

Examen Final

CHM 2532

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Nom d'étudiant(e) _____

Durée: 3 heures

d'étudiant(e) _____

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Instructions: 1. Répondre à chaque question sur les feuilles de l'examen.

2. Calculatrices électroniques sont permises.

3. Ni livres ni notes ne sont permises.

1. One mole of helium gas, initially at 25 °C, is expanded from a volume of 1 L to a final volume of 2 L at 20 °C.

a) Estimate the specific heat of helium.

$$\begin{aligned}
 \bar{C}_V &= \frac{3}{2} R \\
 &= \frac{3}{2} \times 8.31 = 12.5 \text{ J mol}^{-1} \text{K}^{-1}
 \end{aligned}$$

b) Calculate ΔU , assuming that the gas is perfect.

$$\begin{aligned}
 \Delta U &= n \bar{C}_V \Delta T \\
 &= 1 \times 12.5 \times (20 - 25) \\
 &= -62.3 \text{ J}
 \end{aligned}$$

c) Calculate ΔS , assuming that the gas is perfect.

$$\begin{aligned}
 \Delta S &= n \bar{C}_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \\
 &= 1 \left(12.5 \ln \frac{293.15}{278.15} + 8.31 \ln 2 \right) \\
 &= 5.55 \text{ J K}^{-1}
 \end{aligned}$$

d) If the process is carried out irreversibly, what can one say about the magnitudes of ΔU , q , and w ?

$$\begin{aligned}
 \Delta S &\geq \int \frac{dq}{T} \\
 q &\leq T \Delta S = n_{\text{max}}(T_1, T_2) \Delta S = 29815 \times 5.55 \\
 q &< 1659 \text{ J} \\
 W + q &= \Delta U \quad \therefore W = \Delta U - q \\
 &\geq -62.3 - 1659 \\
 &\geq -1716 \text{ J}
 \end{aligned}$$

Alors, toujours

2. The absolute entropy of liquid ethanol at 25 °C is 160.7 J mol⁻¹ K⁻¹. Its specific heat, assumed to be constant all the way up to its boiling point (78.42 °C), is 111.5 J mol⁻¹ K⁻¹. Its heat of vaporization is 42.3 kJ mol⁻¹ K⁻¹. Calculate the absolute entropy of gaseous ethanol at 78.42 °C and 1 atm

$$\begin{aligned}
 S &= S_l^{\circ}(25^{\circ}\text{C}) + \Delta S_l(25 \rightarrow 78.42^{\circ}\text{C}) + \Delta S_{\text{vap}}(78.42) \\
 &= 160.7 + \bar{C}_p \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} \\
 &= 160.7 + 111.5 \ln\left(\frac{351.57}{298.15}\right) + \frac{42310}{357.57} \\
 &= 160.7 + 18.38 + 120.35 \\
 &= 299.4 \text{ J mol}^{-1} \text{ K}^{-1}
 \end{aligned}$$

3. a) 2.0 mL of liquid water is placed in a sealed 20 L container which is then evacuated of all gas, leaving only the water inside. At the initial temperature of 25 °C the vapour pressure of water is 24 mm Hg. The water is allowed to evaporate. How much liquid water remains in the container? Assume that the density of H₂O is 1.0 g cm⁻³

$$\begin{aligned}
 P &= 24 \text{ mmHg} = 24/760 \text{ atm} \\
 V &= 20 \text{ L} \\
 T &= 298.15 \text{ K} \\
 \therefore n_{\text{H}_2\text{O}} &= \frac{PV}{RT} = \frac{24}{760} \times \frac{20}{0.08216 \times 298.15} = 0.0258 \text{ mol} \\
 m_{\text{H}_2\text{O}} &= 0.0258 \times 18 = 0.464 \text{ g} \\
 V_{\text{H}_2\text{O lost}} &= 0.464 \text{ mL} \\
 V_{\text{H}_2\text{O (remaining)}} &= 2.0 - 0.464 = 1.536 \text{ mL}
 \end{aligned}$$

- b) Estimate the specific heat capacity, \bar{C}_v , of gaseous H₂O.

$$\begin{aligned}
 \text{H}_2\text{O is nonlinear} & \quad 3 \\
 \bar{C}_v &= \frac{3}{2}R + \frac{3}{2}R + (3N^{\circ}\Delta^{\circ})R = 3R + 3R = 6R \\
 &= 49.88 \text{ J mol}^{-1} \text{ K}^{-1} \\
 \bar{C}_p &= \bar{C}_v + R = 58.19 \text{ J mol}^{-1} \text{ K}^{-1} - 7R \\
 \gamma &= 7/6
 \end{aligned}$$

- c) The gas in the above-mentioned container is then allowed to expand adiabatically from 24 mm Hg down to 15 mm Hg.

- (i) What is the final volume occupied by the gas?

$$\begin{aligned}
 PV_1^{\gamma} &= P_2 V_2^{\gamma} \\
 \left(\frac{V_2}{V_1}\right)^{\gamma} &= \frac{P_1}{P_2} = \frac{24}{15} = 1.6 \\
 \left(\frac{V_2}{V_1}\right)^{7/6} &= 1.6 \quad \rightarrow \frac{V_2}{V_1} = 1.6^{6/7} = 1.496 \\
 V_2 &= V_1 (1.496) = 20 (1.496) \\
 &= 29.9 \text{ L}
 \end{aligned}$$

(ii) Based on the volume and pressure changes what is the final temperature?

$$T_2 = T_1 \frac{P_2 V_2}{P_1 V_1} = 298.15 \times \left(\frac{15}{24} \right) \left(\frac{299}{20} \right) \\ = 218.6 \text{ K} \\ = 54.3^\circ \text{C}$$

(iii) The heat of vaporization of water is 43.6 kJ mol^{-1} . Based on the Clausius-Clapeyron equation what is the condensation temperature associated with 15 mm Hg? Consequently what do you expect would happen to the water in the container?

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \left(\frac{15}{24} \right) = -\frac{43600}{8.314} \left(\frac{1}{T_2} - \frac{1}{298.15} \right)$$

$$T_2 = 290.39 \text{ K}$$

Since $278.6 \text{ K} < T_{\text{cond}}$, some H_2O vapour will condense

4. In a constant-volume calorimeter, the combustion of fumaric acid releases 1330 kJ mol^{-1} in the form of heat at 291 K . The reaction is



a) Calculate $\Delta \bar{H}$ for this process.

$$\bar{q} = 1330 \text{ kJ mol}^{-1} \\ \Delta \bar{U} = 1330 \text{ kJ mol}^{-1}$$

$$\Delta \bar{H} = \Delta \bar{U} + \Delta(P\bar{V}) = \Delta \bar{U} + \Delta(nRT) = \Delta \bar{U} + RT\Delta n$$

$$\Delta n = +1$$

$$\Delta \bar{H} = 1330000 + 8.314 \times 298.15 = 1332.48 \text{ kJ mol}^{-1}$$

b) The substance which absorbs this heat is assumed to be liquid water (neglecting the gases and the calorimeter housing itself). The specific heat capacity of water is $75.31 \text{ J mol}^{-1} \text{ K}^{-1}$. By how much does the temperature rise?

Take 1 mole of fumaric acid, it produces 2 mol $\text{H}_2\text{O} (\text{l})$

$$q = 1330 \text{ kJ} = n \bar{C}_p \Delta T \\ 1330 \times 10^3 = 2 \times 75.31 \Delta T \\ \Delta T = \frac{1330 \times 10^3}{2 \times 75.31} \\ = 8830 \text{ K}$$

c) What assumption is implied in the formula used to answer part (b). Is this assumption justified? *in this case*

\bar{C}_p constant; otherwise $q = n \int \bar{C}_p dT$ ²⁹⁸
Since ΔT is so large, it is not likely that \bar{C}_p is constant

5. In the bacterium *nitrobacter*, the following reaction occurs:



The following are standard enthalpies and Gibbs free energies of formation at 25 °C:

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$\Delta G_f^\circ / \text{kJ mol}^{-1}$
$\text{NO}_2^-(\text{aq})$	-104.6	-37.2
$\text{NO}_3^-(\text{aq})$	-207.4	-111.3
O_2	0	0

a) Calculate ΔH° , ΔG° , ΔS° , and the equilibrium constant for the reaction

$$\begin{aligned} 2 \quad \Delta H^\circ &= \Delta H_f^\circ(\text{NO}_3^-) - \Delta H_f^\circ(\text{NO}_2^-) \\ &= -207.4 - (-104.6) = \boxed{-102.8 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} 2 \quad \Delta G^\circ &= \Delta G_f^\circ(\text{NO}_3^-) - \Delta G_f^\circ(\text{NO}_2^-) \\ &= -111.3 - (-37.2) = \boxed{-74.1 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} 2 \quad \Delta G^\circ &= \Delta H^\circ + T \Delta S^\circ \\ \therefore \Delta S^\circ &= (\Delta H^\circ - \Delta G^\circ) / T \end{aligned}$$

$$\begin{aligned} &= (-102.8 \text{ kJ} + 74.1 \text{ kJ}) / 298.15 \\ &= \boxed{-96.26 \text{ J mol}^{-1} \text{K}^{-1}} \end{aligned}$$

$$\begin{aligned} 2 \quad K_{\text{eq}} &= \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(+\frac{74100}{8.314 \times 298.15}\right) = e^{+29.89} \\ &= \boxed{9.60 \times 10^{12}} \end{aligned}$$

b) Is the reaction spontaneous under standard conditions?

1 Yes

c) What pressure of O_2 is required for the answer to be the opposite of that in part (b)? if NO_3^- & NO_2^- remain in their standard states

$$\begin{aligned} 3 \quad \Delta G &= \Delta G^\circ + RT \ln\left(\frac{[\text{NO}_3^-]}{[\text{NO}_2^-] P_{\text{O}_2}^{1/2}}\right) > 0 \\ -74100 + 8.314 \times 298.15 \ln\left(\frac{1}{1 \times P_{\text{O}_2}^{1/2}}\right) &> 0 \end{aligned}$$

$$\begin{aligned} -2479.9 \ln P^{1/2} &> 74100 \\ \ln P^{1/2} &< -29.89 \\ P^{1/2} &< 1.041 \times 10^{-13} \\ P &< \boxed{1.084 \times 10^{-26} \text{ atm}} \end{aligned}$$

6. The ionization constant, $[H^+][OH^-]$, for the dissociation of water, $H_2O \rightleftharpoons H^+ + OH^-$, is $1.00 \times 10^{-14} M^2$ at 25 °C, and $1.45 \times 10^{-14} M^2$ at 30 °C.

Calculate ΔH° , ΔG° , and ΔS° at 25 °C.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$2 \quad \ln K_2 = -\frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left(\frac{1.45 \times 10^{-14}}{1.0 \times 10^{-14}} \right) = -\frac{\Delta H^{\circ}}{8.314} \left(\frac{1}{303.15} - \frac{1}{298.15} \right)$$

$$\Delta H^{\circ} = \frac{+0.376 \times 8.314}{0.00005532} = (55.84) \text{ kJ mol}^{-1}$$

$$1 \quad \Delta G^{\circ} = -RT \ln K = -8.314 \times 298.15 \ln 10^{-14} = (79.91) \text{ kJ mol}^{-1}$$

7. A solution of an anionic form of a protein at a concentration of 7.8 g dm^{-3} has an osmotic pressure of $2.3 \times 10^{-3} \text{ atm}$ at 0 °C.

a) Estimate the molecular weight of the protein.

$$[X] = \frac{7.8 \text{ g dm}^{-3}}{M \text{ g mol}^{-1}} \times 1000 \text{ dm}^3/\text{m}^3 = \frac{7800}{M} \text{ mol dm}^{-3}$$

$$\pi = 2.3 \times 10^{-3} \text{ atm} = 2.3 \times 10^{-3} \times 1.01 \times 10^5 \text{ Pa} = RT[X]$$

$$232.3 = 8.314 \times 273.15 \times \frac{7800}{M}$$

$$M = \frac{8.314 \times 273.15 \times 7800}{232.3}$$

$$= (76253) \text{ g mol}^{-1}$$

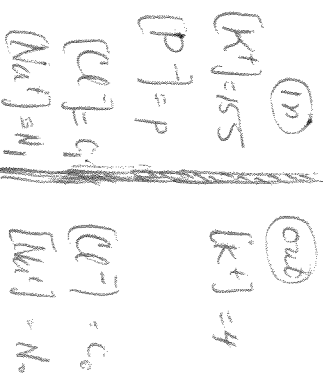
- b) This protein concentrates itself inside a living cell and cannot cross the cell membrane. Its positive counter-ion, K^+ , does diffuse across the membrane. At equilibrium, $[K^+]$ inside the cells is 155 mM, while it is only 4 mM outside the cells. What is the name of the special kind of equilibrium established, and describe qualitatively what happens to the concentration of other major diffusible ions such as Na^+ and Cl^- .

Donnan equilibrium

$$K^+ + N_1 = P + N_2 \quad C_1$$

$$4 + N_2 = C_2$$

$$C_1 + C_2 = N_1 + N_2$$



- c) What is the magnitude of the cell potential which is established across the membrane, neglecting any active transport of ions? at 25 °C

$$2 \quad E = \frac{RT}{nF} \ln \left(\frac{155}{4} \right) = \frac{8.314 \times 298.15}{1 \times 96485} \ln \left(\frac{155}{4} \right)$$

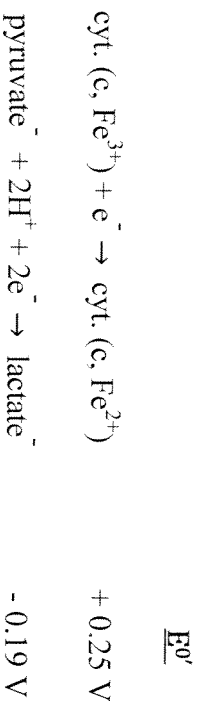
$$= 0.0940 \text{ V}$$

$$= (94.0) \text{ mV}$$

8. Lactate is oxidized by cytochrome (c, Fe^{3+}) to yield pyruvate plus cytochrome (c, Fe^{2+}) according to the following reaction:



The standard reduction potentials at pH 7 and 25 °C are:



- a) Calculate the equilibrium ratio $\frac{[\text{cyt (c, Fe}^{2+})]^2 [\text{pyruvate}^-]}{[\text{cyt (c, Fe}^{3+})]^2 [\text{lactate}^-]}$ at 25 °C and pH 7.

$$E^{\circ} = 0.25 - (-0.19) = 0.44 \text{ V} = \frac{RT}{nF} \ln \left\{ \frac{[\text{cyt (c, Fe}^{2+})]^2 [\text{pyruvate}^-]}{[\text{cyt (c, Fe}^{3+})]^2 [\text{lactate}^-]} \right\}^2$$

$$0.44 = 0.01285 \ln \left\{ \frac{[\text{cyt, Fe}^{2+}]^2 [\text{pyruvate}^-] \times 1}{[\text{cyt, Fe}^{3+}]^2 [\text{lactate}^-]} \right\}$$

$$34.25 = \ln \left\{ \frac{\quad}{\quad} \right\}$$

$$\left\{ \frac{\quad}{\quad} \right\} = 7.51 \times 10^{14}$$

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- b) Recalculate this ratio at 25 °C and pH 6.

Same as above, except $[\text{H}^+] / 10^{-7} = 10^{-6} / 10^{-7} = 10$

$$A \quad 34.25 = \ln \left\{ \frac{\quad}{\quad} \cdot (10)^2 \right\}$$

$$100 \left\{ \frac{\quad}{\quad} \right\} = 7.51 \times 10^{14}$$

$$\left\{ \frac{\quad}{\quad} \right\} = 7.51 \times 10^{12}$$

9. For a solution of 0.05 M in KNO_3 and 0.05 M in KCl

a) Calculate the ionic strength

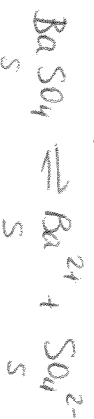
$$I = \frac{1}{2} \left[0.05 \times 1^2 + 0.05 \times 1^2 + 0.05 \times 1^2 + 0.05 \times 1^2 \right] = 0.1$$

b) Some BaSO_4 (which is sparingly soluble) is placed into the above solution. Calculate the mean ionic activity coefficient of the Ba^{2+} and SO_4^{2-} ions.

$$\log_{10} \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I} = -0.509 \times 4 \sqrt{0.1} = -0.6438$$

$$\gamma_{\pm} = 0.5253 \quad 0.226$$

c) Calculate the solubility of BaSO_4 in the above solution.



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

$$s = \frac{\sqrt{K_{sp}}}{\gamma_{\pm}} = \frac{\sqrt{9.2 \times 10^{-11}}}{0.5253} = 1.826 \times 10^{-5} \text{ M}$$

Given that K_{sp} for BaSO_4 is 9.2×10^{-11}

10. In the reversible first order isomerization reaction, $A \rightleftharpoons B$, the following observations were made:

$$[A]_0 = 0.002 \text{ M}, [B]_0 = 0 \text{ M}, [A]_{\text{equilibrium}} = 0.0005 \text{ M}.$$

After 60 seconds the concentration of A drops to 0.001 M.

Calculate the rate constants for the forward and for the reverse reactions.

$$[B]_{\text{eq}} = \Delta[A] = 0.002 - 0.0005 = 0.0015 \text{ M}$$

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{0.0015}{0.0005} = 3 = \frac{k_1}{k_{-1}} = K_{\text{eq}}$$

$$k_{\text{m}} \left(\frac{[A] - [A]_{\text{eq}}}{[A]_0 - [A]_{\text{eq}}} \right) = -(k_1 + k_{-1})t$$

$$k_{\text{m}} \left(\frac{0.001 - 0.0005}{0.002 - 0.0005} \right) = -(k_1 + k_{-1}) \times 60$$

$$k_{\text{m}} \left(\frac{0.0005}{0.0015} \right) = -(k_1 + k_{-1}) \times 60$$

$$(k_1 + k_{-1}) = 1.83 \times 10^{-2}$$

$$3k_{-1} + k_{-1} = 1.83 \times 10^{-2}$$

$$4k_{-1} = 1.83 \times 10^{-2}$$

$$k_{-1} = 4.58 \times 10^{-3} \text{ s}^{-1}$$

$$k_1 = 3k_{-1} = 1.373 \times 10^{-2} \text{ s}^{-1}$$

- 11. An enzyme-catalyzed reaction is found to have a rate of $8.6 \times 10^3 \text{ M s}^{-1}$ at 25°C when it is saturated with substrate. If $[\text{E}]_0 = 1.5 \times 10^{-6} \text{ M}$

a) calculate the rate constant for the formation of products, k_{cat} .

$$v = k_{\text{cat}} [\text{E}]_0 = v_{\text{max}}$$

$$8.6 \times 10^{-3} = k_{\text{cat}} \times 1.5 \times 10^{-6}$$

$$k_{\text{cat}} = \boxed{5733} \text{ s}^{-1}$$

b) If the rate drops to $2.0 \times 10^{-3} \text{ M s}^{-1}$ when $[\text{S}]_0$ drops to $1.0 \times 10^{-4} \text{ M}$, what is the value of the Michaelis-Menten constant?

$$v = \frac{k_{\text{cat}} [\text{E}]_0 [\text{S}]_0}{K_{\text{MH}} + [\text{S}]_0}$$

$$2.0 \times 10^{-3} = \frac{8.6 \times 10^{-3} [\text{S}]_0}{K_{\text{MH}} + [\text{S}]_0}$$

$$\frac{K_{\text{MH}}}{[\text{S}]_0} + 1 = 4.3$$

$$\frac{K_{\text{MH}}}{[\text{S}]_0} = 3.3$$

$$K_{\text{MH}} = 3.3 [\text{S}]_0 = 3.3 \times 1 \times 10^{-4} \text{ M} = \boxed{3.3 \times 10^{-4} \text{ M}}$$

c) If the activation energy is 20 kJ mol^{-1} , what would the rate constant be at 37°C under the saturation conditions of part a)?

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_2}{5733}\right) = -\frac{20000}{8.314} \left(\frac{1}{310.15} - \frac{1}{298.15}\right)$$

$$\ln\left(\frac{k_2}{5733}\right) = +0.3122$$

$$\frac{k_2}{5733} = 1.366$$

$$k_2 = \boxed{7833} \text{ s}^{-1}$$