CHEMISTRY 444.10 **Spring, 2018**
QUIZ 3 **March 2, 2018**
NAME: ____ALEXANDRE DESPLAT___________ **Score ______/20**

[Numbers without decimal points are to be considered infinitely precise. Show reasonable significant figures and proper units. In particular, use generally accepted units for various quantities.]

1. (10 points) The reaction $2\,NO + O_2 \rightarrow 2\,NO_2$ is second order with a temperature-dependent rate constant, k:

T (K)	203.8	222.4	272.2	307.2
k ($cm^3 molecule^{-1} s^{-1}$) / 10^{-15}	2.67	4.17	11.5	20.9

Using these data only, determine $\Delta H^{\neq}$ for this reaction over this range. [An appropriate plot makes the analysis easy.]

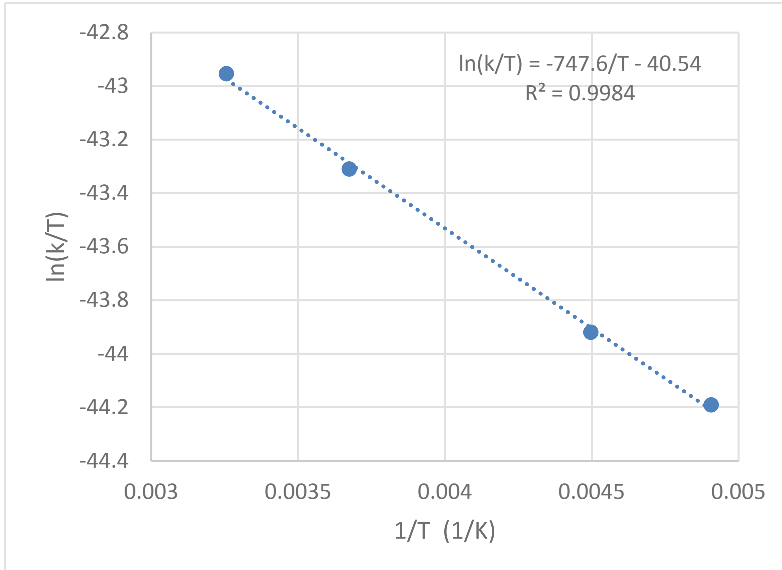
The appropriate equation to plot is the following:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{hc^{\theta}}\right) + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{R}\frac{1}{T}$$

The slope of this plot is related to the enthalpy of activation.

$$\Delta H^{\neq} = 747.6\,K\,(8.3144349\,J\,K^{-1}\,mole^{-1})$$
$$= 6.216\,kJ\,mole^{-1}$$

[Note that the question specifically asked for the enthalpy of activation. It did NOT ask for the activation energy. The two parameters are not the same.]



2. (4 points) The decay of ^{60}Co to form ^{60}Ni by gamma ray emission has been used by physical chemists, such as former Delaware professor Conrad Trumbore, as a gamma-ray source in the study of radiation damage in biological systems. The half-life for the first-order decay of ^{60}Co is 1.9×10^3 days. What is the first-order rate constant for this process?

By rearrangement, one finds the relation: $k = \frac{ln2}{t_{1/2}} = \frac{ln2}{1.9 \times 10^3\,day} = 3.6 \times 10^{-4}\,day^{-1}$

This can be expressed in other time units as $1.5 \times 10^{-5}\,h^{-1} = 2.5 \times 10^{-7}\,min^{-1} = 4.2 \times 10^{-9}\,s^{-1}$.

3. (6 points) Consider a bimolecular solution-phase reaction in water, for which the diffusion coefficient at 298.15 K is $2.25\times10^{-9}\,m^2\,s^{-1}$. [You may assume that all the reactants diffuse similarly to the water.] Assuming the reacting molecules are roughly 1.0 Angstrφm unit <u>in diameter</u>, estimate the maximum rate constant for the reaction under these conditions.

The question is answered by calculating the maximum rate constant for diffusion control:

$$k_D = 4\pi N_0(r_A + r_B)(D_A + D_B)$$
$$= 4\pi(6.02211415 \times 10^{23} mole^{-1})(1 \times 10^{-10}\,m)(2 \times 2.25 \times 10^{-9} m^2 s^{-1})$$
$$= 3.41 \times 10^6 \frac{m^3}{mole * s} = 3.41 \times 10^9 \frac{dm^3}{mole * s}$$