Individual Exam #3: Kinetics, Electrochemistry, and Thermodynamics

1) A galvanic cell is to be constructed using the following half reactions under acidic conditions:

$MnO_4^- | Mn^{2+}$ (ε° = +1.49 V)
$Al^{3+} | Al$ (ε° = −1.66 V)

Given that the potentials are measured against the standard hydrogen electrode (SHE) at 298 K and all ions are present at 1 M concentration, what is the maximum possible work output (in kJ/mol) of this cell?

As this system is a galvanic cell, the ε° should be positive overall, meaning that the reduction half-cell will be the reaction with permanganate, and the oxidation half-cell will have aluminum being reduced to aluminum(III) ion.

$$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)};\ (\varepsilon° = +1.49\text{ V})$$
$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-;\ (\varepsilon° = +1.66\text{ V})$$

To balance the overall reaction, the first equation is multiplied by 3, the second equation is multiplied by 5, and the two reactions are combined into the following:

$$3MnO^-_{4(aq)} + 24H^+_{(aq)} + 5Al_{(s)} \rightarrow 3Mn^{2+}_{(aq)} + 5Al^{3+}_{(aq)} + 12H_2O_{(l)}$$

In combining the reactions, we cancel 15 electrons from each side, meaning that 15 moles of electrons are transferred between the half-cells in one mole of the balanced reaction.

The $\varepsilon°_{\text{reaction}}$ is equal to the sum of the potentials of each half-reaction, so $\varepsilon°_{\text{reaction}} = (+1.49V) + (1.66V) = 3.15V$

The maximum possible work output of this cell is equal to the change in free energy, or ΔG°.

$$\Delta G° = -\left(15\frac{mols\ e^-}{mol\ reaction}\right)\left(96485\frac{C}{mol\ e^-}\right)(3.15V) = -4559.60\frac{kJ}{mol}$$

2) Nitric oxide, NO, reacts with oxygen to give nitrogen dioxide, NO_2, a major air pollutant.

One possible mechanism is proposed for this reaction:

*Note: k with a negative subscript (*e.g.*, k_{-1}) represents a rate constant for the reverse reaction.

Mechanism $\boldsymbol{\alpha}$

$$2\,\mathrm{NO}_{(g)} \overset{k_1}{\underset{k_{-1}}{\rightleftarrows}} \mathrm{N_2O}_{2(g)}$$

$$\mathrm{N_2O}_{2(g)} + \mathrm{O}_{2(g)} \xrightarrow{k_2} 2\mathrm{NO}_{2(g)}$$

Part A: In a multi-step chemical reaction, an intermediate is a compound that is formed, and then later consumed in a later step. An example of an intermediate is N_2O_2 in mechanism α. The intermediate is formed at the rate $\frac{d[N_2O_2]}{dt}$ and consumed at the rate $\frac{-d[N_2O_2]}{dt}$.

If a chemical process involves more than 1 step, and forms at least one intermediate, and if at some point the concentration of the intermediate remains constant, the system has achieved what is known as a "steady state." In other words, under steady state conditions the intermediate is consumed as quickly as it is generated, meaning that $\frac{d[N_2O_2]}{dt} = 0$.

Assume that this mechanism is under steady-state conditions. Derive an expression for the rate of formation of NO_2 gas in terms of the concentrations of reactants and not in terms of any intermediate concentrations.

Part B: A 2nd proposed mechanism for the reaction follows:

Mechanism $\boldsymbol{\beta}$

$$\mathrm{NO}_{(g)} + \mathrm{O}_{2(g)} \overset{k_1}{\underset{k_{-1}}{\rightleftarrows}} \mathrm{NO}_{3(g)}$$

$$\mathrm{NO_{3(g)}} + \mathrm{NO_{(g)}} \xrightarrow{\mathrm{k_2}} \mathrm{2NO_{2(g)}}$$

Solve for the rate law of this second mechanism in a similar manner as you did in part (a). Experiments have shown that the reaction is first order in [NO] and first order in $[O_2]$ when the value of k_2 is much greater than k_{-1}, and when both mechanisms operate under steady-state conditions. Which mechanism is consistent with these experimental observations?

Part A: Determine the rate law for NO_2 production for each of the reactions For mechanism α:

$$\frac{d}{dt}[\mathrm{NO_2}] = 2k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$$

We need to know what the $[N_2O_2]$ is to have a meaningful rate law. Steady state approximation says that the concentration of the intermediate will be small and unchanging, so the net rate of formation is 0 for the intermediate. For mechanism α:

$$\frac{d}{dt}[\mathrm{N_2O_2}] = k_1[\mathrm{NO}]^2 - k_{-1}[\mathrm{N_2O_2}] - k_2[\mathrm{N_2O_2}][\mathrm{O_2}] = 0$$

Solving this equation for $[N_2O_2]$, we obtain:

$$[\mathrm{N_2O_2}] = \frac{k_1[\mathrm{NO}]^2}{k_{-1} + k_2[\mathrm{O_2}]}$$

Now we plug this into the original rate law for NO_2 for mechanism α to get:

$$\boldsymbol{\frac{d}{dt}[\mathrm{NO_2}] = 2k_2[\mathrm{N_2O_2}][\mathrm{O_2}] = \frac{2k_1k_2[\mathrm{NO}]^2[\mathrm{O_2}]}{k_{-1} + k_2[\mathrm{O_2}]}}$$

Part B: We do the same steps for mechanism β and we get:

$$\frac{d}{dt}[\mathrm{NO_3}] = k_1[\mathrm{NO}][\mathrm{O_2}] - k_{-1}[\mathrm{NO_3}] - k_2[\mathrm{NO_3}][\mathrm{NO}] = 0$$

$$[\mathrm{NO_3}] = \frac{k_1[\mathrm{NO}][\mathrm{O_2}]}{k_{-1} + k_2[\mathrm{NO}]}$$

$$\boldsymbol{\frac{d}{dt}[\mathrm{NO_2}] = 2k_2[\mathrm{NO_3}][\mathrm{NO}] = \frac{2k_1k_2[\mathrm{NO}]^2[\mathrm{O_2}]}{k_{-1} + k_2[\mathrm{NO}]}}$$

When k_2 is high compared to k_{-1}, the k_{-1} term in the denominator of the rate law for mechanism α is effectively insignificant compared to $k_2[O_2]$. This means that mechanism α essentially is zero order in O_2 and second order in NO. Mechanism α does not match the experimental results.

In mechanism β, the k_{-1} term will be negligible compared to the $k_2[NO]$ term, meaning that the rate law approaches first order in NO in this case. Also, the reaction remains first order in $O_{2.}$ Thus, mechanism β is consistent with the experimental results.

3) Glucose is an extremely important molecule for humans, and the reactions that turn the glucose from your double cheeseburger into usable energy are among the most important reactions that occur in cells. The first of these reactions is:

$$\text{Glucose}_{(aq)} + \text{PO}_{4(aq)}^{3-} \rightleftharpoons \text{Glucose} - 6 - \text{phosphate}_{(aq)} + \text{H}_2\text{O}_{(l)}$$

a) $\Delta G°$ for this reaction at 37 °C is +14.3 kJ/mol. What is the equilibrium constant, K_{eq}, for this reaction at 37 °C?

$$\Delta G°' = -RT\ln K_{eq}$$

$$K_{eq} = e^{-\frac{\Delta G°'}{RT}}$$

$$K_{eq} = e^{\frac{-14.3\left(\frac{kJ}{mol}\right)}{0.008314\left(\frac{kJ}{mol}*K\right)*310K}} = 0.0039$$

b) The reaction $ATP_{(aq)} + H_2O_{(l)} \rightleftharpoons ADP_{(aq)} + PO_{4(aq)}^{3-}$ is also important in cells, and has $\Delta G°$= –31.0 kJ/mol. Combine these two biological reactions to remove water and unbound phosphate ions, and write the overall reaction.

$$Glucose_{(aq)} + ATP_{(aq)} \rightarrow Glucose - 6 - phosphate_{(aq)} + ADP_{(aq)}$$

c) What is K_{eq} for this combined equation?

$$\Delta G_{rxn}°' = 14.3\frac{kJ}{mol} - 31.0\frac{kJ}{mol} = -16.7\frac{kJ}{mol}$$

$$K_{eq} = e^{-\frac{\Delta G°'}{RT}}$$

$$K_{eq} = e^{\frac{16.7\left(\frac{kJ}{mol}\right)}{0.008314\left(\frac{kJ}{mol}*K\right)*310K}} = 651.70$$

d) The value of ΔG° at a given temperature is measured under standard state conditions, where the concentrations of all aqueous solutions are 1M. However, the concentrations inside living cells are very different from those assumed under standard state conditions. These are typical equilibrium cellular concentrations of the molecules: [Glucose] = 4.5 mM, [Glucose-6-phosphate] = 5 mM, [PO_4^{3-}] = 4.8 mM, [ATP] = 8 mM, [ADP] = 10mM. Calculate ΔG (in kJ/mol) for this reaction using the typical concentrations reported here and 37 °C.

$$K_{eq} = \frac{[Glucose - 6 - phosphate][ADP]}{[Glucose][ATP]} = \frac{(5mM)(10mM)}{(4.5mM)(8mM)} = 1.389$$

$$\Delta G = -RTlnK_{eq}$$

$$\Delta G = -0.008314\frac{kJ}{mol * K}(310K)(ln1.389) = -0.85\, kJ/mol$$

e) At 37 °C, the standard enthalpy change associated with the original reaction ($\mathrm{Glucose + PO_4^{3-} \rightleftharpoons Glucose - 6 - phosphate + H_2O}$) is –8.3 kJ/mol. What is the standard entropy change $\left(\text{in } \frac{\mathrm{J}}{\mathrm{mol\ K}}\right)$ of this reaction at 37 °C? The standard change in free energy, (ΔG°), is given in part (a).

$$\Delta G° = \Delta H° - T\Delta S°$$

$$14.3\frac{kJ}{mol} = -8.3\frac{kJ}{mol} - (310K)\Delta S°$$

$$\Delta S° = -72.90\ \frac{J}{mol * K}$$