Answer Key for Exam A

Section 1. True/False (10×1)

False — As b increases from zero to its maximum value $b_{\max} = r_A + r_B$, the scattering angle θ increases from zero to π.

False — A plot of $\log k$ vs. $1/T$ which is convex downwards is indicative of tunneling.

True — If two reactions with different activation energies have the same rate at room temperature, at the same, higher temperature the reaction with the larger activation energy will be faster, other things being the same.

True — According to collision theory, the pre-exponential factor is proportional to $T^{1/2}$.

True — The entropy change of activation for a bimolecular gaseous reaction is generally negative.

True — The larger the scattering cross section is, the more particles are scattered out of the beam, all other conditions being the same.

False — The kinetic isotope effect is given by $\frac{k_H}{k_D} = e^{-\frac{h\left(\frac{k_{RH}}{\mu_{RH}} - \frac{k_{RD}}{\mu_{RD}}\right)}{4\pi kT}}$.

True — The factor of kT/h in transition state theory is the frequency at which the reactants attempt to get to the activated complex.

True — The energy of the transition state is a maximum in one direction, while in all other directions it is a minimum.

False — Transition state theory assumes that an equilibrium exists between reactants, transition state, and products.

Section 2. Fill in the blanks (5×2)

1. The pre-exponential factor for $NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$ is $3.981 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$. The $\Delta S^\ddagger$ for this reaction at $T = 300.0\,K$ is $R \ln \frac{Ahc^\circ}{e^2 k_B T} = -77.8\,J\,mol^{-1}\,K^{-1}$. (McQuarrie and Simon, example 26-10)

2. If the collision frequency per unit volume between molecules of types A and B with relative speeds in the range u_r and $u_r + du_r$ is $dZ_{AB} = \sigma_{AB}\rho_A\rho_B \left(\frac{\mu}{k_B T}\right)^{3/2} \left(\frac{2}{\pi}\right)^{1/2} e^{-\mu u_r^2/2k_B T} u_r^3\, du_r$, the collision frequency per unit volume in which the relative kinetic energy exceeds some critical value ϵ_c is $\int_{\epsilon_c}^{\infty} dZ_{AB}(\epsilon_r) = \sigma_{AB}\rho_A\rho_B \left(\frac{8k_B T}{\pi\mu}\right)^{1/2} \left(1 + \frac{\epsilon_c}{k_B T}\right) e^{-\epsilon_c/k_B T}$. (McQuarrie and Simon, Example 25-11)

3. Given that the Maxwell-Boltzmann distribution of speeds is $F(u)\,du = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 e^{-\frac{mu^2}{k_B T}}\, du$, the most probable kinetic energy for a molecule is $\frac{d}{d\epsilon}\left(\frac{2\pi}{(\pi k_B T)^{3/2}} \epsilon^{1/2} e^{-\epsilon/k_B T}\right) = \frac{k_B T}{2}$. (McQuarrie and Simon, 25-27)

4. The hard-sphere collision theory rate constant, in $dm^3\,mol^{-1}\,s^{-1}$, for the reaction $NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$ at 300 K is $1000\,dm^3\,m^{-3} N_A \sigma_{AB} \langle u_r \rangle = 2.15 \times 10^{11}\,dm^3\,mol^{-1}\,s^{-1}$. You are given that the diameters of NO and Cl_2 are 370 pm and 540 pm, respectively. (McQuarrie and Simon, 25-1)

5. The activation energy for $NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$ is $84.9\,kJ\,mol^{-1}$. The $\Delta H^\ddagger$ for this reaction at $T = 300.0\,K$ is $E_a - 2RT = 79.9\,kJ\,mol^{-1}$. (McQuarrie and Simon, example 26-10)