **and** the work pages, and **return all pages**! Conceptual questions are **0.5 pts** each, calculation problems **3+1 pts**. Maximum number of points you can get is **50 pts!**)

General Infos:

- No programable calculators, smartphones, smartwatches, tablets, headphones, ... are allowed. Neither any notes or books.
- Any attempt of cheating or other forms of academic dishonesty will result in an automatic "F" for the course.
- **Show a picture ID** when leaving
- Be considerate when you finish early. Consider to stay till end, or at least be quite when leaving earlier to avoid distracting your fellow students!

Conceptual questions:	Problems & Calculations:
1) D	1a) $\frac{M_2}{M_1} = \frac{m_2}{m_1} \cdot \frac{P_1}{[illegible]}$
2) D	1b) 1.2
3) A	2a) $M_{sol} = K \cdot \frac{W_{sol}}{W_{H_2O}} \cdot \frac{1}{\Delta T}$
4) C	2b) 0.0448 kg·mol^{-1}
5) C	3a) $A + 2H^+ + 2e^- \rightarrow AH_2$, $B + 2H^+ + 2e^- \rightarrow BH_2$, $AH_2 + B \rightarrow A + BH_2$
6) B	3b) .35V
7) A	4a) $\lambda_u = t \cdot \Lambda_0$ $u = \frac{\lambda}{F}$
8) C	4b) 8.79x10^{-4} cm^2/sV
9) A	5a) [illegible]
10) B	5b) 200nm
11) C	6a) $E = \frac{h^2}{8ma^3}(1+1+1)$
12) A	6b) 1.81x10^{-7} J
13) B	7a) $\lambda(D) = \lambda(H) \cdot$ [illegible]
14) B	7b) 656.5nm
15) A	8a) $\Delta E \propto \frac{1}{L^2}$, [illegible]
16) C	8b) 1300nm
17) A	9a) $c = \frac{A}{\varepsilon l}$
18) B	9b) 9.059 g/dm^3
19) A	10a) $W(2,1,3) = \frac{6!}{2!1!3!}$, $W(4,1,1) = \frac{6!}{4!1!1!}$
20) A	10b) 60

30

30 < 60 => less likely

CHEM 3523 001 Spring 2023 **Name:** KEY
ID:

Conceptual Questions:

1) When water boils, a phase transition occurs. Which thermodynamic quantity remains the same in both phases at the phase boundary?
   a) Enthalpy H
   b) Volume V
   c) Internal energy U
   d) Gibbs free energy G

2) How many different phases can at most co-exist in a two-component system?
   a) 1
   b) 2
   c) 3
   d) 4
   e) 5
   f) none of a) - e)

3) Adding salt to water
   a) Increases the boiling point
   b) Decreases the boiling point
   c) Has no effect on the boiling point

4) When mixing ideal solutions, which quantity increases?
   a) Mixing Gibbs free energy $\Delta_{mix} G$
   b) Mixing enthalpy $\Delta_{mix} H$
   c) Mixing entropy $\Delta_{mix} S$

5) Suppose we mix two similar liquids A and B. At what mol fraction χ_A of component A would we expect maximal mixing entropy $\Delta_{mix} S$?
   a) $\chi_A < 0.1$
   b) $\chi_A = 1/\pi$
   c) $\chi_A = 0.5$
   d) $\chi_A = 0.666$
   e) $\chi_A \approx 1$

6) The osmotic pressure of a solution
   a) Decreases with increasing solute concentration
   b) Increases with increasing solute concentration
   c) Is independent of solute concentration

7) Which kind of electrolyte can be described already quite good with the Arrhenius theory?
   a) Weak electrolytes
   b) Strong electrolytes
   c) Both are equally well described by the theory
   d) Deviations are for both kinds of electrolytes too large to make the theory useful.

8) The voltage of a battery in which the contents are in chemical equilibrium
   a) Depends on temperature
   b) Depends on concentration of the contents
   c) Is zero

9) The osmotic pressure for electrolytes is
   a) Much higher than that of non-electrolytes
   b) Similar than that of non-electrolytes
   c) Much lower than that of non-electrolytes

10) The De Broglie wavelength of particles traveling with a certain velocity
   a) Is independent from its mass
   b) Decreases with increasing mass
   c) Increases with increasing mass

11) Because of the Pauli-exclusion principle, two electrons
   a) Cannot share the same spatial orbitals
   b) Must have different spin
   c) Must differ in at least one quantum number

12) Which of the following pairs of quantities can be measured together with arbitrary precision?
   a) x and p_y
   b) y and p_y
   c) x and p_x
   d) none of a) – c)

13) With increasing quantum numbers *n* the difference between energy states in a hydrogen atom
   a) Increases
   b) Decreases
   c) Stays constant

14) For a particle in a one-dimensional box, the probability to find the particle is always larger than zero at any place within the box.
   a) True
   b) False

15) Which of the four quantum numbers n, l, m_l, and s, describing the state of an electron in the hydrogen atom, appears already in the Bohr model of the hydrogen atom?

a) n
b) l
c) m_l
d) s
e) none of these four quantities has an equivalent in the Bohr-model

16) A molecule in an excited state can decay to the ground state either by stimulated emission or spontaneous emission. When the frequency of the transition doubles, the probability of spontaneous emission increases relative to that of stimulated emission by a factor

a) 2
b) 4
c) 8
d) does not change
e) none of a)-d)

17) The absorbance A of a solution depends on the concentration of solute

a) True
b) False

18) If a system of non-interacting particles is constrained by the requirement that the average energy of particles $<\varepsilon>$ = const (i.e. T=const), the probability distribution of particle energies p_i is

a) Constant
b) Proportional to $\exp(-\varepsilon_i/k_BT)$ (k_B is the Boltzmann constant)
c) Proportional to $-\varepsilon_i/k_BT$
d) None of a) – c)

19) The sum over the probabilities of all possible microstates of a system in a certain macrostate is called its partition function Z. In the case of a system with T = const, $Z = \Sigma_l \exp(-E_i/k_BT)$. All thermodynamics quantities can be calculated from the partition function.

a) True
b) False

20) Suppose you have two systems that differ only in that the first system is made of distinguishable particles, and the other of indistinguishable particles.

a) The system made of distinguishable particles has a higher multiplicity than the one made of indistinguishable particles
b) The system made of distinguishable particles has a smaller multiplicity than the one made of indistinguishable particles
c) The two systems have the same multiplicity

Problems and Calculations:

1. Components 1 and 2 form an ideal solution. The pressure of pure component 1 is 13.0 kPa at 298 K; and that of component 2 approximately zero. If addition of 1.00 g of component 2 to 10.00 g of component 1 reduces the total vapor pressure to 12.0 kPa, what is the ratio of the molar mass of component 2 to that of component 1?

$$\frac{P_1}{P_1^*} = x_1 \implies 1 - \frac{P_1}{P_1^*} = 1 - x_1 = x_2 \implies x_2 = \frac{P_1^* - P_1}{P_1^*}$$

$$x_2 = \frac{m_2/M_2}{m_1/M_1 + m_2/M_2} = \frac{1}{\frac{m_1}{M_1}\frac{M_2}{m_2} + 1}$$

$$\implies \frac{1}{x_2} = \frac{m_1}{m_2}\frac{M_2}{M_1} + 1 \implies \frac{1}{x_2} - 1 = \frac{1 - x_2}{x_2} = \frac{x_1}{x_2} = \frac{m_1}{m_2}\frac{M_2}{M_1}$$

$$\implies \frac{M_2}{M_1} = \frac{m_2}{m_1}\frac{x_1}{x_2} = \frac{m_2}{m_1} \cdot \frac{P_1}{P_1^*}\frac{P_1^*}{P_1^* - P_1} = \frac{m_2}{m_1}\frac{P_1}{P_1^* - P_1}$$

$$= \frac{1}{10}\frac{12.0}{13.0 - 12.0}$$

$$= \frac{12.0}{10}$$

$$= 1.2$$

2. When 5 g of a nonvolatile solute is dissolved in 250.0 g of water, the freezing point depression is 0.75 K. Calculate the molar mass of the compound assuming a freezing point depression coefficient K_f = 1.68 K*kg/mol. Use that the molality $m=n/W_{solvent}=W_{solute}/(M_{Solute} *W_{solvent})$ with W the total mass of solute/solvent and M the molar mass

$$\Delta_{fre} T = K_F m_S = K_F \frac{W_{solute}}{M_{solute} \cdot W_{H_2O}}$$

$$\Rightarrow M_{solute} = K_F \cdot \frac{W_{solute}}{W_{H_2O}} \cdot \frac{1}{\Delta_{fre} T}$$

$$= 1.68 \, K \frac{kg}{mol} \times \frac{5g}{250g} \times \frac{1}{0.75 K}$$

$$= 0.0448 \frac{kg}{mol}$$

3. Under standard conditions, a solution containing A and its reduced form AH_2 has a standard electrode potential of -0.5 V. A solution containing B and BH_2 has a standard potential of -0.15 V. If a cell were constructed with these two systems as half-cells, would AH_2 be oxidized by B or BH_2 oxidized by A? What would be the reversible emf of the cell?

$A + 2H^+ + 2e^- \rightarrow AH_2 \quad E_0 = -0.50V$

$B + 2H^+ + 2e^- \rightarrow BH_2 \quad E_0 = -0.15V$

$AH_2 + B \rightarrow A + B$[illegible]

AH_2 is oxidized by B

reversible emf of cell: $-0.15V - (-0.5V) = 0.35V$

4. **The transport numbers of HCl at infinite dilution are estimated to be t^+ = 0.801 and t^- = 0.199. The molar conductivity 426.16 S cm²/mol. Calculate the ionic conductivities and mobilities of the hydrogen and chloride ions.**

$$\lambda_{H_+} = t^+ \cdot 426.16 \frac{S\,cm^2}{mol} = 0.801 \cdot 426.16 \frac{S\,cm^2}{mol} = 341.13 \frac{S\,cm^2}{mol}$$

$$\lambda_{Cl_-} = t^- \cdot 426.16 \frac{S\,cm^2}{mol} = 0.199 \cdot 426.16 \frac{S\,cm^2}{mol} = 84.81 \frac{S\,cm^2}{mol}$$

$$u_+ = \frac{\lambda_+}{F} = \frac{341.13}{96456} = 3.54 \times 10^{-3} \frac{cm^2}{SV}$$

$$u_- = \frac{\lambda_-}{F} = \frac{84.81}{96456} = 8.79 \times 10^{-4} \frac{cm^2}{SV}$$

5. **When a photon with the wavelength of 190 nm hits a certain metal, it can eject an electron with a kinetic energy of 2.8 x 10⁻¹⁹J. What would be the largest wave length with that a photon could still eject an electron?**

$h\nu = E_{Kin} + W \Rightarrow W = h\nu_0 \quad (E^0_{Kin} = 0)$

$\Rightarrow h\nu_0 = h\nu - E_{Kin}$

$\Rightarrow \nu_0 = \nu - \frac{E_{Kin}}{h}$

$\Rightarrow \frac{c}{\lambda_{max}} = \frac{c}{\lambda} - \frac{E_{Kin}}{h} = \left(\frac{2.988 \times 10^{8}}{190 \times 10^{-9}} - \frac{2.8 \times 10^{-19}}{6.626 \times 10^{-34}}\right)\frac{1}{s}$

$= \left(\frac{2.988}{1.9} \cdot 10^{15} - 0.423 \times 10^{15}\right)\frac{1}{s}$

$= (1.573 - 0.423) \cdot 10^{15}$ Hz

$= 1.1496 \times 10^{15}$ Hz

$\Rightarrow \lambda_{max} = \frac{c}{1.1496 \cdot 10^{15}}$ m

$= \frac{2.988 \times 10^{8}}{1.1496 \cdot 10^{15}}$ m

$= 2.0 \times 10^{-7}$ m

$= 200$ nm

2.61×10^{-7}

~ 260 nm

6. Calculate the lowest possible energy for an electron confined to a cube of sides equal to 10^{-10} m.

Lowest energy $n_x = n_y = n_z = 1$ $a = 10^{-10}$ m

$$E = \frac{h^2}{8ma^3}(1+1+1) = \frac{3\cdot(6.626\times10^{-34})^2}{8\cdot9.18\times10^{-31}\cdot(10^{-10})^3} \text{ J}$$

$$= 1.81\times10^{-7} \text{ J}$$

7. The Balmer spectrum of hydrogen (transitions into n=2) has a line of wavelength 656.7 nm. What is the wavelength of the corresponding line of deuterium? (m_D = 3.3434 x 10^{-27} kg; m_H = 1.6727 x 10^{-27} kg; m_e = 9.1095 x 10^{-31} kg)

$$\mu_H = \frac{m_e m_H}{m_e + m_H} = 9.1046 \times 10^{-31}\ Kg$$

$$\mu_D = \frac{m_e m_D}{m_e + m_D} = 9.1070 \times 10^{-31}\ Kg$$

$$\frac{1}{\lambda} = \frac{Z^2 e^2}{8 \pi \varepsilon_0 a_0 h} \left(\frac{1}{n_2} - \frac{1}{4}\right) \Rightarrow \frac{1}{\lambda} \propto \frac{1}{a_0}$$

$$a_0 = \frac{h \varepsilon_0}{\pi e^2 \mu} \Rightarrow a_0 \propto \frac{1}{\mu}$$

$$\frac{1}{\lambda} \propto \mu \Rightarrow \lambda \propto \frac{1}{\mu}$$

$$\Rightarrow \frac{\lambda(D)}{\lambda(H)} = \frac{\mu_H}{\mu_D}$$

$$\Rightarrow \lambda(D) = \lambda(H) \cdot \frac{\mu_H}{\mu_D} = 656.7\,nm \cdot 0.9997$$

$$= 656.5\ nm$$

8. A diatomic molecule HCl undergoing a rotational transition from J=4 to J=5 in the gas phase emits light with a wavelength of 650nm. Hydrogen has an atomic mass of 1 and Chloride one of 35. What would be the wavelength for this transition if the hydrogen is replaced by deuterium? Deuterium is twice as heavy as hydrogen. Assume that the bond length of the molecule does not change, and that the effective mass μ_{DCl} of DCl is twice the effective mass μ_{HCl} of HCl.

$$\Delta E_{J \to J+1} = \frac{\hbar^2}{I}(J+1) = \frac{\hbar^2}{I} \cdot 5 \,, \quad I = \mu d^2$$

$$\Rightarrow \Delta E \propto \frac{1}{\mu}$$

$$\text{and} \quad \Delta E \propto \frac{1}{\lambda}$$

$$\lambda \propto \mu \,, \quad \mu_{DCl} = 2\mu_{HCl}$$

$$\Rightarrow \lambda_{DCl} = 2\,\lambda_{HCl}$$

$$= 1300\ nm$$

9. The molar absorption coefficient of human hemoglobin (molecular weight 64,000) is 532 dm³/(cm*mol) at 440 nm. A solution of hemoglobin in a cuvette having a light path of 2 cm was found at that wavelength to have a transmittance of 70.7%. Calculate the concentration in g/dm³.

$$T = \frac{I}{I_0} = 0.707 \qquad A = \log_{10}\frac{I_0}{I} = -\log_{10} 0.707$$

$$= 0.1506$$

$$A = \varepsilon \cdot c \cdot l \Rightarrow c = \frac{A}{\varepsilon l} = \frac{0.1506}{532 \frac{dm^3}{cm \cdot mol} \cdot 2\,cm}$$

$$= 1.4152 \times 10^{-4} \frac{mol}{dm^3}$$

$$= 1.4152 \times 10^{-4} \cdot 64000 \times 1.661 \times 10^{-27} \times 6.022 \times 10^{23} \frac{kg}{dm^3}$$

$$= 9.058 \times 10^{-3} \frac{kg}{dm^3}$$

$$= 9.058 \frac{g}{dm^3}$$

10. Putting six **indistinguishable** particles into three different containers (E, 2E, 3E) such that the first container has two particles, the second container one particles and the third container three particles, i.e., the configuration is (2,1,3), what is the multiplicity of this configuration? If the occupation changes to (4,1,1), what is the multiplicity of the new configuration? Will the new configuration occur more likely than the old one?

$$W(2,1,3) = \frac{6!}{2!\cdot 1!\cdot 3!} = 60$$

$$W(4,1,1) = \frac{6!}{4!\cdot 1!\cdot 1!} = 30 < 60$$

Less likely