Department of Chemistry
University of Texas at Austin

Name:_______________

Nuclear Chemistry/Kinetics Unit Activity – Readiness Assessment Quiz KEY

Please work in small groups and be prepared to answer via clicker.

Discussion Point I: Thinking about nuclear change… what is the macroscopic observable, and what is the microscopic model?

1. Pt-200 undergoes beta emission. Please write the balanced nuclear decay equation.

Since the question only states "beta emission," we assume this is a negative beta emission, an electron.

The atomic numbers on the right hand side must add up to the atomic number on the left hand side.

We find that a neutron has been converted to a proton and an electron and write the equation below:

$$^{200}_{78}Pt \rightarrow {}^{0}_{-1}\beta + {}^{200}_{79}Au$$

2. Write the rate law and the integrated rate law for this decay.

Since this is a radioactive decay, we know it is 1st Order. We will use the generic symbol, A, to represent the species that is undergoing decay (Pt in this case).

Rate = k[A]

$[A]_t = [A]_o e^{-kt}$

Alternatively, we could write it like this: $\ln[A]_t = -kt + \ln[A]_0$

3. The half-life of Pt-200 is 12 hours. Assuming you start with 2.0 Ci, how many Ci will be left after 2 hours?

Starting with the half-life equation for first-order kinetics: $t_{1/2} = \frac{\ln(2)}{k}$

We find k = 0.05776 hours^{-1}

Now using: $[A]_t = [A]_o e^{-kt}$

We can plug in our values for the initial Pt-200, k, and time

$[A]_t = (2.0\text{Ci})e^{-(0.05776)*2}$

$[A]_t$ = 1.78 Ci

4. Assume you have acquired 0.12 g of Pt-200. Assume that each time a certain mass of Pt-200 undergoes decay, 0.1 % of the mass is converted to energy. How much energy in units of kJ will be given off over one 24-hour period?

After 24 hours, the Pt-200 will have gone through 2 half-lives. The sample will lose 0.09 grams of material and will be left with 0.03 grams remaining. (0.12g/2 = 0.06 g and then again 0.06g/2 = 0.03g).

Our energy comes from the 0.09 grams of material that decayed, so we start with this, converting to kg AND multiplying by 0.001, for the 0.1% of the mass that was converted to energy.

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$$\Delta m = 0.09g \times \frac{1kg}{1000g} \times 0.001 = 9.0 \times 10^{-8} kg$$

$E = mc^2$

$E = (9\times10^{-8}kg)(3.00\times10^{8}m/s)^2$

Remember, $J = kg\frac{m^2}{s^2}$

$E = 8.1 \times 10^{9}$ J

$E = 8.1 \times 10^{6}$ kJ

Discussion Point II: Thinking about the kinetics of chemical change, what is the macroscopic observable and what is the microscopic model?

The following questions will refer to the following gas phase reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

5. Can you determine the rate law by inspecting this reaction? Why or Why not?
No, we cannot determine the rate law by looking at this reaction alone. We must know if there are elementary steps that lead to this overall reaction. There may be intermediate species that need to collide for the reaction to take place.

6. Predict the rate law based on the following data:

Initial μM NO	Initial μM O_2	Initial Rate μM*s^{-1}
100	100	2
300	100	18
250	250	31.3

7. Calculate the value of the rate constant for the predicted rate law.
Let's do some analysis:
Rate = $k[NO]^x[O_2]^y$

We can determine the value of k and the x and y exponents by comparing experiments. We need hold one of the reactant concentrations constant while changing the other. First, compare experiments 1 and 2.

The concentration of NO tripled from 100 to 300 and the rate increased by a factor of 9 times!!! So the exponent of the NO concentration must be a "2."

For a more mathematical approach, divide the rates:

$\underline{\text{Rate1} = 2\mu M{*}s^{-1} = k[100\mu M]^x[100\mu M]^y}$

$\text{Rate2} = 18\mu M{*}s^{-1} = k[300\mu M]^x[100\mu M]^y$

The O_2 concentrations and the k cancel, leaving:
$(1/9) = (1/3)^x$ therefore, x must equal 2.

Now that we know the value of x, we can use this mathematical approach again to find y. In fact, we must use this approach because there are no two experiments where the value of O_2 is changing, but the value of NO is constant.

Divide experiments 2 and 3, let's but 3 on the numerator for easier math:

$$\frac{\text{Rate3} = 31.3\mu M*s^{-1} = k[250\mu M]^2[250\mu M]^y}{\text{Rate2} = 18\mu M*s^{-1} = k[300\mu M]^2[100\mu M]^y}$$

The k cancels, leaving:
$1.74 = (0.833)^2(2.5)^y$
$2.5 = (2.5)^y$ therefore, y must equal 1.

Now that we finally have our exponents, we just choose any experiment, plug in the values and solve for k.
$\text{Rate2} = 18\mu M*s^{-1} = k[300\mu M]^2[100\mu M]^1$
$\text{Rate2} = 18\mu M*s^{-1} = k\,(9000000\ \mu M^3)$
$k = (18\mu M*s^{-1})/(9000000\ \mu M^3)$
$k = 2.0\text{x}10^{-6}\ \mu M^{-2}*s^{-1}$

8. Determine the rate laws for each of the proposed mechanisms below.
For each of these mechanisms, the SLOW step will be the rate-limiting or rate-determining step. Write down the rate from the slow step. Then, if there are intermediates in this rate, we will eliminate them using an equilibrium constant expression!

a) $NO + NO \rightarrow N_2O_2$ (slow)
$N_2O_2 + O_2 \rightarrow 2NO_2$ (fast)
Overall reaction: $2NO + O_2 \rightarrow 2NO_2$
Rate = $k[NO]^2$

b) $NO + O_2 \rightarrow NO_3$ (slow)
$NO_3 + NO \rightarrow 2NO_2$ (fast)
Overall reaction: $2NO + O_2 \rightarrow 2NO_2$
Rate = $k[NO]^1[O_2]^1$

c) $NO + O_2 \leftarrow\rightarrow NO_3$ (fast, eq)
$NO_3 + NO \rightarrow 2NO_2$ (slow)
Overall reaction: $2NO + O_2 \rightarrow 2NO_2$
Rate = $k[NO_3]^1[NO]^1$ We cannot stop here because NO_3 is an intermediate

Write the equilibrium constant expression for the step with equilibrium:
$K = \underline{\quad [NO_3] \quad}$

$[NO][O_2]$

Now, solve for the intermediate, NO_3, by rearranging:

$[NO_3] = K[NO][O_2]$

Substitute this expression back into the rate law:

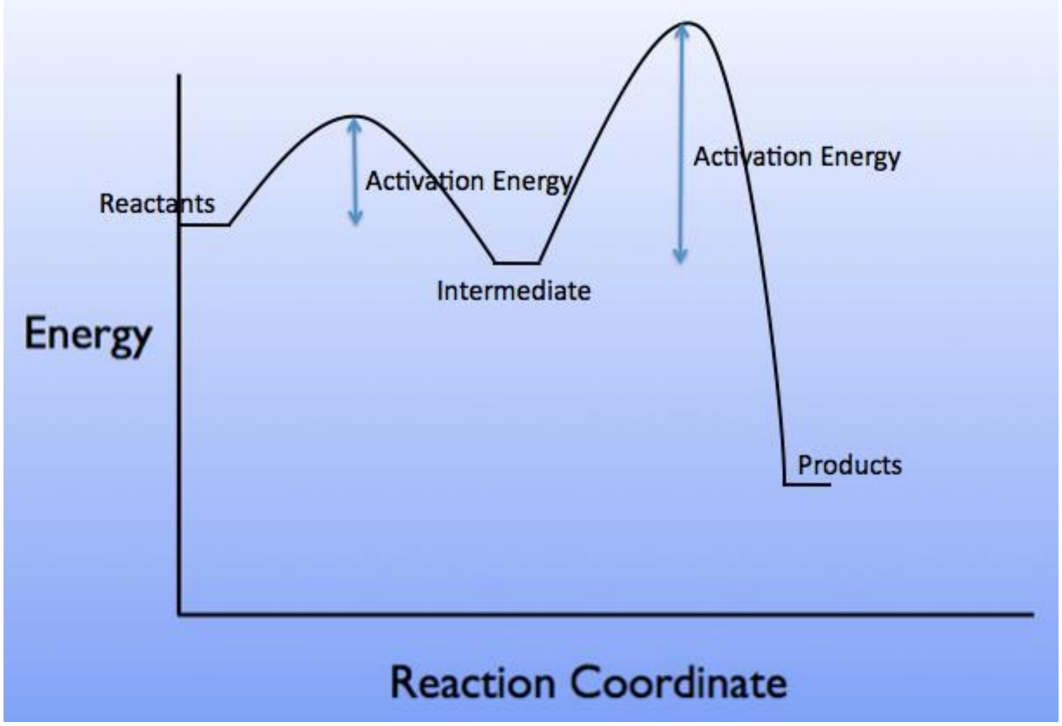
Rate = $k[NO](K[NO][O_2])$

The multiplication of k, the rate constant, and K, the equilibrium constant, will simply give just another constant which we can call k'.

Rate = $k'[NO]^2[O_2]$

9. Which of the proposed mechanisms are possible given the experimentally determined rate law?
   Mechanism c, it results in a rate law that matches the experimentally determined rate law.

10. Given that the reaction is exothermic, draw a viable reaction coordinate diagram based on the experimentally supported reaction mechanism.



There are TWO steps in this mechanism and the second step is the slow step. Overall we know that an exothermic reaction would have reactants that are higher in energy than the products, but on the way from overall reactant to overall products we have intermediates. The second step will have a bigger "energy hill" to overcome because a slow step will require a greater activation energy.

11. When Pt metal is used as a catalyst for this reaction, the mechanism changes and the reaction is much faster. With the catalyst the activation energy is found to be 80 kJ mol^{-1}. How much would you have to raise the temperature to get the reaction to run 100 times faster than it does at room temperature with the catalyst?

$k = Ae^{-E_a/RT}$ can be rearranged into $\ln(k) = \ln(A) - (E_a/RT)$

We would like to imagine a rate constant that is 100 times the current k, which we can call k_1. The activation energy will remain the same for the reaction because we will be using the same catalyst each time.

$\ln(k_1) = \ln(A) - (E_a/RT_1)$
$\ln(k_2) = \ln(A) - (E_a/RT_2)$

$\ln(k_2) - \ln(k_1) = (\ln(A) - (E_a/RT_2)) - (\ln(A) - (E_a/RT_1))$
$\ln(k_2/k_1) = -(E_a/RT_2) + (E_a/RT_1)$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Now we know that $k_2 = 100k_1$ so the ratio of k_2 over k_1 will just be 100. Room temperature is 298 K and the value of R is 8.314 J/molK (we have to convert activation energy to 80,000 joules if we use this value for R).

$$\ln(100) = \frac{-80{,}000J}{8.314\frac{J}{molK}}\left[\frac{1}{T_2} - \frac{1}{298K}\right]$$

$$-4.786\text{x}10^{-4}\ K^{-1} = \left[\frac{1}{T_2} - \frac{1}{298K}\right]$$

$$\left[\frac{1}{T_2}\right] = -4.786\text{x}10^{-4}\ K^{-1} + (1/298K) = 0.00288\ K^{-1}$$

T_2 = 347.57 K or about 74°C