

CHEM 103 TEST 2 KEY

Average  $\pm$  std deviation = 88 (59%)  $\pm$  27 (18%) Highest score = 147/150 (98%)

Rough corresponding grade: A = 120 and above; B = 105 + , C = 70 +

Part I

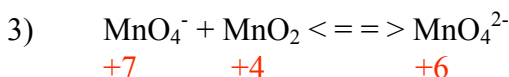
1 B	5 A	8 C
2 E	6 C	9 C
3 D	7 B	10 C
4 E		

Part II

1)

At  $T=232\text{K}$ ,  $\Delta G^\circ=0$ :  $0=\Delta H^\circ-T\Delta S^\circ \Rightarrow \Delta S^\circ = \Delta H^\circ/T = (2290\text{J/mol})/(232\text{K}) = 9.87 \text{ J/molK}$

2) ATP hydrolysis is used to drive nonspontaneous reactions. To do this, it is coupled to the reaction with the help of enzymes. Together the reactions have a net  $\Delta G < 0$  thus allowing the reaction to occur.



(i)  $1 e^- + \text{MnO}_4^- \rightarrow \text{MnO}_4^{2-}$  and (ii)  $\text{MnO}_2 \rightarrow \text{MnO}_4^{2-} + 2 e^-$ ; note that (i) is already balance. (ii)  $\text{MnO}_2 + 4 \text{OH}^- \rightarrow \text{MnO}_4^{2-} + 2e^- + 2 \text{H}_2\text{O}$ . Add 2x(i) + (ii):



4) Solution:  $E_{\text{cell}} = E_{\text{red,+}} - E_{\text{red,-}} = -(0.0592/2) \log(1/2.5) - (-0.0592/2) \log(1/2.5 \times 10^{-6})$   
 $= .0296 \log(2.5) - 0.0296 \log(2.5 \times 10^{-6}) = .0296 \log(2/5/2.5 \times 10^{-6}) = .0296(6) = 0.18 \text{ V}$

5) Solution: we need to reverse (ii) first:  $\text{Eu}^{2+} + 2e^- \rightarrow \text{Eu} \quad -2.81 \text{ V}$  then we can add it to (i) to get the desired half reaction, For, E we need to first all E's as  $\Delta G$ 's, add the  $\Delta G$ 's and then revert back to E:  $-0.35 \text{ V}$  becomes  $+0.35 \text{ F}$ ;  $-2.81 \text{ V}$  becomes  $-(2.81)(-2)\text{F} = +5.62\text{F}$ . Add them to get  $\Delta G_{\text{net}} = (0.35+5.62)\text{F} = 5.98 \text{ F}$ . Convert back to E:  $E = (5.98\text{F})/(-3\text{F}) = -1.99 \text{ V}$

6) Solution:  $\text{Ag}_2\text{C}_2\text{O}_4(\text{s}) \rightleftharpoons 2 \text{Ag}^+ + \text{C}_2\text{O}_4^{2-} \quad K_{\text{sp}} = [\text{Ag}^+]^2[\text{C}_2\text{O}_4^{2-}]$   
 $= (2(7.0 \times 10^{-5}))^2(7.0 \times 10^{-5}) = 1.37 \times 10^{-12}$

7)

Solution:  $\text{Fe}(\text{OH})_3 \rightleftharpoons \text{Fe}^{3+} + 3 \text{OH}^- \quad K_{\text{sp}} = 4.0 \times 10^{-38} = [\text{Fe}^{3+}][\text{OH}^-]^3 =$   
 $= \frac{1.0 \times 10^{-3}}{[\text{OH}^-]} [\text{OH}^-]^3 = 4.0 \times 10^{-38} \Rightarrow [\text{OH}^-] = 3.4 \times 10^{-12} \Rightarrow \text{pOH} = 11.46 \Rightarrow \text{pH} = 2.54$

8) solution:  $\text{Ca}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Ca}^{2+} + 2 \text{OH}^- \quad K_{\text{sp}} = 6.5 \times 10^{-6}$   
 $\text{Ca}^{2+} + \text{Ac}^- \rightleftharpoons \text{Ca}(\text{Ac})^+ \quad K_{\text{f}} = 1.7 \times 10^1$

Net:  $\text{Ca}(\text{OH})_2 + \text{Ac}^- \rightleftharpoons \text{Ca}(\text{Ac})^+ + 2 \text{OH}^- \quad K_{\text{net}} = 1.1 \times 10^{-4}$   
 $\begin{matrix} 1.00 & & x & & 2x \end{matrix}$

$K_{\text{net}} = K_{\text{sp}}K_{\text{f}} = (6.5 \times 10^{-6})(1.7 \times 10^1) = 1.1 \times 10^{-4} = (x)(2x)^2/1.00 \Rightarrow 4x^3 = 1.1 \times 10^{-4}$   
 And  $x = \sqrt[3]{(1.1 \times 10^{-4}/4)} = 0.030 \text{ M}$

### Part III

1) Solution: This is a concentration cell.  $E_{\text{cell}} = -0.0592/1 (\log(1/[\text{Ag}^+]) - \log(1/x))$   
 $= -0.0592 \log( (1/1.00) / 1/x ) = -0.0592 \text{ V} \log(x) = 0.230 \text{ V} = \log x = -3.885$   
 $x = 10^{-3.885} \Rightarrow x = 1.3 \times 10^{-4}$ ; and  $\text{Ag}_3\text{PO}_4 \rightleftharpoons 3 \text{Ag}^+ + \text{PO}_4^{3-}$   
so that  $[\text{Ag}^+] = 1.3 \times 10^{-4}$ ;  $[\text{PO}_4^{3-}] = (1.3 \times 10^{-4})/3 = 4.34 \times 10^{-5}$   
and so  $K_{\text{sp}} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] = (1.3 \times 10^{-4})^3(4.3 \times 10^{-5}) = \mathbf{9.4 \times 10^{-17}}$

2)

a) solution:

$$\Delta G^\circ = 3(-394.359) - 2(-742.2) = -1183.077 + 1484.4 = +301.323 \text{ kJ/mol}$$

$$= 301.323 \times 10^3 \text{ J/mol}$$

$$\Rightarrow K_p = \exp(-\Delta G^\circ/RT) = \exp(-(301.323 \times 10^3 \text{ J/mol}) / ((8.314 \text{ J/molK})(298 \text{ K}))) = \exp(-122)$$

$$\mathbf{K_p = 1.52 \times 10^{-53}}$$

b) (let's solve for the values of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ )

$$\Delta H^\circ = 3(-393.509) - 2(-824.2) = 467.873 \text{ kJ/mol} = 467.873 \times 10^3 \text{ J/mol}$$

$$\Delta S^\circ = 3(213.74) + 4(27.78) - 2(87.4) - 3(5.74) = 641.22 + 111.12 - 174.8 - 17.22 = 560.32$$

J/molK

$$T = 547 + 273 = 820 \text{ K} \Rightarrow \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 467.873 \times 10^3 - (820)(560.32) = 8410.6$$

J/mol

$$K_p = \exp(-(8410) / ((8.314)(820))) = \exp(-3.38) = 0.0336$$

$$\text{But: } K_p = P_{\text{CO}_2}^3 = x^3 \Rightarrow x = \sqrt[3]{K_p} = \sqrt[3]{(0.0336)} = \mathbf{0.323 \text{ bar}}$$

c) Solution: at this T,  $\Delta G^\circ = 0 \Rightarrow 0 = \Delta H^\circ - T\Delta S^\circ$

$$\Rightarrow T = \Delta H^\circ / \Delta S^\circ = (467.873 \times 10^3 \text{ J/mol}) / (560.32 \text{ J/molK}) = 835 \text{ K} = \mathbf{562 \text{ }^\circ\text{C}}$$