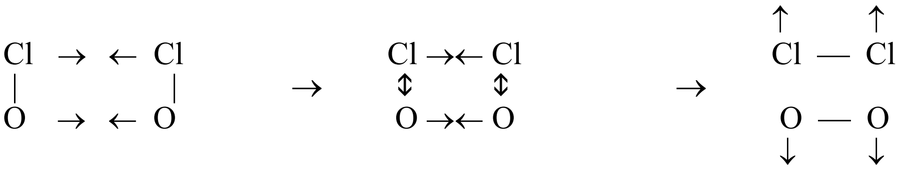
Chapter 32: Reaction Dynamics Problems

1. One possible geometry of the activated complex for the 2 ClO → $Cl_2 + O_2$ reaction is shown in Table 32.1.1. Is this square geometry consistent with the expectation that the reaction coordinate is an unstable asymmetric stretch?

Answer: The plan is to follow the motion of the atoms during the collision.
The reaction coordinate is:



This motion is exactly what you would expect for the asymmetric stretch of a square planar molecule.

2. The lifetime of the transition state is typically on the order of a single vibration period. Calculate the period of a vibration of wave number 500 cm^{-1}.

Answer: The period is the inverse of the frequency:

$$L = 1/\tilde{\nu}c = (500\ cm^{-1}\ 2.997x10^{10}\ cm\ s^{-1})^{-1} = 6.7x10^{-14}\ s = 67\ fs$$

3. Use Activated Complex Theory to discuss the reaction:

$$H + F–F \rightleftarrows [\, H\text{--}F\text{--}F\,]^{\dagger} \rightarrow H–F + F$$

(a). Do the translational partition functions favor or hinder the rate of the reaction? Why?
(b). Do the rotational partition functions favor or hinder the rate of the reaction? Why?

Answer: The plan is to focus on the formation of the activated complex. The products are irrelevant in this analysis. As a result, the plan is to use statistical mechanical arguments to determine factors that favor the formation of the activated complex through the reaction $H + F–F \rightleftarrows [\, H\text{--}F\text{--}F\,]^{\dagger}$. The larger the concentration of the activated complex, the faster the formation of products.

(a). The translational degree of freedom hinders the overall reaction rate. The translational part has only one translational partition function in the numerator and two translational partition functions in the denominator: specifically from Eq. 32.1.14°:

$$\frac{q_t^{\circ\neq}/N_A}{q_t^{\circ}(H)/N_A\ q_t^{\circ}(F_2)/N_A} \qquad \text{(translation only)}$$

Each partition function is on the order of $q_t/N_A \cong 10^6–10^7$, see Eq. 30.4.5°. The translational partition functions dominate the unfavorable entropy of formation of the activated complex: two collision partners combine to form one activated complex.

(b). The rotational partition functions favor the rate of the reaction. The rotational part has one rotational partition function in the numerator and one rotational partition function in the denominator, since one of the reactants is atomic: specifically from Eq. 32.1.14°:

$$\frac{q_r^{o\neq}}{q_r^o(F_2)} = \frac{1/\sigma^{\neq}\tilde{B}^{\neq}}{1/\sigma(F_2)\tilde{B}(F_2)} \qquad \text{with} \quad \tilde{B} = \frac{\hbar}{4\pi Ic} \qquad (24.5.41)$$

where $\sigma^{\neq}$ and $\tilde{B}^{\neq}$ are the rotational symmetry number and rotational constant of the activated complex and $\sigma(F_2)$ and $\tilde{B}(F_2)$ are the rotational symmetry number and rotational constant of the diatomic reactant. The symmetry number of F_2 is $\sigma = 2$, which decreases the number of accessible states of the reactants, which increases the ratio of rotational partition functions, favoring the formation of the activated complex. More importantly, even for more complex reactions, the activated complex is larger than either of the reactants individually and larger because of the loose association in the activated complex. In other words, the reactive asymmetric stretch is "loose and floppy" in the activated complex, $[\text{ H--F--F }]^{\dagger}$. Both effects make the moment of inertia of the activated complex larger than the reactants, giving smaller rotational constants for the activated complex, and therefore larger number of accessible states for the activated complex, compared to the reactants.

4. Use Activated Complex Theory to discuss the reaction:

$$\text{H} + \text{F–F} \rightleftarrows [\text{ H--F--F }]^{\dagger} \rightarrow \text{H–F} + \text{F}$$

Consider the shift in reaction rate, faster or slower, after making the following changes. (a). The bond length of F_2 is increased. (b). F_2 is changed from a homonuclear to a heteronuclear diatomic. (c). The symmetric stretch force constant of the activated complex is increased. (d). The bond dissociation energy of F_2 is increased. (e). The ^{1}H-atom is changed to deuterium, ^{2}H, considering translation only. [In reality changing just one molecular parameter is impossible, bond strength changes have multiple effects. However, for the purposes of this exercise assume that the given change is done without changes in other parameters.]

Answer: The plan is to focus on the formation of the activated complex. The products are irrelevant in this analysis. As a result, the plan is to consider the change in number of accessible states as we did for the calculation of the equilibrium constant in Example 30.5.5, but this time in the context of activated complex theory, as based on Eq. 32.1.14°:

$$k_2 = \frac{kT}{h}\left(\frac{q^{\neq o'}/N_A}{q^{o}(\text{H})/N_A \; q^{o}(F_2)/N_A}\right)\left(\frac{RT}{P^{o}}\right) e^{-\Delta E_o^{\neq}/kT} \qquad (32.1.14°)$$

Each change makes the reaction *slower*:

(a). The rotational partition function of a diatomic is $q_r = kT/\sigma\tilde{B}hc$, Eq. 30.2.33. If the bond length of F_2 is increased, the rotational constant of F_2 is decreased: $\tilde{B} = \hbar/4\pi\mu R_o^2 c$. If the

rotational constant is decreased, the number of accessible rotational states of the reactants is increased, and the rate of formation of the activated complex is decreased.
(b). The rotational symmetry number of a homonuclear diatomic is $\sigma = 2$, but for a heteronuclear diatomic is $\sigma = 1$. If F_2 is changed from a homonuclear to a heteronuclear diatomic, the symmetry number decreases, increasing the number of accessible rotational states of the reactants, and decreasing the rate of formation of the activated complex.
(c). If the symmetric stretch force constant of the activated complex is increased, the number of accessible vibrational states of the activated complex decreases, and the rate of formation of the activated complex decreases. See Eq. 30.2.27.
(d). If the bond dissociation energy, D_o, of F_2 is increased, the zero point energy shift term increases:

$$\Delta E^{\neq}_{o} = [-D_o(HFF^{\neq})] - [-D_o(F_2)] \qquad \textit{increases, so that } e^{-\Delta E^{\neq}_{o}/kT} \textit{ decreases}$$

In other words, if the bond dissociation energy of F_2 increases, the reactant becomes more stable, giving more accessible states to the reactants, and decreasing the rate of formation of the activated complex.
(e). The translational partition function is $q_t = (2\pi mkT)^{3/2}V/h^3$, Eq. 30.2.19°. The effect of the change in isotope is an increase in the mass, m. With increasing mass, the energy spacing of the particle in a box translational energy levels decreases. If the ^{1}H-atom is changed to deuterium, considering translation only, the number of accessible translational states of both the reactants and activated complex increases. The translational partition function factor in activated complex theory for ^{1}H is:

$$\frac{q_t^{\circ\neq}/N_A}{q_t^{\circ}(H)/N_A\, q_t^{\circ}(F_2)/N_A} = \left[\frac{\mathcal{M}(HFF)}{\mathcal{M}(H)\mathcal{M}(F_2)}\right]^{3/2} \frac{N_A}{(2\pi kT/1000\text{ g kg}^{-1}N_A)^{3/2}\, RT/P^{\circ}h^3}$$

Changing the ^{1}H atom to ^{2}H effects only the mass ratio; the second factor remains unchanged. Changing the ^{1}H atom to ^{2}H doubles the denominator in the mass ratio, but has a smaller fractional change in the numerator, which decreases the rate of formation of the activated complex for ^{2}H. Numerically these factors are:

$$\left[\frac{\mathcal{M}(HFF)}{\mathcal{M}(H)\mathcal{M}(F_2)}\right]^{3/2} = \left[\frac{39}{(1)\,(38)}\right]^{3/2} = 1.039 \qquad \left[\frac{\mathcal{M}(DFF)}{\mathcal{M}(D)\mathcal{M}(F_2)}\right]^{3/2} = \left[\frac{40}{(2)\,(38)}\right]^{3/2} = 0.526^{3/2} = 0.381$$

The change from ^{1}H to ^{2}H increases the number of accessible states of the reactants more than the activated complex, decreasing the reaction rate. This translation-only approximation neglects any changes to the vibrational zero point energies of the activated complex. This problem's approach to the isotope effect is specific to this particular reaction, with atomic hydrogen as a reactant. The **primary isotope effect** for H-atom transfer is more commonly referenced and is developed in a subsequent problem.

5. In the derivation of the Eyring equation, Eq. 32.1.24°, what is the source of the kT/h term?

Answer: The kT/h term relates back to the vibrational partition function of the reactive asymmetric stretch, which gives the reaction coordinate. An increase in temperature partitions more energy into the reactive asymmetric stretch thereby increasing the rate of formation of the activated complex. The explicit form as kT/h results from the use of the high temperature approximation to give the vibrational partition function as $kT/h\nu^{\neq}$, Eq. 30.4.20.

6. (a). Find the activation enthalpy, entropy, and Gibbs energy of the reaction:

$$2\ NO_2\ (g) \rightarrow 2\ NO\ (g) + O_2\ (g)$$

at 600.0 K. The Arrhenius pre-exponential factor is $3.06\text{x}10^{12}\ s^{-1}$. The activation energy is 110.9 kJ mol^{-1}. (b). The reaction does not necessarily proceed by a single step mechanism. Is the activation entropy consistent with a bimolecular transition state for the rate limiting step?

Answer: The plan is to follow Example 32.1.2 and then compare the activation entropy to the value of -80 J K^{-1} mol^{-1} that is typical for a bimolecular process.

At 600.0 K, the transmission factor and standard state molar volume are:

$$\frac{kT}{h} = 1.2502\text{x}10^{13}\ s^{-1} \quad \text{and} \quad \left(\frac{RT}{P°}\right) = \frac{0.0831446\ \text{L bar K}^{-1}\ \text{mol}^{-1}(600.0\ \text{K})}{1.000\ \text{bar}} = 49.887\ \text{L mol}^{-1}$$

Using Eq. 32.1.30° for the bimolecular pre-exponential factor with the given experimental value, $A = 3.06\text{x}10^{12}\ M^{-1}\ s^{-1}$, results in:

$$A = \frac{kT}{h}\left(\frac{RT}{P°}\right) e^2\, e^{\Delta_r S^{\circ\neq}/R}$$

$$= 1.2502\text{x}10^{13}\ s^{-1}\ (49.887\ \text{L mol}^{-1})(2.7183)^2\ e^{\Delta_r S^{\circ\neq}/R} = 3.06\text{x}10^{12}\ \text{L mol}^{-1}\ s^{-1}$$

or $e^{\Delta_r S^{\circ\neq}/R} = 6.640\text{x}10^{-4}$

Solving for the activation entropy:

$$\Delta_r S^{\circ\neq} = 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\ \ln(4.043\text{x}10^{-3}) = -60.84\ \text{J K}^{-1}\ \text{mol}^{-1}$$

With Eq. 32.1.28°: $\Delta_r H^{\circ\neq} = E_a - 2RT$

$$\Delta_r H^{\circ\neq} = 110.9\ \text{kJ mol}^{-1} - 2(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(600.0\ \text{K})(1\ \text{kJ}/1000\ \text{J})$$
$$= 110.9\ \text{kJ mol}^{-1} - 9.9774\ \text{kJ mol}^{-1} = 100.92\ \text{kJ mol}^{-1}$$

With Eq. 32.1.23: $\Delta_r G^{\circ\neq} \equiv \Delta_r H^{\circ\neq} - T\Delta_r S^{\circ\neq}$

$$\Delta_r G^{\circ\neq} = 100.92\ \text{kJ mol}^{-1} - (600.0\ \text{K})(-60.84\ \text{J K}^{-1}\ \text{mol}^{-1})(1\ \text{kJ}/1000\ \text{J}) = 137.4\ \text{kJ mol}^{-1}$$

For pre-exponential factors in the range $A \sim 10^{10} - 10^{11}$ the entropy of activation is in the range:

$$e^{\Delta_r S^{\circ\neq}/R} = 8.79\text{x}10^{-6} \text{ to } 8.79\text{x}10^{-5} \quad \text{giving} \quad \Delta_r S^{\circ\neq} = -96.8 \text{ to } -77.7\ \text{J K}^{-1}\ \text{mol}^{-1}$$

or in round numbers ~ -80 J K^{-1} mol^{-1}. The value for this reaction is likewise strongly negative, but not as negative as expected. The value is much more negative than expected for a unimolecular process. The activation entropy of -60.8 J K^{-1} mol^{-1} provides support for a bimolecular transition state, but one that has relaxed steric requirements. The relaxed steric requirements might result from orientation independence, long range forces that increase the effective collision cross section, or relaxed collision timing requirements for the reactive asymmetric stretch.

7. The pre-exponential factor for the reaction $CH_3Br + Cl^- \rightarrow CH_3Cl + Br^-$ in acetone solution is $2.0\text{x}10^9$ L mol^{-1} s^{-1} and the activation energy is 65.7 kJ mol^{-1}. What are the Gibbs energy, entropy, and enthalpy of activation at 298.15 K?

Answer: The plan is to follow Example 32.1.2, but based on Eqs. 32.1.31°-32.1.34°, since the reaction is in solution.

At 298.15 K, the transmission factor is: $\frac{kT}{h} = \frac{1.38064\text{x}10^{-23}\text{ J K}^{-1}(298.15\text{ K})}{6.62608\text{x}10^{-34}\text{ J s}} = 6.2124\text{x}10^{12}\text{ s}^{-1}$

Using Eq. 32.1.34° for the solution phase pre-exponential factor with the given experimental value, $A = 2.0\text{x}10^9$ L mol^{-1} s^{-1}, results in:

$$A = \frac{kT}{h}\, e\, e^{\Delta_r S^{\circ\neq}/R}$$

$$= 6.2124\text{x}10^{12}\text{ s}^{-1}\ (2.7183)\ e^{\Delta_r S^{\circ\neq}/R} = 2.0\text{x}10^9\text{ L mol}^{-1}\text{ s}^{-1}$$

or $e^{\Delta_r S^{\circ\neq}/R} = 1.184\text{x}10^{-4}$

Solving for the activation entropy:

$$\Delta_r S^{\circ\neq} = 8.3145\text{ J K}^{-1}\text{ mol}^{-1}\ \ln(1.184\text{x}10^{-4}) = -75.2\text{ J K}^{-1}\text{ mol}^{-1}$$

Since $\Delta_r n_g = 0$, Eq. 32.1.32, $\Delta_r H^{\circ\neq} = E_a - RT$

$$\Delta_r H^{\circ\neq} = 65.7\text{ kJ mol}^{-1} - 8.3145\text{ J K}^{-1}\text{ mol}^{-1}(298.15\text{ K})(1\text{ kJ}/1000\text{ J})$$

$$= 65.7\text{ kJ mol}^{-1} - 2.4790\text{ kJ mol}^{-1} = 63.22\text{ kJ mol}^{-1}$$

With Eq. 32.1.23: $\Delta_r G^{\circ\neq} \equiv \Delta_r H^{\circ\neq} - T\Delta_r S^{\circ\neq}$

$$\Delta_r G^{\circ\neq} = 63.22\text{ kJ mol}^{-1} - (298.15\text{ K})(-75.2\text{ J K}^{-1}\text{ mol}^{-1})(1\text{ kJ}/1000\text{ J}) = 85.6\text{ kJ mol}^{-1}$$

For pre-exponential factors in the range $A \sim 10^{10} - 10^{11}$ the entropy of activation is in the range:

$$e^{\Delta_r S^{\circ\neq}/R} = 8.79\text{x}10^{-6}\text{ to }8.79\text{x}10^{-5}\quad\text{giving}\quad \Delta_r S^{\circ\neq} = -96.8\text{ to }-77.7\text{ J K}^{-1}\text{ mol}^{-1}$$

or in round numbers ~ -80 J K^{-1} mol^{-1}. The value for this reaction is a little below typical, indicating a little more forgiving steric constraints than normal for a bimolecular gas phase reaction. Collision timing constraints are often relaxed because of the cage effect in solution.

8. Find the activation enthalpy, entropy, and Gibbs energy of the gas phase isomerization:

trans-CHCl=CHCl → *cis*-CHCl=CHCl

at 800.0 K. The Arrhenius pre-exponential factor is $5.0\text{x}10^{12}$ s^{-1}. The activation energy is 27.8 kJ mol^{-1}:

Answer: The plan is to follow Example 32.1.2, noting that the reaction is unimolecular, giving $\Delta_r n_g = 0$ for the formation of the transition state.

At 800.0 K, the transmission factor is: $\frac{kT}{h} = 1.6669\text{x}10^{13}\text{ s}^{-1}$

Using Eq. 32.1.35° for the unimolecular pre-exponential factor with the given experimental pre-exponential factor of $A = 5.0\text{x}10^{12}$ s^{-1} results in:

$$A = \frac{kT}{h}\, e\, e^{\Delta_r S^{\circ\neq}/R} \qquad 1$$

$$= 1.6669\text{x}10^{13}\ \text{s}^{-1}\ (2.7183)\ e^{\Delta_r S^{\circ\neq}/R} = 5.0\text{x}10^{12}\ \text{s}^{-1}$$

or $e^{\Delta_r S^{\circ\neq}/R} = 0.11035$ 2

Solving for the activation entropy: $\Delta_r S^{\circ\neq} = 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\ \ln(0.11035) = -18.33\ \text{J K}^{-1}\ \text{mol}^{-1}$

The entropy of activation is seen to be a moderate value, compared to the "garden variety" -80 J K^{-1} mol^{-1} that is expected for a bimolecular gas phase reaction.

With $\Delta_r n_g = 0$, $\Delta_r H^{\circ\neq} = \Delta_r U^{\circ\neq}$ and then $\Delta_r H^{\circ\neq} = E_a - RT$, from Eq. 32.1.32:

$$\Delta_r H^{\circ\neq} = 27.8\ \text{kJ mol}^{-1} - 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}(800.0\ \text{K})(1\ \text{kJ}/1000\ \text{J})$$
$$= 27.8\ \text{kJ mol}^{-1} - 6.652\ \text{kJ mol}^{-1} = 21.15\ \text{kJ mol}^{-1} \qquad 3$$

With Eq. 32.1.23, $\Delta_r G^{\circ\neq} \equiv \Delta_r H^{\circ\neq} - T\Delta_r S^{\circ\neq}$:

$$\Delta_r G^{\circ\neq} = 21.15\ \text{kJ mol}^{-1} - (800.0\ \text{K})(-18.33\ \text{J K}^{-1}\ \text{mol}^{-1})(1\ \text{kJ}/1000\ \text{J}) = 35.8\ \text{kJ mol}^{-1} \qquad 4$$

Alternatively for $\Delta_r G^{\circ\neq}$ we can use the corresponding equation to Eqs. 32.1.20 and 32.1.22°¸which for $\Delta_r n_g = 0$ gives $K_p^{\neq} = K_c^{\neq}$ and:

$$k_1 = \frac{kT}{h}\, e^{-\Delta_r G^{\circ\neq}/RT} \qquad 5$$

To use this approach, we require the value of the unimolecular rate constant at 800.0 K:

$$k_1 = A\, e^{-E_a/RT} = 5.0\text{x}10^{12}\ \text{s}^{-1}\ e^{-27800\ \text{J}/8.3145\ \text{J K}^{-1}\text{mol}^{-1}(800.0\ \text{K})} = 7.653\text{x}10^{10}\ \text{s}^{-1} \qquad 6$$

Substituting this value for k_1 into Eq. 5 gives:

$$e^{-\Delta_r G^{\circ\neq}/RT} = 7.653\text{x}10^{10}\ \text{s}^{-1}/1.6669\text{x}10^{13}\ \text{s}^{-1} = 4.591\text{x}10^{-3} \qquad 7$$

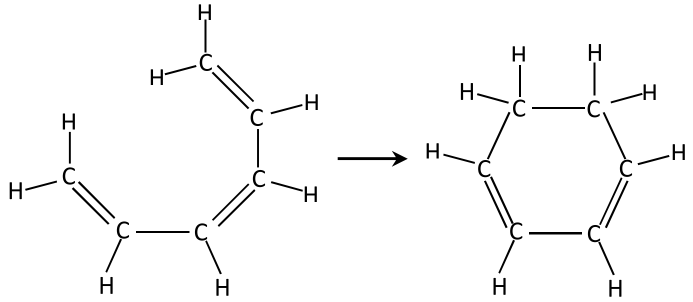
and $\Delta_r G^{\circ\neq} = -\ 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\ (800.0\ \text{K}) \ln(4.591\text{x}10^{-3})\ (1\ \text{kJ}/1000\ \text{J}) = 35.8\ \text{kJ mol}^{-1}$

which matches Eq. 4.

9. The gas phase reaction: *cis*-1,3,5-hexatriene → 1,3-cyclohexadiene has an activation enthalpy of 121.5 kJ mol^{-1} and an entropy of activation of -30.4 J K^{-1} mol^{-1}. Comment on the ease of formation of the transition state.

Answer: The plan is to compare the activation parameters to the values in Table 32.1.1, the "garden variety" activation energy of ~ 50 kJ mol^{-1} given in Sec. 3.5, and the typical bimolecular activation entropy of -80 J K^{-1} mol^{-1} given in Sec. 32.1.

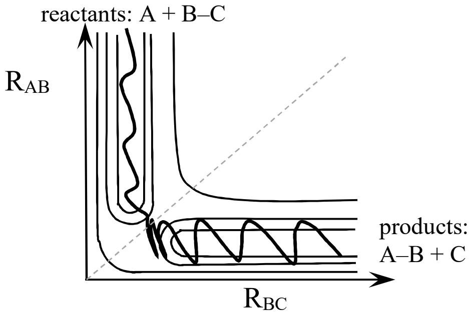
The reaction is diagrammed below:



The activation enthalpy is related to the activation energy through $\Delta_r H^{\circ\neq} = E_a - RT$. In other words, the activation energy and enthalpy differ by only 2.5 kJ mol^{-1} at 298.15 K. The large activation energy suggests the approach to the transition state is dominated by a bond cleavage. The activation entropy is intermediate between "loose and floppy" unimolecular transition states and typical bimolecular transition states. As a result we expect some considerable steric restraints in the formation of the transition state. These results seem reasonable because the process is more complicated than a simple ring closure. The relatively large activation entropy (for a unimolecular process) suggests that the formation of the transition state involves a concerted ring closure and hydride transfer.

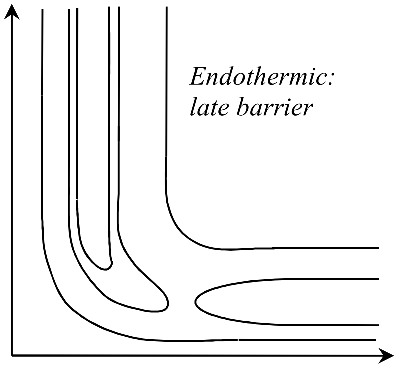
10. Draw the trajectory, on the potential energy surface below, of a reactive atom-diatom collision that experiences multiple crossings and produces a product in a highly excited vibrational state. Label the side of the graph that corresponds to the reactants and specify the corresponding reaction, choosing from either A + B–C → A–B + C or A–B + C → A + B–C.

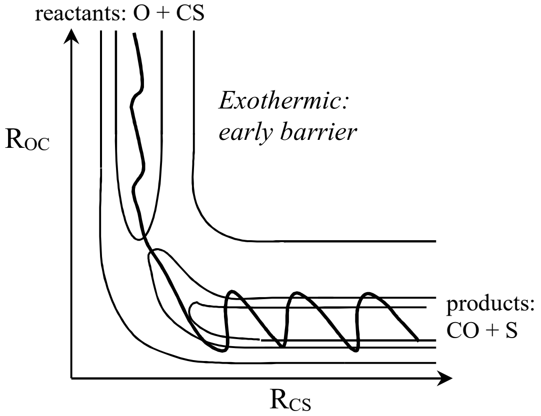
Answer: Choosing the reaction A + B–C → A–B + C and the given axis labels, the reactant well is at the top of the potential energy surface. The trajectory crosses the 45° line more than once and the amplitude of the product vibrations is large.



11. Consider the exothermic gas phase reaction: $O(^3P) + CS \rightarrow CO + S(^3P)$. Is the reaction likely to have an early or late barrier? Does translational or vibrational energy in the collision favor the formation of products? Choose the corresponding energy surface, below. Label the axes with either R_{OC} or R_{CS}. Label the reactant and product valleys. Draw an example of a trajectory that has the favorable combination of translational and vibrational energy for the collision. (You will use only one of the surfaces).

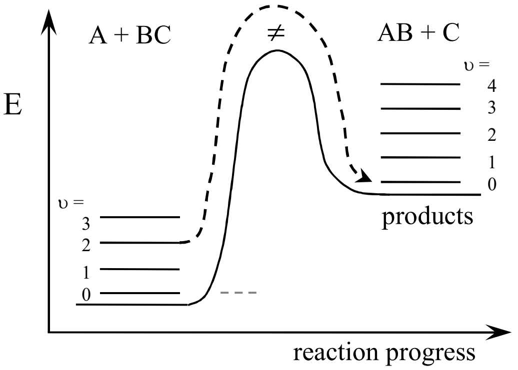
Answer: Exothermic reactions often have early barriers, as in the potential energy surface at right. Initial translational energy favors the formation of products. To explain why, consider standing in the reactant valley looking towards the transition state barrier. The barrier is straight ahead, instead of being a bit around the corner to the left. The best approach to the transition state is then to go straight ahead. Translational energy moves you straight ahead, but vibrational energy moves you to the left and right, perpendicular to the minimum energy path. The amplitude of the initial vibration is small, showing that the energy is primarily in translation. Exothermic reactions are more likely to give products in excited vibrational states than endothermic reactions. Consistent with this expectation, the trajectory in the product valley is shown with a large amplitude, but this choice is not necessary for this problem.

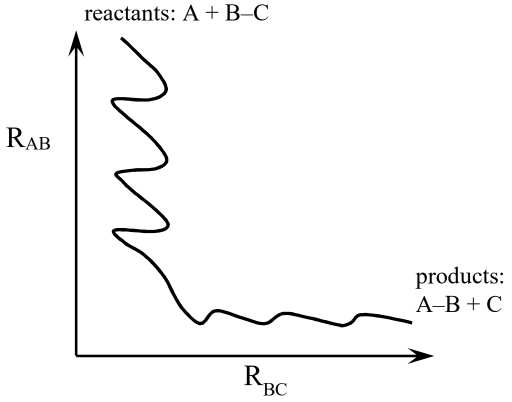




12. The reaction profile of an atom-diatom collision is shown below, including the vibrational levels. Draw a corresponding trajectory for the collision. Label the reactant and product sides.

Answer: Given the reaction A + B–C → A–B + C and the given axis labels, the reactant well is at the top of the potential energy surface. The reaction begins in an excited vibrational state and ends in the ground vibrational state. The amplitude of the vibrations in the reactant well is then large and in the product well is small (at the minimum amplitude given $\upsilon = 0$).





13. Use collision theory to calculate the theoretical value of the bimolecular rate constant of the reaction $H_2\ (g) + I_2\ (g) \rightarrow 2\ HI\ (g)$ at 650 K. The collision cross-section is 0.36 nm^2, the reduced mass is $3.32\text{x}10^{-27}$ kg, and the activation energy is 171. kJ mol^{-1}

Answer: The plan is to use Eq. 32.7.18 with the given cross-section: $\sigma = \pi b_{max}^2 = 0.36\ \text{nm}^2$.
The relative collision speed is, Eq. 31.3.14:

$$\bar{c}_{rel} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} = \left(\frac{8(1.38065\text{x}10^{-23}\ \text{J K}^{-1})(650\ \text{K})}{\pi\ 3.32\text{x}10^{-27}\ \text{kg}}\right)^{1/2} = 2624.\ \text{m s}^{-1}$$

The pre-exponential factor is using Eq. 32.7.18 and converting σ to m^2:

$$A = \pi b_{max}^2\ \bar{c}_{rel}\ (1000\ \text{L/m}^3)N_A$$
$$A = 0.36\ \text{nm}^2\ (1\text{x}10^{-9}\ \text{m/ 1nm})^2(2624.\ \text{m s}^{-1})\ (1000\ \text{L/m}^3)\ 6.022\text{x}10^{23}\ \text{mol}^{-1}$$
$$= 5.7\text{x}10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

14. The rate constant of an aqueous ionic reaction with $z_A = 2$ and $z_B = -1$ at zero ionic strength is $k_{(I=0)}$. Calculate the ratio of the rate constant of the reaction done in 0.1 M NaCl, k, to the rate constant at zero ionic strength: $k/k_{(I=0)}$ at 298 K.

Answer: The plan is to use Eq. 32.6.6 to estimate the kinetic salt effect.
The difference of the logs cancels the leading term in Eq. 32.6.6:

$$\log k_2 - \log k_{(I=0)} = \log\left(\frac{kT}{h} K_c^{\ddagger\prime}\ c^{o-1}\right) + 0.509\ (2z_Az_B)\ I^{1/2} - \log\left(\frac{kT}{h} K_c^{\ddagger\prime}\ c^{o-1}\right)$$
$$= 0.509\ (2z_Az_B)\ I^{1/2}$$

Solving for the ratio gives:

$$k/k_{(I=0)} = 10^{0.509\ (2z_Az_B)\ I^{1/2}}$$

The ionic strength is given by Eq. 19.4.22. Assume that the ionic strength is dominated by the NaCl. For 0.1 M NaCl, because NaCl is a 1:1 electrolyte, $I = m/m^o = 0.1$. Given $z_A = +2$ and $z_B = -1$ for the reacting ions gives:

$$k/k_{(I=0)} = 10^{0.509\ (2(+2)(-1))(0.1)^{1/2}} = 0.227$$

The reaction is slower at higher ionic strength because the ionic atmosphere decreases the attraction of the two reactant ions.

15. Use Eq. 32.7.13 to prove that the hard-core collision cross section is $\sigma_{HC} = \pi d_{HC}^2$, where d_{HC} is the hard-core collision diameter.

Answer: The plan is to assume the reaction probability is a function of the impact parameter only, $P(\varepsilon_{rel},b) = P(b)$, which in turn is defined as unity for an impact parameter less than the hard-core collision diameter in Eq. 32.7.13.

The probability that a collision with relative kinetic energy ε_{rel} and impact parameter b gives products is $P(\varepsilon_{rel},b)$. The reaction cross-section is then the integral of the reaction probability over the impact parameter, Eq. 32.7.13:

$$\sigma(\varepsilon_{rel}) = 2\pi \int_o^\infty P(\varepsilon_{rel},b)\, b\, db \qquad (32.7.13)$$

Assuming that the reaction probability is unity for every collision with impact parameter $b \le d_{HC}$, $P(\varepsilon_{rel},b) = 1$, and zero for any greater impact parameter gives the cross-section as:

$$\sigma(\varepsilon_{rel}) = 2\pi \int_o^{d_{HC}} b\, db = \pi b^2\Big|_o^{d_{HC}} = \pi d_{HC}^2$$

This result shows that the more general definition in Eq. 32.7.13 is consistent with the KMT model.

16. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). In atom-diatom collisions, $A + BC \rightarrow AB + C$, the reaction coordinate is an unstable asymmetric stretch.

(b). Once the transition state surface is crossed, the activated complex does not return to reactants.

(c). Activated Complex Theory assumes a Boltzmann distribution among vibrations and rotations in the reactants and the activated complex.

(d). Excluding the reactive asymmetric stretch, the vibrations and rotations of the activated complex do not have an effect on the reaction rate.

(e). Reactions are more likely with excess energy in translation rather than vibration.

(f). Exothermic reactions are more likely to give products in excited vibrational states than endothermic reactions.

(g). The common existence of chemical reactions that are much slower than the corresponding kinetic molecular theory hard-core collision rate is evidence of long-lived transition states.

(h). In the RRKM theory of unimolecular processes, the vibrational and rotational states of the reactants are treated as a continuum while the vibrational and rotational states of the critical configuration are treated as discrete and countable.

(i). In the RRKM theory of unimolecular processes, the critical configuration never returns to the activated reactant.

(j). Non-adiabatic transitions occur by avoided curve crossing.

(k). The Born-Oppenheimer approximation is valid for the progression of the transition state to give products.

(l). Experimental reaction cross-sections are never larger than the hard-core collision cross-sections, although the experimental reaction cross-sections is often smaller than the hard-core collision cross-section.

(m). In collision theory, the line of centers velocity and kinetic energy increase with decreasing impact parameter.

(n). In collision theory, the reaction cross section is independent of the collision relative kinetic energy.

(o). In solution, equilibrium constants are functions of the activities of the reactants and products, rather than the concentrations. Reaction rates are functions of the solution concentrations, and not the activities.

Answers: (a). *True*.

(b). *False*, multiple crossings can occur, which increase the probability of the return to reactants.

(c). *True, but too restrictive*. Activated Complex Theory also assumes a Boltzmann distribution of the available energy into the reactive asymmetric stretch, which is represented by the kT/h factor. We also must consider the electronic degrees of freedom in the reactants and the activated complex. For many reactions the electronic partition functions are equal to the ground state degeneracies, and the ground state degeneracies are often singlets. However, this simplification is not always true, especially if a reactant is atomic, Table 30.2.2.

(d). *False*. The bimolecular rate constant is the number of accessible states in the activated complex divided by the product of the number of accessible states in the reactants. The vibrations and rotations of the activated complex increase the number of accessible states of the activated complex.

(e). *Sometimes true and sometimes false*. Endothermic reactions with late barriers are more likely with excess energy in vibration rather than translation. Exothermic reactions with early barriers are more likely with excess energy in translation rather than vibration.

(f). *True*. Exothermic reactions are more likely to give products in excited vibrational states than endothermic reactions.

(g). *False*: The traversal of the transition state region is typically very fast – tens of femtoseconds. The sluggishness of many reactions is a reflection of the improbability of collisions with sufficient relative kinetic energy, proper orientation, and timing with respect to the progress of the vibrations of the reactants.

(h). *True*.

(i). *False*: The critical configuration is considered to be in equilibrium with the reactants, Eq. 32.5.3, which can only occur if the formation of the critical configuration is reversible from the perspective of the reactants.

(j). *True*.

(k). *False*: Classical trajectory calculations do calculate the potential energy surface of a collision within the Born-Oppenheimer approximation. Never-the-less, the Born-Oppenheimer approximation is violated from the perspective of the bound-vibrational potential energy wells of the reactants and products. The unstable transition state maximum in energy cannot be represented in the bound-state product potential energy functions. The Born-Oppenheimer approximation is violated for the progression of the transition state to give products.

(l). *False*: Attractive intermolecular potentials can result in reaction cross-sections that are larger than the hard-core collision cross-sections. Reactions that have little or no activation energy are commonly in this category. However, it is *true* that the experimental reaction cross-section is often smaller than the hard-core collision cross-section.

(m). *True*, see Eq. 32.7.11.

(n). *False*: In collision theory, the reaction cross section can be strongly dependent on the collision relative kinetic energy, Figure 32.7.4.

(o). *False*: Reaction rates in real gases and in solution are functions of the gas phase fugacities or solution activities and not the concentrations. The thermodynamic activity of a solute differs from the concentration because of intermolecular forces. Intermolecular forces play an important role in molecular dynamics.