Chemistry 1B, Exam II
March 18, 2009
Professor R.J. Saykally

Name KEY

TA ______________________

1. (10) ____________
2. (10) ____________
3. (40) ____________
4. (20) ____________
5. (10) ____________
6. (10) ____________

TOTAL EXAM SCORE (100) ____________

Rules:

- Work all problems to 3 significant figures
- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit
- Periodic Table, Tables of Physical Constants, Conversion Factors, and Key Equations included

1. **(10 points)** A thermodynamic engine operates cyclically and reversibly between two temperature reservoirs, absorbing heat from the high-temperature bath at 450 K and discharging heat to the low-temperature bath at 300 K. How much heat is discarded to the low-temperature bath if 1500 J of heat is absorbed from the high-temperature bath during each cycle?

$$\frac{q_H}{T_H} = \frac{q_L}{T_L} \rightarrow q_L = \frac{q_H}{T_H} \cdot T_L$$

$$= \frac{1500\,J \cdot 300\,K}{450\,K}$$

$$= \boxed{1000\,J}$$

$(1.00 \times 10^3\,J$ w/ 3 sf$)$

2. **(10 points)** The strongest known chemical bond is that in carbon monoxide, CO, with bond enthalpy of 1.05×10^3 kJ mol^{-1}. Furthermore, the entropy increase in a gaseous dissociation of the kind $AB \leftrightarrows A + B$ is about 110 J mol^{-1} K^{-1}. These factors establish a temperature above which there is essentially no chemistry of molecules. Show why this is so, and find the temperature.

$\Delta G = \Delta H - T\Delta S = 0$ @ equilibrium

↳ above this temperature, the forward rxn will dominate $AB \rightarrow A + B$ $(\Delta G < 0)$

$$T = \frac{\Delta H}{\Delta S} = \frac{1.05 \times 10^3\,kJ/mol}{0.110\,kJ/mol \cdot K} = 9545\,K$$

$$= \boxed{9500\,K}$$

$(9550\,K$ w/ 3 s.f.$)$

3. (8 points each) Consider the combustion of methane (CH_4) occurring at 2500 K:

A) Calculate the <u>total</u> maximum work that can be extracted from the reaction.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

$$W_{max(total)} = \Delta A = \Delta H - T\Delta S - P\Delta V$$
$$= \Delta H - T\Delta S - \Delta n RT$$
$$= -802340\ J - 2500K(-5.14\ \tfrac{J}{K}) - 0$$
$$= -789490\ J$$
$$= \boxed{-789\ kJ}$$

$\Delta H = [1(-393.51) + 2(-241.82)] - [1(-74.8$
$= -802.34\ kJ$
$\Delta S = [1(213.63) + 2(188.72)] - [1(186.15) + 2(205.1$
$= -5.14\ J/K$
$\Delta n = [1+2] - [1+2] = 0$

B) If this reaction is used to drive an internal combustion engine wherein the exhaust is removed to a cold reservoir at T = 1000 K, calculate the <u>maximum work</u> that this engine could perform

$$W_{max} = W_{max(total)} \times \epsilon$$
$$= W_{max(total)} \times 1 - \frac{T_L}{T_H}$$
$$= -789\ kJ\left(1 - \frac{1000K}{2500K}\right) = \boxed{-473\ kJ}$$

C) Calculate the <u>electrical work</u> that could be extracted from the reaction in a fuel cell (at 2500 K).

$$W_{max(elec)} = \Delta G = \Delta H - T\Delta S = \boxed{-789\ kJ}$$ (same as part (a))

D) Calculate the voltage output of this fuel cell.

$\Delta G = -nF\Delta\epsilon$ $\quad n = \#\ e^- = 8$

$8e^-$: $\overset{-4}{C}H_4 \rightarrow \overset{+4}{C}O_2$

$$\Delta\epsilon = -\frac{\Delta G}{nF}$$
$$= \frac{789 \times 10^3\ J}{(8\ mole^-)(96485\ C/mole^-)} = \boxed{1.02\ V}$$

E) If this fuel cell can produce 50 amps of <u>current</u>, what is the <u>power</u> that it can produce?

$$P = I\Delta\epsilon = \left(50\ \tfrac{C}{s}\right)\left(1.02\ \tfrac{J}{C}\right) = \boxed{51\ W}$$

4. (10+10 points)

A) A Ni|Ni^{2+}||Ag^{+}|Ag galvanic cell is constructed in which the standard cell voltage is 1.03 V. Calculate the free energy change at 25°C when 1.00 g of silver plates out, if all concentrations remain at their standard valve of 1 M throughout the process.

$$\Delta G = -nF\Delta \mathcal{E}^\circ \qquad Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$$

$$= -(2\text{ mol } e^-)(96485 \tfrac{C}{\text{mol } e^-})(1.03\text{ V})$$

$$= -199\text{ kJ per mol rxn}$$

$$\frac{-199\text{ kJ}}{\text{mol rxn}} \cdot \frac{1\text{ mol rxn}}{2\text{ mol Ag}} \cdot \frac{1\text{ mol Ag}}{107.87\text{ g Ag}} \times 1.00\text{ g Ag} = -0.922\text{ kJ}$$

$$= \boxed{-922\text{ J}}$$

B) What is the maximum electrical work done by the cell on its surroundings during this experiment if the ion concentrations drop to 0.20 M?

$$\Delta \mathcal{E} = \Delta \mathcal{E}^\circ - \frac{0.0592}{n}\log Q \qquad Q = \frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.03\text{ V} - \frac{0.0592}{2}\log\frac{(0.2\text{ M})}{(0.2\text{ M})^2}$$

$$= 1.01\text{ V}$$

$$\Delta G = -nF\Delta \mathcal{E} = -(2\text{ mol } e^-)(96485 \tfrac{C}{\text{mol } e^-})(1.01\text{ V})$$

$$= \boxed{-195\text{ kJ}}$$

5. (2 points each) Briefly rationalize the following observations regarding the cosmic abundance of the elements:

A) Even Z nuclei are more abundant than odd Z nuclei nuclear shell theory (spin pairing of protons).

B) H and He comprise 88.6% and 11.3% of the atoms in the Universe originated in the big bang.

C) In the lighter elements, those with mass number divisible by 4 are more abundant formed from $^{4}_{2}He$ fusion cycle.

D) ^{56}Fe is considerably more abundant than adjacent mass number elements it has the most stable nucleus.

E) Li, Be, and B are very rare compared to neighboring elements very short lived and used to create heavier elements

6. (5 points each) Write balanced equations that represent the following nuclear reactions.

A) Beta emission by $^{39}_{17}Cl$

$$^{39}_{17}Cl \rightarrow ^{0}_{-1}e + ^{39}_{18}Ar$$

B) Alpha emission by $^{224}_{88}Ra$

$$^{224}_{88}Ra \rightarrow ^{4}_{2}He + ^{220}_{86}Rn$$