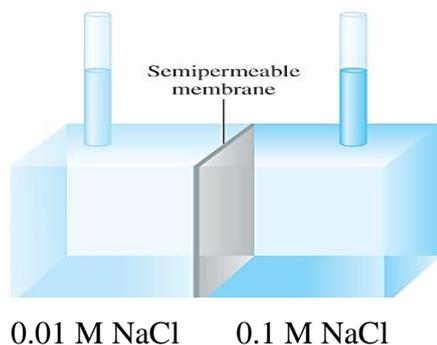


4. (a) Explain in terms of molecular interactions why the temperature-composition phase diagram for chloroform CHCl_3 and acetone $(\text{CH}_3)_2\text{CO}$ possesses a high-boiling azeotrope. (b) Explain why the maximum obtainable purity of ethanol is 95 percent when you try to purify an ethanol-water mixture by fractional distillation. (3+3 pt)
5. Why does the vapor pressure of a solvent decrease when a nonvolatile solute is added? (assume it is an ideal solution) (5 pt)

6.



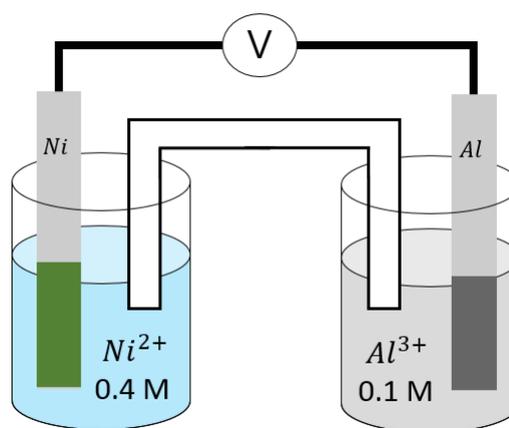
In the apparatus shown above, what will happen if the membrane is (a) permeable to both water and the Na^+ and Cl^- ions, (b) permeable to water and Na^+ but not to Cl^- ions, (c) permeable to water only? (2+2+2 pt)

7. (a) What is the K_P at 1273°C for the reaction $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$ if the K_c is 2.24×10^{-22} at the same temperature? (3 pt)
- (b) At equilibrium, the pressure of the reacting mixture $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is 0.106 bar at 350°C . Calculate K_P and K_c for this reaction. (4 pt)
8. The equilibrium constant K for the reaction $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ is 4.40 at 2000 K. (a) Calculate ΔG°_r for the reaction. (b) Calculate ΔG_r for the reaction when the partial pressures are $P(\text{H}_2) = 0.25$ bar, $P(\text{CO}_2) = 0.78$ bar, $P(\text{H}_2\text{O}) = 0.67$ bar, and $P(\text{CO}) = 1.21$ bar. (4+4 pt)
9. Consider the decomposition of calcium carbonate: $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$. Calculate the pressure in bar of CO_2 in an equilibrium process (a) at 25°C and (b) at 800°C . Assume that $\Delta H^\circ_r = 177.8$ kJ/mol and $\Delta S^\circ_r = 160.5$ J/mol·K for the temperature range. (4+4 pt)
10. Consider the following equilibrium process: $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$. Predict the direction of the shift in equilibrium when (a) the temperature is raised; (b) the pressure on the gases is increased; or (c) He gas is added to the reaction mixture. (2+2+2 pt)

Thermodynamic Data at 25°C (ΔH_f° is **independent** on temperature)

	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)
$\text{Al}^{3+} (aq)$	-531.0	-485.0
$\text{Ni}^{2+} (aq)$	-54.0	-45.6
$\text{CH}_4 (g)$	-74.6	-50.8
$\text{CO}_2 (g)$	-393.5	-394.4
$\text{H}_2\text{O} (l)$	-285.8	-237.1
$\text{OH}^- (aq)$	-229.94	-157.30

11. (a) Considering only the cost of electricity, would it be cheaper to produce 1 kg of sodium (Na) or 1 kg of aluminum (Al) by electrolysis. (b) Please calculate the mole of electrons required to prove your answer. (2+3 pt)
12. If the combustion of methane (CH_4) is used in the fuel cell and operates at 25°C, please answer the following questions. The products of the fuel cell are water and carbon dioxide.
- (a) Please identify the half-cell reactions at the anode and cathode. Here, the electrolytes of the anode and cathode are treated as acid solutions. (6 pt)
- (b) Please use the thermodynamic data at 25°C to calculate ΔG_r° of the combustion reaction in the fuel cell. (3 pt)
- (c) Please calculate E° of the fuel cell. (3 pt)
13. In order to attend the competition for the most powerful cell, Angela designed a new cell which would be larger than E° of the copper-zinc cell (=1.10 V). The figure of the new cell is drawn below.



- (a) Please use the thermodynamic data at 25°C to determine which electrode is the anode and which one is the cathode. Then, write the half-cell reactions at the anode and cathode. Explain your answer briefly. (2+2+2 pt)
- (b) Please calculate E° of the new cell at 25°C to see whether larger than E° of the copper-zinc cell (=1.10 V). (4 pt)
- (c) If $[\text{Ni}^{2+}] = 0.4 \text{ M}$ and $[\text{Al}^{3+}] = 0.1 \text{ M}$, please calculate E of the new cell at 25°C. (3 pt)
- (d) Please calculate E° of the new cell at 80°C. (4%)

103B Chemistry (II) midterm

Answer

1. (a) The molar volume $V_m(\text{ice}) = 18/0.918 = 0.0196$ (L/mol)
 $V_m(\text{water}) = 18/1.000 = 0.0180$ (L/mol)
 use Clapeyron equation $[dP/dT] = \Delta H_{\text{fusion}}/T\Delta V$
 $\Delta V_{\text{fus}} = V_{\text{liquid}} - V_{\text{solid}} = 0.0180 - 0.0196 = -0.0016$ (L/mol)
 $[dP/dT] \approx \Delta P/\Delta T = 6010/(273.15 \times (-0.0016)) = -1.38 \times 10^4$ J/L·K = -138 bar /K
 $\Delta T = \Delta P/(-138) = (500 - 1.01) / (-138) = -3.6$ (K) (3 pt)
 $T_m = 273.15 - 3.6 = 269.5$ K
- (b) from 273 K to 0 K, $\Delta T = -273$ K ; $\Delta P = (-138) \times (-273) = 3.8 \times 10^4$ (bar) (1 pt)
 The prediction is not reasonable. Because (1) Liquid water cannot exist at 0 K. (2) ΔH_{fus} and ΔV_{fus} were assumed to be constant, which is a good approximation to make over small temperature ranges, but is not valid over large temperature ranges. (2 pt)
2. (a) Application of the Clausius-Clapeyron Equation $\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
 $\rightarrow P(298\text{K}) = 107$ mmHg (4 pt)
- (b) $\ln \frac{23.8}{760} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{373} - \frac{1}{298} \right) \rightarrow \Delta H_{\text{vap}} = 42.7$ kJ/mol (4 pt)
3. Henry's law: $c = kP$, $k = (5.6 \times 10^{-4})/0.8 = 7.0 \times 10^{-4}$ (mol/L·bar)
 the solubility N_2 in blood at 4.0 bar $(7.0 \times 10^{-4}) \times 4.0 = 2.8 \times 10^{-3}$ (mol/L)
 the number of moles of N_2 in 5.0 L of blood at 0.80 bar $(5.6 \times 10^{-4}) \times 5.0 = 2.8 \times 10^{-3}$ (mol)
 the number of moles of N_2 in 5.0 L of blood at 4.0 bar $(2.8 \times 10^{-4}) \times 5.0 = 1.4 \times 10^{-2}$ (mol)
 the amount of N_2 released in moles $(1.4 \times 10^{-2}) - (2.8 \times 10^{-3}) = 1.1 \times 10^{-2}$ (mol)
 $V(\text{N}_2) = (1.1 \times 10^{-2}) \times 0.08314 \times (273+37)/1 = 0.28$ (L) (6 pt)
4. (a) Systems that possess a high-boiling azeotrope exhibit a strong negative deviation from Raoult's law, meaning that the intermolecular forces between $(\text{CH}_3)\text{CO}$ and CHCl_3 are stronger than the intermolecular forces amongst the like molecules. This leads to a lower vapor pressure than calculated using Raoult's law assuming an ideal solution. (3 pt)
- (b) The ethanol-water system forms a low-boiling azeotrope and the distillation process will always converge to the azeotrope. (3 pt)
5. For ideal solution, $\Delta H_{\text{mix}} = 0$, $\Delta S_{\text{mix}} > 0$. So $\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}} < 0$, the Gibbs free energy of the solution decreases. While the vapor of the solvent will be in equilibrium with the solvent, hence its Gibbs free energy will decrease accordingly. At constant temperature, the only way is to lower

its pressure. (5 pt)

6. (a) → two solutions of equal NaCl concentration (the same as just removing the membrane) (2 pt)

(b) The movement of one ion but not the other would result in one side of the apparatus acquiring a positive electric charge and the other side becoming equally negative. This has never been known to happen, so we must conclude that migrating ions always drag other ions of the opposite charge with them. → only water would move through the membrane from the dilute to the more concentrated side (2 pt)

(c) → Water would move through the membrane from the dilute to the concentrated side. (2 pt)

7. (a) $K_P = K_c(RT)^{\Delta n} = K_c(0.08314T)^{\Delta n}$, $\Delta n = 2 - (2+1) = -1$, $T = 1273+273 = 1546$ (K)
 $K_P = (2.24 \times 10^{22})(0.08314 \times 1546)^{-1} = 1.74 \times 10^{20}$ (3 pt)

(b) $K_P = P(\text{CO}_2) = 0.106$ (2 pt)

$$K_c = 0.106 / (0.08314 \times 623)^{(1-0)} = 2.05 \times 10^{-3} \quad (2 \text{ pt})$$

8. (a) $\Delta G^\circ = -RT \ln K = -8.314 \times 2000 \times \ln 4.40 = -2.46 \times 10^4 \text{ J/mol} = -24.6 \text{ kJ/mol}$

(b) Under non-standard-state conditions, $\Delta G = \Delta G^\circ + RT \ln Q$ (4 pt)

$$\Delta G = -2464 + 8.314 \times 2000 \times \ln((0.67 \times 1.21) / (0.25 \times 0.78)) = -947 \text{ J/mol} \\ = -0.947 \text{ kJ/mol} \quad (4 \text{ pt})$$

9. $K_P = (\approx) P(\text{CO}_2)$

(a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3) - 298 \times 160.5 = 130.0 \times 10^3 \text{ J/mol}$

$$P(\text{CO}_2) = \exp(-\Delta G^\circ / RT) = \exp(-52.47) = 1.63 \times 10^{-23} \text{ bar} \quad (4 \text{ pt})$$

(b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3) - 1073 \times 160.5 = 5.585580 \times 10^3 \text{ J/mol}$

$$P(\text{CO}_2) = \exp(-\Delta G^\circ / RT) = \exp(-0.625) = 0.535 \text{ bar} \quad (4 \text{ pt})$$

10. (a) an endothermic reaction (decomposition, cleavage of N-N bond) → from left to right (2 pt)

(b) from right to left (2 pt)

(c) no effect (2 pt)

11. (a) It is cheaper to produce 1 kg of Na. (2 pt)

(b) for Na : $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$, $\frac{1000 \text{ g Na}}{23.0 \frac{\text{g}}{\text{mol of Na}}} \times 1 = 43.5 \text{ mole } \text{e}^-$

for Al : $\text{Al}^+ + 3\text{e}^- \rightarrow \text{Al}$, $\frac{1000 \text{ g Al}}{27.0 \frac{\text{g}}{\text{mol of Al}}} \times 3 = 111.1 \text{ mole } \text{e}^-$

It is cheaper to prepare 1 kg of sodium by electrolysis. (3 pt)

12. (a) Anode(oxidation half reaction): $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$
 Cathode(reduction half reaction): $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ (各 3 pt)
- (b) The overall reaction is equal to 1×(the oxidation half reactions) + 2×(the reduction half reaction) :
- $$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)$$
- $$\Delta G_r^\circ = \Delta G_f^\circ(H_2O(l)) \times 2 + \Delta G_f^\circ(CO_2(g)) \times 1 - \Delta G_f^\circ(CH_4(g)) \times 1 - \Delta G_f^\circ(O_2(g)) \times 2$$
- $$= (-237.1) \times 2 + (-394.4) \times 1 - (-50.8) \times 1 - (0) \times 2 = -817.8 \text{ kJ/mol} \quad (3 \text{ pt})$$
- (c) $E^\circ = \frac{\Delta G_r^\circ}{-nF} = \frac{-817.8 \times 10^3}{-8 \times 96485} = 1.06 \text{ V} \quad (3 \text{ pt})$

13.

- (a) Anode (Al electrode, the oxidation half reaction): $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$ (2 pt)
 Cathode (Ni electrode, the reduction half reaction): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ (2 pt)
 overall reaction $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$
- $$\Delta G_r^\circ = \Delta G_f^\circ(Al^{3+}(aq)) \times 2 + \Delta G_f^\circ(Ni(s)) \times 3 - \Delta G_f^\circ(Al(s)) \times 2 - \Delta G_f^\circ(Ni^{2+}(aq)) \times 3$$
- $$= (-485.0) \times 2 + (0.0) \times 3 - (0.0) \times 2 - (-45.6) \times 3 = -833.2 \text{ kJ/mol}$$

Because the Gibbs free the overall reaction at 25°C is small than zero, the spontaneous direction the reaction is from reactants towards the production. (2 pt)

- (b) $E^\circ = \frac{\Delta G_r^\circ}{-nF} = \frac{-833.2 \times 10^3}{-6 \times 96485} = 1.439 \text{ V} \quad (3 \text{ pt})$

Yes, Eo of the new cell at 25°C is larger than Eo of the copper-zinc cell (=1.10 V). (1 pt)

- (c) use the Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln(Q) = 1.439 - \frac{8.314 \times 298}{6 \times 96485} \ln\left(\frac{[Al^{3+}]^2 \cdot 1^3}{1^2 \cdot [Ni^{2+}]^3}\right) = 1.439 - \frac{8.314 \times 298}{6 \times 96485} \ln\left(\frac{0.1^2}{0.4^3}\right) =$$

$$1.447 \text{ V} \quad (3 \text{ pt})$$

- (d) $\Delta H_r^\circ = \Delta H_f^\circ(Al^{3+}(aq)) \times 2 + \Delta H_f^\circ(Ni(s)) \times 3 - \Delta H_f^\circ(Al(s)) \times 2 - \Delta H_f^\circ(Ni^{2+}(aq)) \times 3$
 $= (-531.0) \times 2 + 0 \times 3 - 0 \times 2 - (-54.0) \times 3 = -954.0 \text{ kJ/mol}$

$$\Delta S_r^\circ = (\Delta H_r^\circ - \Delta G_r^\circ)/T = (-954.0 - (-833.2)) \times 10^3 / 298 = -405.4 \text{ J/mol} \cdot K$$

$$\text{use } \frac{E_{T_2}^\circ}{T_2} - \frac{E_{T_1}^\circ}{T_1} = \frac{\Delta H^\circ}{nF} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \quad E_{T_2}^\circ = E_{T_1}^\circ + \frac{\Delta S^\circ}{nF} (T_2 - T_1) \quad (2 \text{ pt})$$

$$E^\circ(80^\circ\text{C}, 353 \text{ K}) = 1.400 \text{ V} \quad (2 \text{ pt})$$