

# Minor 2 Solutions

March 22, 2016

## I True/False

1. The entropy change of activation for a bimolecular gaseous reaction is generally negative.  
True. When two reactants form an activated complex, some of the degrees of freedom are decreased as a result of which the entropy of activation is usually negative.
2. The larger the scattering cross section is, the more particles are scattered out of the beam, all other conditions being the same.  
True. The scattering or reaction cross section,  $\sigma = \pi r^2$ , is an effective area measuring the likelihood of a scattering event and hence higher it is the more particles are scattered out of the beam.
3. As  $b$  increases from zero to its maximum value  $b_{\max} = r_A + r_B$ , the scattering angle  $\theta$  increases from zero to  $\pi$ .  
False. The impact parameter,  $b$ , is the distance of closest approach between two colliding particles. Head-on collision corresponds to  $b = 0$  for which the scattering angle is  $\pi$ . The minimum value of the scattering angle is zero, and corresponds to no deflection.
4. The kinetic isotope effect is given by  $\frac{k_H}{k_D} = e^{-\frac{h\left(\frac{k_{RH}}{\mu_{RH}} - \frac{k_{RD}}{\mu_{RD}}\right)}{4\pi kT}}$ .  
False. Does not have the negative sign.
5. The energy of the transition state is a maximum in one direction, while in all other directions it is a minimum.  
True. Along the reaction coordinate the TS is at an energy maximum, while in all other directions it is at a minimum.
6. A plot of  $\log k$  vs.  $1/T$  which is convex downwards is indicative of tunneling.  
False. The observed rate constant,  $k_{\text{obs}}$  can be written as  $k_{\text{Arrh}} + k_{\text{T}}$ , where the first term shows Arrhenius dependence on temperature while the second term, the tunneling contribution, is temperature independent. At low temperatures, the tunneling contribution dominates and the  $\log k$  vs.  $1/T$  is concave upwards.
7. According to collision theory, the pre-exponential factor is proportional to  $T^{1/2}$ .  
True. According to collision theory,  $k \propto \bar{Z}$ , which is related to the average velocity factor, which in turn is proportional to  $T^{1/2}$ .
8. Transition state theory assumes that an equilibrium exists between reactants, transition state, and products.  
False. Transition state theory assumes that an equilibrium exists between reactants and the transition state.
9. 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. Might appear counter-intuitive at first sight, but if we plot  $\ln k$  vs.  $1/T$  we find that the one with the higher activation energy has a more negative slope. This implies that at high temperature, which is closer to the origin, the line with the more negative slope will be higher than the line with the less negative slope.

10. The factor of  $kT/h$  in transition state theory is the frequency at which the reactants attempt to get to the activated complex.  
True. Because that is what it is!

## 2 Fill in the blanks

1. The hard-sphere collision theory rate constant, in  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ , for the reaction  $\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{NOCl}(\text{g}) + \text{Cl}(\text{g})$  at 300 K is \_\_\_\_\_. You are given that the diameters of NO and  $\text{Cl}_2$  are 370 pm and 540 pm, respectively. (McQuarrie and Simon, 25-1)  
The hard sphere collision theory rate constant (in the required units) is

$$k_{\text{theor}} = 1000 \text{ dm}^3 \text{ m}^{-3} N_A \sigma_{\text{AB}} \langle u_r \rangle.$$

$$\sigma_{\text{AB}} = \pi d_{\text{AB}}^2 = \pi \left( \frac{370 \text{ pm} + 540 \text{ pm}}{2} \right)^2 = 6.50 \times 10^{-19} \text{ m}^2$$

$$\langle u_r \rangle = \left( \frac{8k_{\text{B}}T}{\pi\mu} \right)^{1/2} = \left\{ \frac{8 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}}{\pi \left[ \frac{(70.906 \text{ amu})(30.006 \text{ amu})}{(100.912 \text{ amu})} \right]} \right\}^{1/2} = 549 \text{ m s}^{-1}$$

$$k_{\text{theor}} = 1000 \text{ dm}^3 \text{ m}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times 6.50 \times 10^{-19} \text{ m}^2 \times 549 \text{ m s}^{-1} = 2.15 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

2. Given that the Maxwell-Boltzmann distribution of speeds is  $F(u) du = 4\pi \left( \frac{m}{2\pi k_{\text{B}}T} \right)^{3/2} u^2 e^{-\frac{mu^2}{k_{\text{B}}T}} du$ , the most probable kinetic energy for a molecule is \_\_\_\_\_.  
The distribution is first expressed in terms of the kinetic energy,  $\epsilon = 1/2 mu^2$ . This means that  $d\epsilon = mu du$  or  $du = \frac{1}{\sqrt{2m\epsilon}} d\epsilon$ . Hence  $F(\epsilon) d\epsilon = 4\pi \left( \frac{m}{2\pi k_{\text{B}}T} \right)^{3/2} \frac{2\epsilon}{m} e^{-\epsilon/k_{\text{B}}T} \frac{d\epsilon}{(2m\epsilon)^{1/2}}$ . Differentiating  $F(\epsilon)$  with respect to  $\epsilon$ , setting it to zero, and solving for  $\epsilon$  gives the desired result.

$$\frac{dF(\epsilon)}{d\epsilon} = \frac{2\pi}{(\pi k_{\text{B}}T)^{3/2}} \left[ \frac{\epsilon^{-1/2} e^{-\epsilon/k_{\text{B}}T}}{2} - \frac{\epsilon^{1/2} e^{-\epsilon/k_{\text{B}}T}}{k_{\text{B}}T} \right]$$

$$0 = \frac{2\pi e^{-\epsilon/k_{\text{B}}T}}{(\pi k_{\text{B}}T)^{3/2}} \left[ \frac{1}{2\epsilon^{1/2}} - \frac{\epsilon^{1/2}}{k_{\text{B}}T} \right]$$

$$\epsilon_{\text{mp}} = \frac{k_{\text{B}}T}{2}.$$

3. 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

$$dZ_{\text{AB}} = \sigma_{\text{AB}} \rho_{\text{A}} \rho_{\text{B}} \left( \frac{\mu}{k_{\text{B}}T} \right)^{3/2} \left( \frac{2}{\pi} \right)^{1/2} e^{-\mu u_r^2 / 2k_{\text{B}}T} u_r^3 du_r,$$

the collision frequency per unit volume in which the relative kinetic energy exceeds some critical value  $\epsilon_c$  is \_\_\_\_\_.

As in problem 2, we first express the collision frequency with relative speeds in the range  $u_r$  and  $u_r + du_r$  as the collision frequency with relative kinetic energy in the range  $\epsilon_r$  and  $\epsilon_r + d\epsilon_r$ . This gives

$$dZ_{\text{AB}} = \sigma_{\text{AB}} \rho_{\text{A}} \rho_{\text{B}} \left( \frac{8}{\pi\mu} \right)^{1/2} \left( \frac{1}{k_{\text{B}}T} \right)^{3/2} \epsilon_r e^{-\epsilon_r/k_{\text{B}}T} d\epsilon_r$$

Integrating  $dZ_{\text{AB}}$  from  $\epsilon_r = \epsilon_c$  to  $\infty$  gives the desired result. This integration requires that we know

$$\int_{\epsilon_c}^{\infty} \epsilon_r e^{-\epsilon_r/k_{\text{B}}T} = (k_{\text{B}}T)^2 \left( 1 + \frac{\epsilon_c}{k_{\text{B}}T} \right) e^{-\epsilon_c/k_{\text{B}}T}.$$

You could argue that I was supposed to provide this integral, but then again we had discussed in class how to determine this! The result is

$$Z_{\text{AB}} = \sigma_{\text{AB}} \rho_{\text{A}} \rho_{\text{B}} \left( \frac{8k_{\text{B}}T}{\pi\mu} \right)^{1/2} \left( 1 + \frac{\epsilon_c}{k_{\text{B}}T} \right) e^{-\epsilon_c/k_{\text{B}}T}.$$

4. The activation energy for  $\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{NOCl}(\text{g}) + \text{Cl}(\text{g})$  is  $84.9 \text{ kJ mol}^{-1}$ . The  $\Delta H^\ddagger$  for this reaction at  $T = 300.0 \text{ K}$  is \_\_\_\_\_.

For a bimolecular reaction,  $\Delta H^\ddagger = E_a - 2RT$ . At  $300 \text{ K}$ ,  $RT \approx 2.5 \text{ kJ}$  and so  $\Delta H^\ddagger = 79.9 \text{ kJ mol}^{-1}$ .

5. The pre-exponential factor for  $\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{NOCl}(\text{g}) + \text{Cl}(\text{g})$  is  $3.981 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The  $\Delta S^\ddagger$  for this reaction at  $T = 300.0 \text{ K}$  is \_\_\_\_\_.

We have  $A = \frac{kT}{h} e^{\Delta S^\ddagger/R}$ , so that  $\Delta S^\ddagger = R \ln \frac{Ahc^\circ}{kT}$ . Here  $c^\circ = 1.0 \text{ mol dm}^{-3}$  ensures that the argument of  $\ln$  is unitless. Plugging in the values, one finds  $\Delta S^\ddagger = -77.8 \text{ J mol}^{-1} \text{ K}^{-1}$ .