Chemistry 1B, Exam II
March 8, 2007
Professor R.J. Saykally

Name KEY

TA ____________________

1. (10) ____________

2. (10) ____________

3. (20) ____________

4. (20) ____________

5. (25) ____________

6. (15) ____________

TOTAL EXAM SCORE (100) ____________

Rules:

- Work all problems to 2 significant figures
- No lecture notes or books permitted
- No word processing calculators
- Time: 90 minutes
- Show all work to get partial credit
- Periodic Table, Tables of Physical Constants, and Conversion Factors included

1. **(10 points)** Suppose that the following redox couple is joined to form a galvanic cell that generates a current under standard conditions. Identify the oxidizing agent and the reducing agent, write a cell diagram, and calculate the standard cell emf.

Co^{2+}/Co and Ti^{3+}/Ti^{2+}

$Co^{2+} + 2e^- \rightarrow Co(s)$ $E_o = -0.28V$
$Ti^{3+} + e^- \rightarrow Ti^{2+}$ $E_o = 0.00V$

$$\underbrace{Co(s)}_{\text{reducing agent}} | Co^{2+}(aq) || \underbrace{Ti^{3+}(aq)}_{\text{oxidizing agent}}, Ti^{2+}(aq) | Pt(s)$$

$$E^\circ = 0.00V - (-0.28V) = \boxed{0.28V}$$

2. **(2 points each)** The total world energy consumption is __14 TW__, which is increasing at a rate of __5%__ per year, corresponding to a doubling time of __14__ years. Transportation accounts for __27__% of this energy use. A typical gasoline auto engine operates at a maximum efficiency near __30 - 50 %__, wasting much of this energy.

thermal

14% also accepted

3. (5 points each) Consider the following chemical reaction (note: 6 electrons are transferred) as a potential source of abundant clean energy for the world:

$$CH_3OH(\ell) + \frac{3}{2}O_2(g) \rightarrow 2H_2O(g) + CO_2(g) \qquad \Delta H° = -726 \text{ kJ/mole}$$

$S°$ ($H_2O(g)$) = 189 JK^{-1} $mole^{-1}$
$S°$ ($CO_2(g)$) = 198 JK^{-1} $mole^{-1}$
$S°$ ($O_2(g)$) = 205 JK^{-1} $mole^{-1}$
$S°$ ($CH_3OH(\ell)$) = 127 JK^{-1} $mole^{-1}$

Partial pressures are 1 bar

a) Calculate the maximum possible efficiency for using this reaction in an internal combustion engine operating between temperatures of 2800K and 800K with a compression ratio of 15.

$$eff = 1 - \frac{T_c}{T_h} = 1 - \frac{800K}{2800K} = 0.714$$

$$\boxed{71.4\%}$$

b) Calculate the maximum electrical work obtainable from a methanol fuel cell operating at 1000K.

$$w_{e_{max}} = \Delta G = \Delta H - T\Delta S$$

$$= -726 \text{ kJ/mol} - (1000K)\Big(2(189 \text{ J/mol K}) + 198 \text{ J/mol K} - 127 \text{ J/mol K} - \tfrac{3}{2}(205 \text{ J/mol K})\Big)$$

$$= \boxed{-868 \text{ kJ/mol}}$$

c) Calculate the maximum electrical power obtainable from the fuel cell above if it can produce a current of 1.0 amperes.

$$P = IE$$

$$\Delta G° = -nFE°$$

$$E° = -\frac{\Delta G°}{nF} = \frac{-(-868 \text{ kJ/mol})}{6(96485 \text{ C/mol } e^-)} = 1.50V$$

$$E = E° - \frac{RT}{nF}\ln Q$$

$$Q = \frac{(1 \text{ bar})^2(1 \text{ bar})}{(1 \text{ bar})^{3/2}} = 1 \Rightarrow \ln Q = 0$$

$$\Rightarrow E = E°$$

$$P = (1A)(1.5V) = \boxed{1.5W}$$

d) Calculate the maximum total work obtainable from this reaction at 1000K and 1 atm pressure (hint: use ideal gas approximation).

$$W_{Tot} = W_{elec} + W_{PV}$$

$$W_{PV} = P\Delta V = \Delta nRT = (1.5 \text{ mol})(8.314 \text{ J/mol K})(1000 \text{ K})$$

$$= 12,5 \text{ kJ/mol}$$

$$W_{Tot} = -868 \text{ kJ/mol} - 12.5 \text{ kJ/mol} = \boxed{-880 \text{ kJ/mol}}$$

4. (5 points each)

a) Complete and balance the equation for the nuclear reaction:

$${}^{243}_{95}\text{Am} + {}^{1}_{0}\text{n} \rightarrow {}^{244}_{96}\text{Cm} + ? + \gamma$$

$${}^{243}_{95}\text{Am} + {}^{1}_{0}\text{n} \longrightarrow {}^{244}_{96}\text{Cm} + {}^{0}_{-1}e^{-} + \gamma$$

or β^{-}

b) Calculate the energy liberated in this reaction (kJ/mol). Use attached table.

$$\Delta m = (244.063 \text{ u})(1.6605 \times 10^{-27} \text{ kg/u}) + 9.109390 \times 10^{-31} \text{ kg}$$

$$- [(243.061 \text{ u})(1.6605 \times 10^{-27} \text{ kg/u}) + 1.674929 \times 10^{-27} \text{ kg}]$$

$$= -1.08 \times 10^{-29} \text{ kg} \Rightarrow E = \Delta m c^2 = (-1.08 \times 10^{-29} \text{ kg})(3 \times 10^{8} \text{ m/s})^2$$

$$\boxed{E = 5.83 \times 10^{8} \text{ kJ/mol}}$$

c) Write the balanced equation for α decay of gold – 185.

$$^{185}_{79}Au \longrightarrow {}^{181}_{77}Ir + {}^{4}_{2}\alpha$$

or α

or He^{2+}

d) Write the balanced equation for the β^- decay of uranium –233.

$$^{233}_{92}U \longrightarrow {}^{233}_{93}Np + \beta^-$$

or ${}^{0}_{-1}e^-$

5. (10+5+10 points)

a) Determine the emf of the following cell (T = 298K):
$Sn(s)|Sn^{2+}(aq, 0.277\ mol{\cdot}L^{-1})||Sn^{4+}(aq, 0.867\ mol.L^{-1}), Sn^{2+}(aq, 0.55\ mol{\cdot}L^{-1})|Pt(s)$

$Sn^{2+} + 2e^- \rightarrow Sn$ $E° = -0.136V$
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ $E° = +0.150V$

$$E° = 0.150V - (-0.136V) = 0.286V$$

$$E = E° - \frac{RT}{2F} \ln \frac{[Sn^{2+}][Sn^{2+}]}{[Sn^{4+}]}$$

$$Sn + Sn^{4+} \rightarrow Sn^{2+} + Sn^{2+}$$

$$= 0.286V - \frac{(8.314\ J{\cdot}K^{-1}mol^{-1})(298K)}{2(96485\ C{\cdot}mol^{-1})} \ln \frac{(0.277)(0.55)}{(0.867)}$$

$\Longrightarrow E =$ ~~0.308~~ $\boxed{0.31V}$

b) Calculate the maximum electrical work that can be produced by this cell.

$$\Delta G = -nFE$$

$$= -2\,(96485\ C\cdot mol^{-1})(0.31V)$$

$$\Delta G = \boxed{-60.3\ kJ/mol}$$

c) Calculate the equilibrium constant for the overall cell reaction.

$$\ln K = \frac{nFE^\circ}{RT} = \frac{2\,(96485\ C\cdot mol^{-1})(0.286V)}{(8.314\ J/mol\,K)(298K)} = 22.3$$

$$\Longrightarrow \boxed{K = 4.7\times 10^{9}}$$

6. (10+5 points) The relevant half-reactions for the fully charged lead-acid battery (written as reductions) are:

$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$ $E^o = -0.356V$

$PbSO_2(s) + 4\ H_3O^+ + 2e^- \rightarrow PbSO_4(s) + 6\ H_2O$ $E^o = +1.685V$

$([H^+] = [SO_4^{2-}] = 6.0\ \underline{M})$

a) Calculate the maximum electrical power available from this battery if a current of 120 amps is produced at 298K.

$$E^\circ = 1.685\,V - (-0.356V) = 2.041\,V$$

$$E = E^\circ - \frac{RT}{nF}\ln Q = 2.041V - \frac{(8.314)(298)}{2(96485)}\ln\left(\frac{1}{\underset{H^+}{6^4}\cdot\underset{SO_4^{2-}}{6}}\right)$$

$$E = 2.156V$$

$$P = IE = (120A)(2.156V) = \boxed{260W}$$

b) Estimate the energy equivalent (EE) for this battery (assume it is all Pb).

$$\Delta G = -nFE = -2\,(96485\ \mathrm{C \cdot mol^{-1}})(2{,}156\ \mathrm{V})$$

$$= 416\ \mathrm{kJ/_{mol\ Pb}}$$

$$\left(\frac{416\ \mathrm{kJ}}{1\ \mathrm{mol\ Pb}}\right)\left(\frac{1\ \mathrm{mol\ Pb}}{207.2\ \mathrm{g\ Pb}}\right) = 2.0 \times 10^{3}\ \mathrm{kJ/_{kg\ Pb}}$$