# Chemistry 4000 Fall 2012 Test 2

**Time:** 50 minutes
**Marks:** 38
**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. Define **any three** of the following terms, and **briefly** explain the role of the corresponding concepts in theoretical kinetics (what theory or theories these concepts appear in, how they are used). [4 marks each]
   (a) Intramolecular vibrational relaxation
   (b) Microcanonical rate constant
   (c) Active mode
   (d) Transition rate
   (e) Detailed balance

2. One variation on the Lindemann mechanism involves the formation of an exciplex, an excited complex, which then goes on to react:

$$\mathrm{A} + \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}_2^*$$
$$\mathrm{A}_2^* \xrightarrow{k_2} \mathrm{A} + \text{products}$$

   (a) Derive a rate law for this mechanism. Is this mechanism consistent with experimental observations of the kinetics of gas-phase unimolecular reactions? Explain briefly. [10 marks]
   (b) For reactions where this mechanism is a possibility, it should compete with the ordinary Lindemann mechanism in which there is collisional activation but the molecules do not stick together. It should be possible to treat the second step of this reaction ($\mathrm{A}_2^* \rightarrow \mathrm{A}$ + products) using RRK theory. Which rate constant would you expect to be larger, the one for the exciplex mechanism, or the rate constant for the normal Lindemann pathway, $\mathrm{A}^* \rightarrow$ products? What does this imply in terms of the likelihood that the exciplex pathway will operate for typical reactions? Explain briefly. [6 marks]

3. The chemical master equation can be written

$$\frac{dP(\mathbf{N},t)}{dt} = \sum_{r\in\mathcal{R}} a_r(\mathbf{N}-\boldsymbol{\nu}_r)P(\mathbf{N}-\boldsymbol{\nu}_r,t) - \sum_{r\in\mathcal{R}} a_r(\mathbf{N})P(\mathbf{N},t)$$

Explain the meanings of all the symbols in this equation ($\mathbf{N}$, $P(\mathbf{N},t)$, etc.). Also explain the physical meanings of the two sums on the right-hand side of the equation. [10 marks]

## Formulas and data

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

$$k_1 = \frac{A_{\rm ct}}{(s-1)!}\left(\frac{E_a}{k_BT}\right)^{s-1}\exp\left(-\frac{E_a}{k_BT}\right)$$

$$k_{2K} = k^\ddagger\left(\frac{E-E^\ddagger}{E}\right)^{s-1}$$

$$k_{\rm RRK} = \int_{E^\ddagger}^{\infty}\frac{\frac{\nu^\ddagger[\mathrm{M}]}{k_BT(s-1)!}\left(\frac{E-E^\ddagger}{k_BT}\right)^{s-1}\exp\left(-\frac{E}{k_BT}\right)}{[\mathrm{M}]+\frac{\nu^\ddagger}{k_{-1}}\left(\frac{E-E^\ddagger}{E}\right)^{s-1}}\,dE$$

$$\frac{dP_s}{dt} = \sum_{r\neq s} w_{rs}P_r - \sum_{r\neq s} w_{sr}P_s$$

$$\frac{w_{sr}}{w_{rs}} = \exp\left(-\frac{E_r-E_s}{k_BT}\right)$$

| **Reaction type** | $\boldsymbol{a}$ | $\boldsymbol{\kappa}$ |
|---|---|---|
| $\mathrm{A}\rightarrow$ | $\kappa N_A$ | $k$ |
| $\mathrm{A}+\mathrm{B}\rightarrow$ | $\kappa N_A N_B$ | $k/LV$ |
| $\mathrm{A}+\mathrm{A}\rightarrow$ | $\kappa N_A(N_A-1)/2$ | $2k/LV$ |