Chem 1422 – Exam # 1 (Feb 19, 2009)

Thermo, Kinetics & 1st part of Equilibrium

Put a big X this box if you want your graded exam put out in the public racks outside Prof. Stanley’s office after grading. If you don’t check it, Prof. Stanley will keep your exam and you will have to stop by to pick it up from him personally.

1. (5 pts) Qualitatively, for which of the following reactions will $\Delta S_{rxn}$ increase the most? Circle the correct answer and provide clear justification/reasoning for your choice in the space to the left of the answers.

   a) $\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$
   
   b) $\text{AgCl}(s) + \text{Br}^-(aq) \rightarrow \text{AgBr}(s) + \text{Cl}^-(aq)$
   
   c) $3\text{C}_2\text{H}_2(g) \rightarrow \text{C}_6\text{H}_6(l)$
   
   d) $2\text{HgO}(s) \rightarrow 2\text{Hg}(l) + \text{O}_2(g)$
   
   e) $2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$

2. (5 pts) Which of the following substances has the highest absolute Entropy? Circle the correct answer and provide clear justification/reasoning for your choice in the space to the right of the answers.

   a) $\text{H}_2\text{Te}(g)$
   
   b) $\text{H}_2\text{S}(g)$
   
   c) $\text{NH}_3(g)$
   
   d) $\text{H}_2\text{O}(l)$
   
   e) $\text{LiBH}_4(s)$

3. (5 pts) What is $\Delta H^\circ_{rxn}$ for the following reaction? $\Delta H_f^\circ(\text{PCl}_3) = -320 \text{ kJ/mol}$. $\text{P}_4 = \text{elemental P}$. Circle the correct answer and provide clear justification/reasoning for your choice in the space to the right of the answers.

   $\text{P}_4(s) + 6\text{Cl}_2(g) \rightarrow 4\text{PCl}_3(l)$

   a) 1280 kJ/mol
   
   b) 320 kJ/mol
   
   c) 0 kJ/mol
   
   d) $-320 \text{ kJ/mol}$
   
   e) $-1280 \text{ kJ/mol}$

5. (5 pts) Calculate $\Delta S_{rxn}$ for: $3\text{O}_2(g) \rightarrow 2\text{O}_3(g)$

   $\Delta S^\circ(\text{O}_2) = 205 \text{ J/mol-K}$, $\Delta S^\circ(\text{O}_3) = 240 \text{ J/mol-K}$ Circle the correct answer and provide clear justification/ reasoning for your choice in the space to the right of the answers.

   a) 620 J/mol-K
   
   b) 310 J/mol-K
   
   c) $-135 \text{ J/mol-K}$
   
   d) $-310 \text{ J/mol-K}$
   
   e) $-620 \text{ J/mol-K}$
The following potential energy (PE) diagrams are to be used for problems 6 - 8. They can be used more than once.

6. (5 pts) Which potential energy diagram best represents a spontaneous reaction that will have the largest temperature dependence with regards to its rate of reaction? Indicate the letter for the diagram and provide clear justification/reasoning for your choice.

C It is spontaneous (products lower in energy than reactants) and has the largest activation energy barrier so it will be the most dependent on temperature and temperature changes. Rxns with small or no activation energies are fast and not as affected by temperature.

7. (5 pts) Consider the following reaction mechanism for converting reactants A + B + C into product F. Indicate the letter for the potential energy diagram that best matches this spontaneous reaction and provide clear justification/reasoning for your choice.

Step # 1: A + B → D (slow step)
Step # 2: D + C → E (fast; species E observable)
Step # 3: E → F

F It is spontaneous (products lower in energy than reactants) and has two intermediates (dips or valleys) in the potential energy curve that correspond to species D and E. The largest activation barrier for the rxn is the first one that will define the slowest rxn step (A + B forms intermediate D). There is a smaller activation energy for the second step indicating a fast rxn step. The well (dip or valley) for intermediate E is deeper than that for D indicating that it should be more stable than D.

8. (5 pts) Which potential energy diagram best represents the reaction that will rapidly form an equilibrium mixture with roughly equal amounts of reactants and products? Indicate the letter for the PE diagram and provide clear justification/reasoning for your choice.

B The reactants and products have about the same energy so they should be present in approximately similar amounts. This reaction also has a small activation energy indicating that the rxn between reactants and products (the equilibrium) is fast.

9. (5 pts) What is the kinetic rate law for the following data. Circle the correct answer and provide clear justification/reasoning for your choice.

<table>
<thead>
<tr>
<th>Exp #</th>
<th>[A]</th>
<th>[B]</th>
<th>Rate (Msec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.5</td>
<td>0.2</td>
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<td>2</td>
<td>1.5</td>
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</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>4.5</td>
<td>3.6</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>3.0</td>
<td>1.6</td>
</tr>
</tbody>
</table>

In going from Exp # 1 to # 2, the concentration of B doubles, but the rate increases by a factor of 4. That indicates a square power on [B]². For Exp # 2 and # 4, the concentration of A doubles and the rate doubles. That indicates a first order power relationship. So the rate law is \( k[A][B]^2 \)
10. (5 pts) Consider the following rxn: \(4C_3H_5N_3O_9(l) \rightarrow 6N_2(g) + 12CO_2(g) + 10H_2O(g) + O_2(g)\)

\(\Delta H^\circ_{rxn} = -5646 \text{ kJ/mol} \) and \(E_a = 10 \text{ kJ}\). Based on this thermodynamic and kinetic data what can you tell me about the reaction: energy given off (or absorbed), likely form of the energy (heat, light, nuclear, electrical, etc), spontaneity, and likely speed of the reaction. Would you want to be around 10 moles of the reactant when it “reacts”?

This reaction is extremely exothermic and should release most of the energy as heat, probably also with some light if the rxn is fast (which it will be). Lots of gas is produced so there will be a large increase in volume. No nuclear energy for chemical reactions! Electricity can only be generated when the reactants transferring electrons are separated from one another. The reaction is also highly spontaneous because the entropy of rxn is increasing a lot. This will add to the \(\Delta H_{rxn}\) term making \(\Delta G_{rxn}\) even more negative and energy releasing. The small value of the \(E_a\) (activation energy) indicates that this reaction should be very fast. A very fast rxn that releases a lot of energy is usually an explosion.

10 moles of the material will release (10 mol)(−5646 kJ/mol) = 56,460 kJ of energy!! Very quickly due to the small \(E_a\) value. So this should be a large explosion and NO, I do not want to be near it.

FYI: \(C_3H_5N_3O_9(l) = \text{nitroglycerine}\)

11. (10 pts) The second law of thermodynamics says that the entropy of the universe always increases for a spontaneous reaction. But a spontaneous reaction can have a \(\Delta S_{rxn}\) term that is negative, i.e., the entropy of the reaction decreases. Explain why this does not violate the second law of thermodynamics.

The key here is that the entropy of reaction is not the same as the entropy of the universe. The entropy of the universe is the entropy of the system (your reaction) plus the entropy of the surroundings (everything else): \(\Delta S_{universe} = \Delta S_{system(rxn)} + \Delta S_{surroundings}\)

It is OK for the entropy of a spontaneous reaction to decrease so long as the reaction is exothermic enough to compensate. The heat from the exothermic reaction increases the temperature of both the system & surroundings and this increases the entropy of the universe enough (if the reaction is exothermic enough) to compensate for the decreasing “local” entropy of the reaction. This is why we have the formula:

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \] to quantitatively account for the effects of \(\Delta H^\circ\) on the surroundings.

12. (10 pts) I did the burning Mg demonstration outside for the class: \(Mg(s) + CO_2(g) \rightarrow MgO(s) + C(s)\)

\(\Delta H^\circ_{rxn} = -811 \text{ kJ/mol}\). When I used the propane torch to light the Mg(s) sitting on the paper on top of the dry ice, \(CO_2(s)\) (temp = −79°C; \(CO_2(s) \rightleftharpoons CO_2(g)\)), the Mg barely started burning. But as soon as I dropped more dry ice onto the Mg pile it really took off and reacted vigorously. There are two kinetic factors that work in opposite directions that affect this rxn, but one is clearly more important. What are these two kinetic factors and how do they affect the rxn rate?

The two kinetic factors are:

1) Concentration: by dropping the dry ice (CO\(_2\)) onto the hot Mg we increased the concentration of CO\(_2\) so it could increase the rate of reaction with the Mg. The paper below the Mg was keeping CO\(_2\)(g) from the dry ice below it from easily accessing the Mg. This is the major factor for increasing the rate of rxn.

2) Temperature: increasing temperature increases the rxn rate. But the dry ice is very cold so it will lower the temperature and slow the reaction rate. The concentration effect more than compensates for this, as you saw from the very exothermic overall rxn. The heat given off due to \(\Delta H_{rxn}\) also more than compensates for the cold dry ice and works to increase the temperature and speed up the rxn.

The activation energy is not one of the answers since we do not know what it is – although it must be rather large due to the fact that we need to ignite the Mg with a propane torch to initiate the reaction.

There is also a small thermodynamic factor involved. Since the rxn is exothermic, heat is one of the products. The cold dry ice will help remove heat and favor the formation of products. But that is a thermodynamic factor, which usually does not affect rxn rates.
13. (10 pts) Calculate the rate constant for the following reaction. Clearly show all your work.

\[ 2\text{C}_2\text{H}_4(\text{OH})_2(aq) + 5\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(g) \]

First you must determine the rate law:

In going from Exp # 1 to # 2, the concentration of \( \text{O}_2 \) doubles, but the rate increases by a factor of 4. That indicates a square power on \( [\text{O}_2]^2 \). For Exp # 3 and # 4, the concentration of \( \text{C}_2\text{H}_4(\text{OH})_2 \) increases by a factor of 4 and the rate also increases by a factor of 4. That indicates a first order power relationship. So the rate law is \( k [\text{C}_2\text{H}_4(\text{OH})_2][\text{O}_2]^2 \)

Now you can calculate the rate constant by plugging in one set of data from any of the 4 experiments. I will pick # 1:

\[ 2.1 \times 10^{-4} \text{ M/sec} = k [\text{C}_2\text{H}_4(\text{OH})_2][\text{O}_2]^2 \]

\[ k = \frac{2.1 \times 10^{-4} \text{ M/sec}}{(0.1 \text{ M})(0.01 \text{ M})^2} = \frac{2.1 \times 10^{-4} \text{ M/sec}}{(1 \times 10^{-5} \text{ M}^3)} = 21 \text{ M}^{-2} \text{ sec}^{-1} \]

<table>
<thead>
<tr>
<th>Exp #</th>
<th>([-\text{C}_2\text{H}_4(\text{OH})_2])</th>
<th>([-\text{O}_2])</th>
<th>Rate (M/sec^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.01</td>
<td>(2.1 \times 10^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.02</td>
<td>(8.4 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.03</td>
<td>(1.9 \times 10^{-3})</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>0.03</td>
<td>(7.6 \times 10^{-3})</td>
</tr>
</tbody>
</table>

14. (10 pts) Consider the following equilibrium: \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \)

The initial concentrations are: \([\text{N}_2] = 2 \text{ M}; [\text{H}_2] = 1 \text{ M}; [\text{NH}_3] = 10 \text{ M}\). At equilibrium \([\text{N}_2] = 3 \text{ M}\)? Calculate \(K_{eq}\) for this reaction. Clearly show all your work.

Initial: 2 1 10
\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

@Eq: 2 + x 1 + 3x 10 − 2x

Since I gave you one of the final equilibrium values, you can easily calculate what x is and the other equilibrium values from that:

\[ 2 + x = 3, \ x = 1 \]

Substitute into the algebraic expressions:

\[ K_{eq} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(8)^2}{(3)(4)^3} = \frac{64}{(3)(64)} = \frac{1}{3} = 0.33 \]

\[ K_{eq} = 0.33 \]

15. (10 pts) Consider the reaction: \( \text{F}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{FCl}(g) \quad K_{eq} = 64 \)

If one starts with \([\text{F}_2] = [\text{Cl}_2] = 0\), and \([\text{FCl}] = 10 \text{ M}\), what will be the concentration of \(\text{FCl}\) @ equilibrium? Clearly show all your work!

Initial: 0 M 0 M 10 M
\[ \text{F}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{FCl}(g) \]

@eq: \( x \) \( x \) 10 − 2x

\[ K_{eq} = 64 \]

Now plug the algebraic equilibrium concentrations into the equilibrium expression and solve for x:

\[ K_{eq} = \frac{(\text{FCl})^2}{(\text{F}_2)(\text{Cl}_2)} = \frac{(10 − 2x)^2}{(x)^2} = 64 \]

now take the square root of each side: \( \frac{10 − 2x}{x} = 8 \)

Rearrange and solve for x: \( 10 − 2x = 8x; \ 10 = 10x; \ x = 1 \)

The concentration of \([\text{FCl}]\) at equilibrium, therefore, is \([\text{FCl}] = 10 − 2x = 10 − (2)(1) = 8 \text{ M}\)

So, \([\text{FCl}] = 8 \text{ M}\)