Chemistry 4000 Fall 2012 Test 1

Time: 50 minutes
Marks: 42
Aids allowed: calculator
Formulas and data are given on the reverse of this page.
Instructions: You can answer the questions in any order, but make sure that you clearly label each of your answers with the question number in your exam booklet(s).
In questions where you have a choice, **do not answer more than the required number of questions**. Extra answers will not be marked. If you start answering one question and decide to answer another, cross out the one you do not want marked.

1. The elementary reaction $H + CO_2 \rightarrow OH + CO$ is important in combustion chemistry. How many vibrational modes would be included in the partition function $Q^{\ddagger}$? The transition state of this reaction is bent. [2 marks]

2. The elementary reaction $CO + O_2 \rightarrow CO_2 + O$ has an experimentally determined preexponential factor of $3.5 \times 10^9\,\mathrm{L\,mol^{-1}s^{-1}}$ over the temperature range 2400–3000 K.

   (a) Arrhenius theory treats the preexponential factor as a constant. Is this reasonable? Discuss this issue briefly using the theories presented in class. Do *any* of them lead to a temperature-independent preexponential factor? [5 marks]

   (b) The hard-sphere radii of O_2 and CO are, respectively, 1.8 and 1.9 Å, and their molar masses are, again respectively, 32.00 and $28.01\,\mathrm{g\,mol^{-1}}$. Estimate the preexponential factor of this reaction. (Pick a reasonable temperature given the data provided.) How does your calculated rate constant compare to the experimental value? What does this tell us about the reaction? [14 marks]

3. Briefly explain what tunneling is and why this phenomenon poses a problem for transition-state theory. [6 marks]

4. Describe **one** of the following experimental techniques. Feel free to use a diagram if that would be helpful. [5 marks]

   - Velocity selection
   - Infrared chemiluminescence
   - Laser induced fluorescence

5. Choose any **two** of the following theories, and compare them. How are they similar? How are they different? What data do we need in order to apply them? [10 marks]

   - Simple collision theory
   - Theory of reactive scattering
   - Transition-state theory

Formulas and data

$L = 6.022\,141\,29 \times 10^{23}\,\mathrm{mol^{-1}}$
$R = 8.314\,4621\,\mathrm{J\,K^{-1}mol^{-1}}$
$1\,\text{Å} = 10^{-10}\,\mathrm{m}$
$1\,\mathrm{m}^3 = 1000\,\mathrm{L}$

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

$$A_{\mathrm{ct}} = \sigma \bar{v}_r L \qquad \bar{v}_r = \sqrt{\frac{8RT}{\pi \mu_m}} \qquad \frac{1}{\mu_m} = \frac{1}{M_A} + \frac{1}{M_B}$$

$$k = 4\pi L \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \int_0^\infty \sigma_R(v_r) v_r^3 \exp\left(-\frac{\mu v_r^2}{2k_B T}\right)\, dv_r$$

$$k = \frac{4L}{k_B T}\left[2\pi \mu k_B T\right]^{-1/2} \int_0^\infty \sigma_R(K_r) K_r \exp\left(-\frac{K_r}{k_B T}\right)\, dK_r$$

$$k = \frac{k_B T}{c^\circ h} \frac{Q^\ddagger}{Q_{\mathrm{X}}\, Q_{\mathrm{Y}}} N \exp\left(-\frac{\Delta E_0}{RT}\right)$$

$$k = \frac{k_B T}{c^\circ h}\, \exp\left(\frac{\Delta^\ddagger S_m^\circ}{R}\right) \exp\left(-\frac{\Delta^\ddagger H_m^\circ}{RT}\right)$$

$$E_a = \Delta^\ddagger H_m^\circ + RT\left(1 - \Delta^\ddagger n_{\mathrm{gas}}\right)$$

$$A = \frac{k_B T}{c^\circ h}\, \exp\left(\frac{\Delta^\ddagger S_m^\circ}{R}\right) \exp(1 - \Delta^\ddagger n_{\mathrm{gas}})$$