

Topic 7D - Models of Reactions

Theories of Chemical Reactions

Effect of Temperature on Reaction Rates

Arrhenius Equation (exponential dependence of rates on temperature):

$$k = A e^{-E_a/RT}$$

or

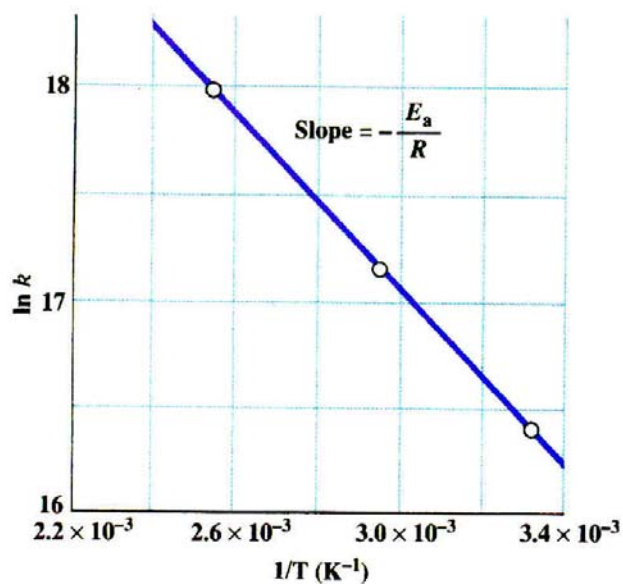
$$\ln k = \ln A - \frac{E_a}{RT}$$

where **k** is the rate constant, **A** is the pre-exponential factor, and **E_a** is the activation energy.

Thus, a plot of **ln k vs. 1/T** should yield a straight line, with **Slope = -E_a/R** and **Intercept = ln A**, enabling both **E_a** and **A** to be separately determined.

If **E_a** and **A** are known, it is possible to compare rates at two different temperatures (where **T₂ > T₁**):

$$\frac{k_2}{k_1} = e^{-\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$
$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

**Figure 11-9**

An Arrhenius plot of $\ln k$ against $1/T$ for the reaction of benzene vapor with oxygen atoms. An extrapolation to $1/T = 0$ gives the constant $\ln A$ from the intercept of this line.

$$k = Ae^{-E_a/RT}$$

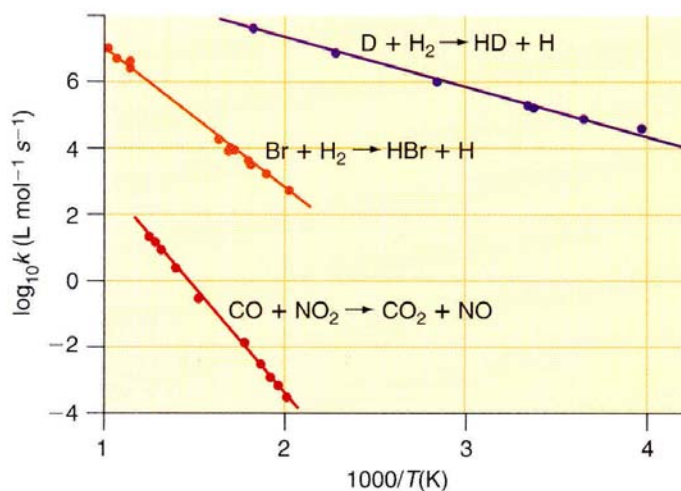
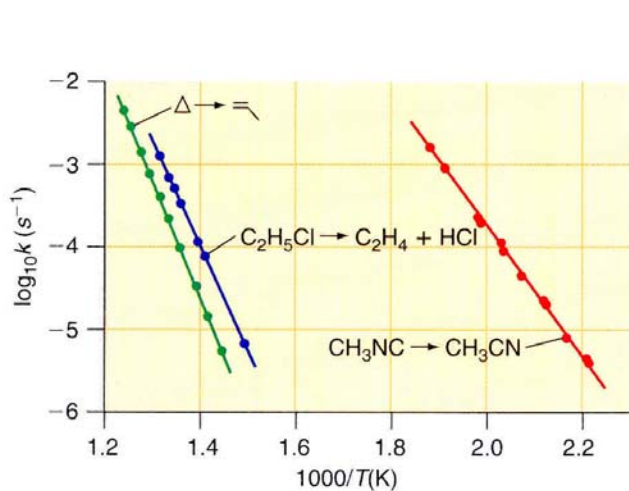
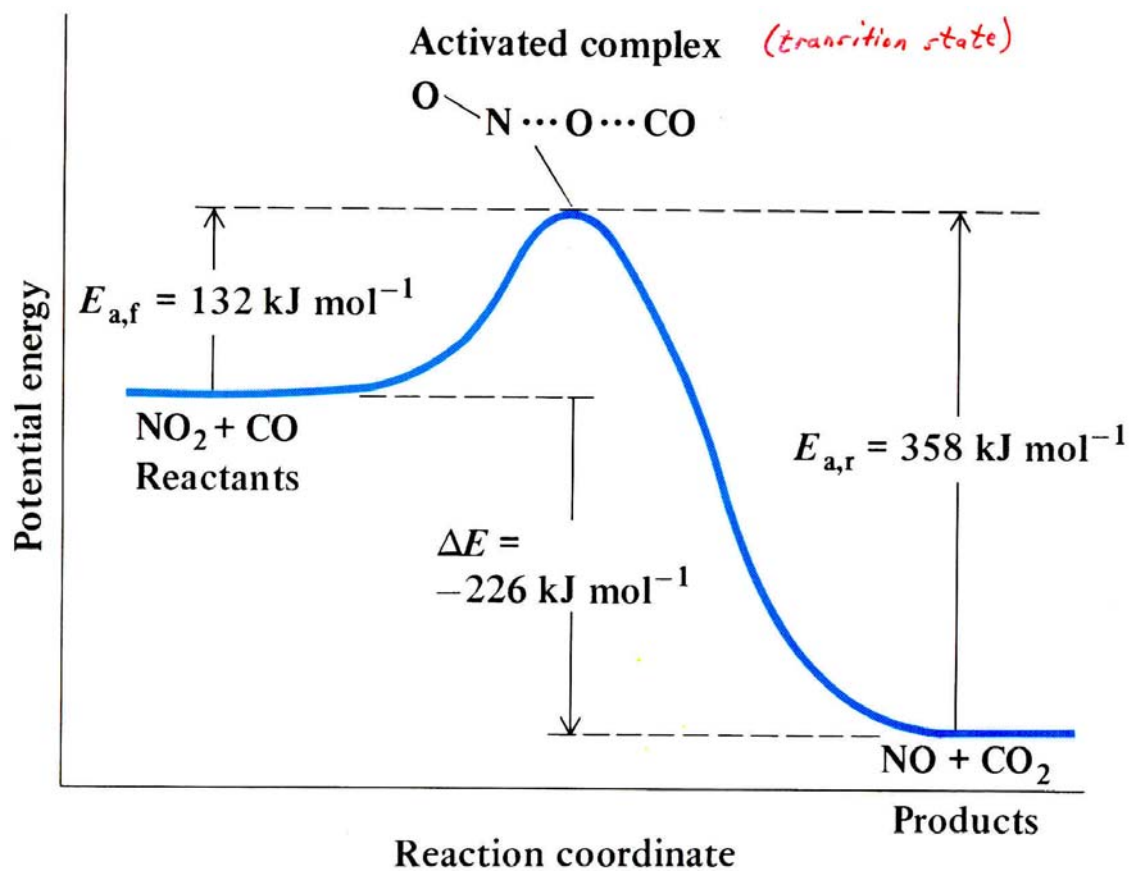
Figure 15.8: Arrhenius Plots

Table 15.4: Arrhenius Parameters for Selected Reactions**TABLE 15.4****Arrhenius parameters for selected bimolecular gas-phase reactions^a**

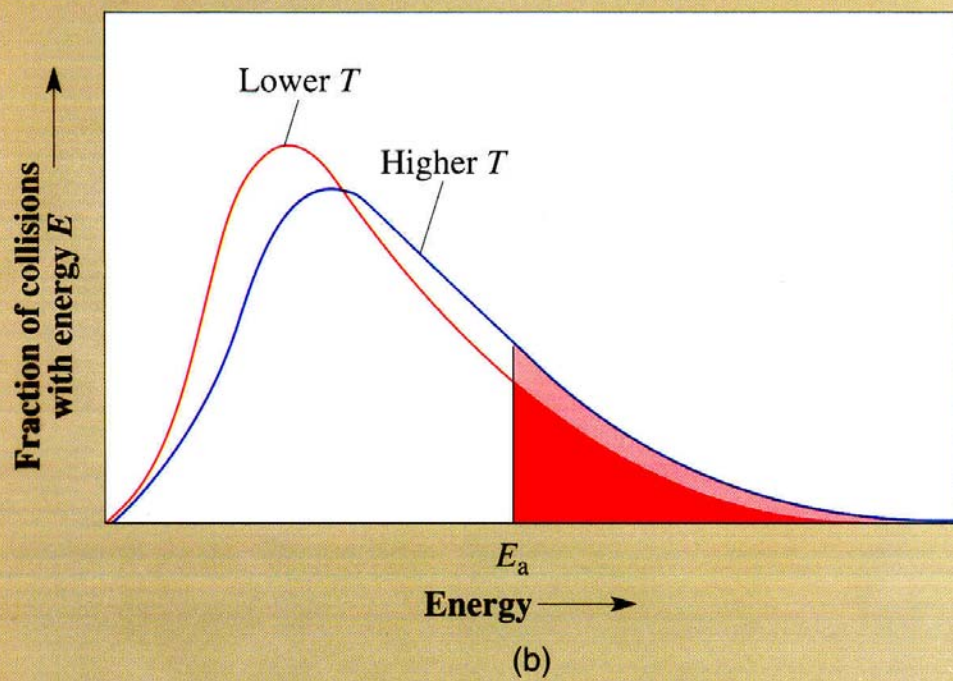
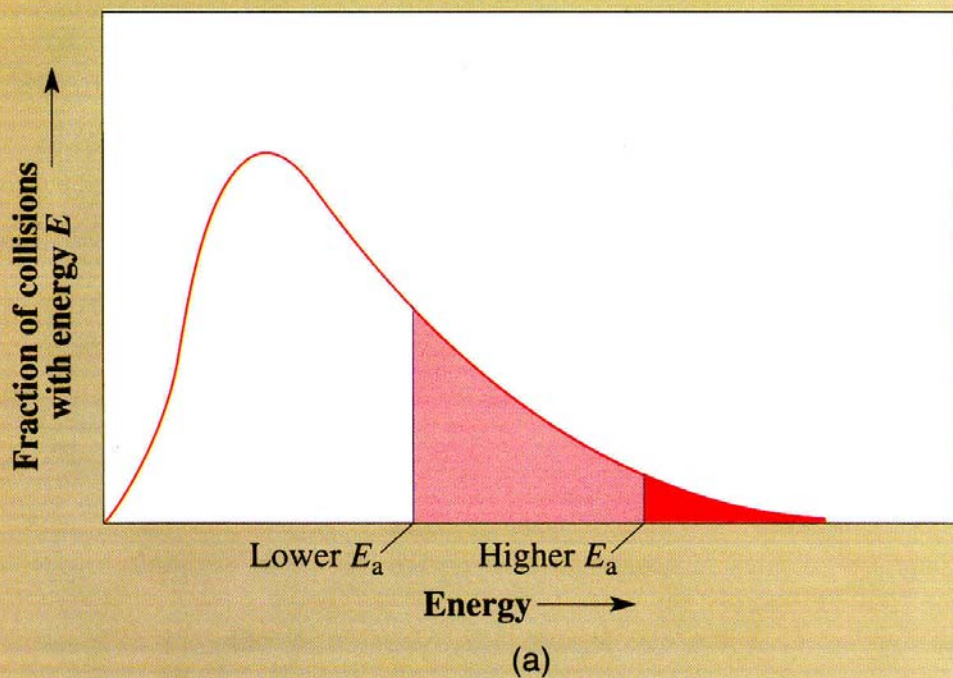
Reaction	E_a	$\log_{10}A$	$\log_{10}A_{\text{ct}}$	Steric factor p
$\text{Na} + \text{Cl}_2 \longrightarrow \text{NaCl} + \text{Cl}$	0	11.6	11.58	1.0
$\text{K} + \text{Br}_2 \longrightarrow \text{KBr} + \text{Br}$	0	12.0	11.47	3.4
$\text{K} + \text{HBr} \longrightarrow \text{KBr} + \text{H}$	0.2	11.6	11.46	1.3
$\text{Br} + \text{H}_2 \longrightarrow \text{HBr} + \text{H}$	19.7	11.43	11.60	0.7
$\text{Cl} + \text{H}_2 \longrightarrow \text{HCl} + \text{H}$	4.3	10.92	11.59	0.22
$\text{F} + \text{H}_2 \longrightarrow \text{HF} + \text{H}$	1.13	11.06	11.55	0.32
$\text{O} + \text{H}_2 \longrightarrow \text{OH} + \text{H}$	11.3	10.4	11.53	0.07
$\text{D} + \text{H}_2 \longrightarrow \text{HD} + \text{H}$	7.61	10.64	11.60	0.11
$\text{O} + \text{ClO} \longrightarrow \text{O}_2 + \text{Cl}$	0.1	10.35	11.06	0.19
$\text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2$	0.5	10.21	11.22	0.10
$\text{O} + \text{O}_3 \longrightarrow \text{O}_2 + \text{O}_2$	4.09	9.68	11.27	0.026
$\text{O} + \text{NO}_2 \longrightarrow \text{O}_2 + \text{NO}$	0.24	9.59	11.24	0.022
$\text{O} + \text{CO}_2 \longrightarrow \text{O}_2 + \text{CO}$	54.2	10.28	11.28	0.10
$\text{OH} + \text{H}_2 \longrightarrow \text{H}_2\text{O} + \text{H}$	4.17	9.67	11.63	0.011
$\text{OH} + \text{CO} \longrightarrow \text{CO}_2 + \text{H}$	1.08	8.62	11.33	0.0019
$\text{CO} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{O}$	51.0	9.54	11.34	0.004
$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$	2.72	9.04	11.35	0.005
$\text{CO} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$	27.8	8.75	11.35	0.0025
$\text{C}_2\text{H}_4 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_6$	43.0	6.09	11.81	0.0000019

^a Activation energy E_a in kcal/mol and A in $\text{L mol}^{-1} \text{s}^{-1}$. A_{ct} prediction of collision theory (Equation 15.42 at $T = 298 \text{ K}$) using molecular diameters d derived from viscosity measurements. Rate constants at a given T may be generated from $\log_{10}k = 1000E_a/(2.303RT) + \log_{10}A$, generally reproducing actual experimental values within 20%.

Collision Theory**Boltzmann Distribution****Activation Energy****Activated Complex (transition state)****Steric Effect****Potential Energy Surfaces**



Energy Distribution Curves for Colliding Molecules



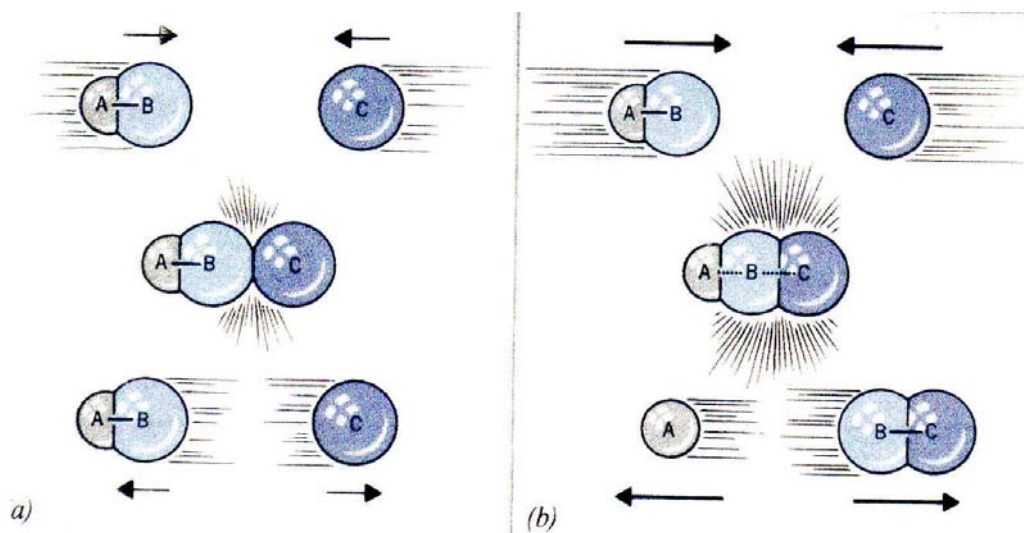
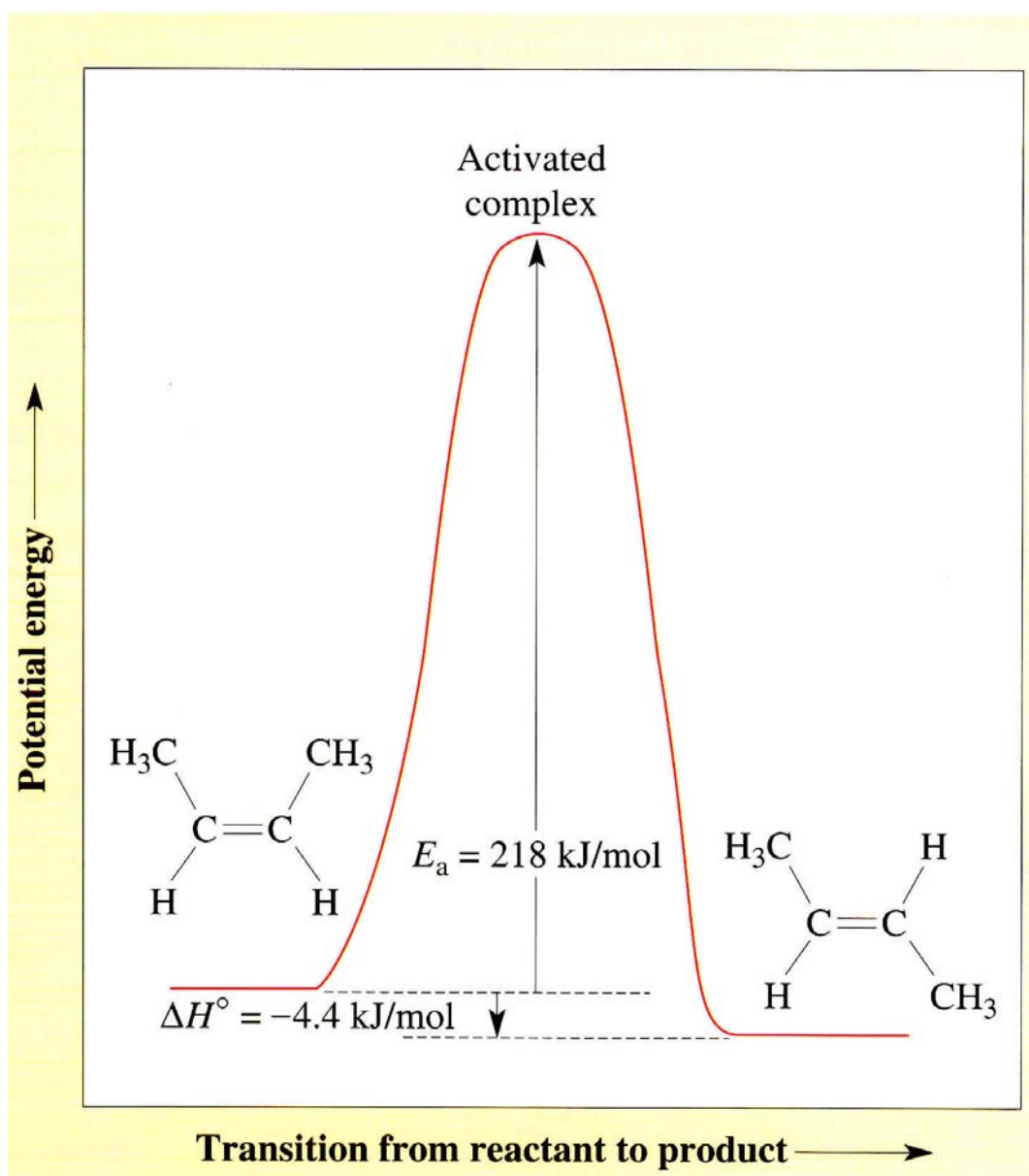
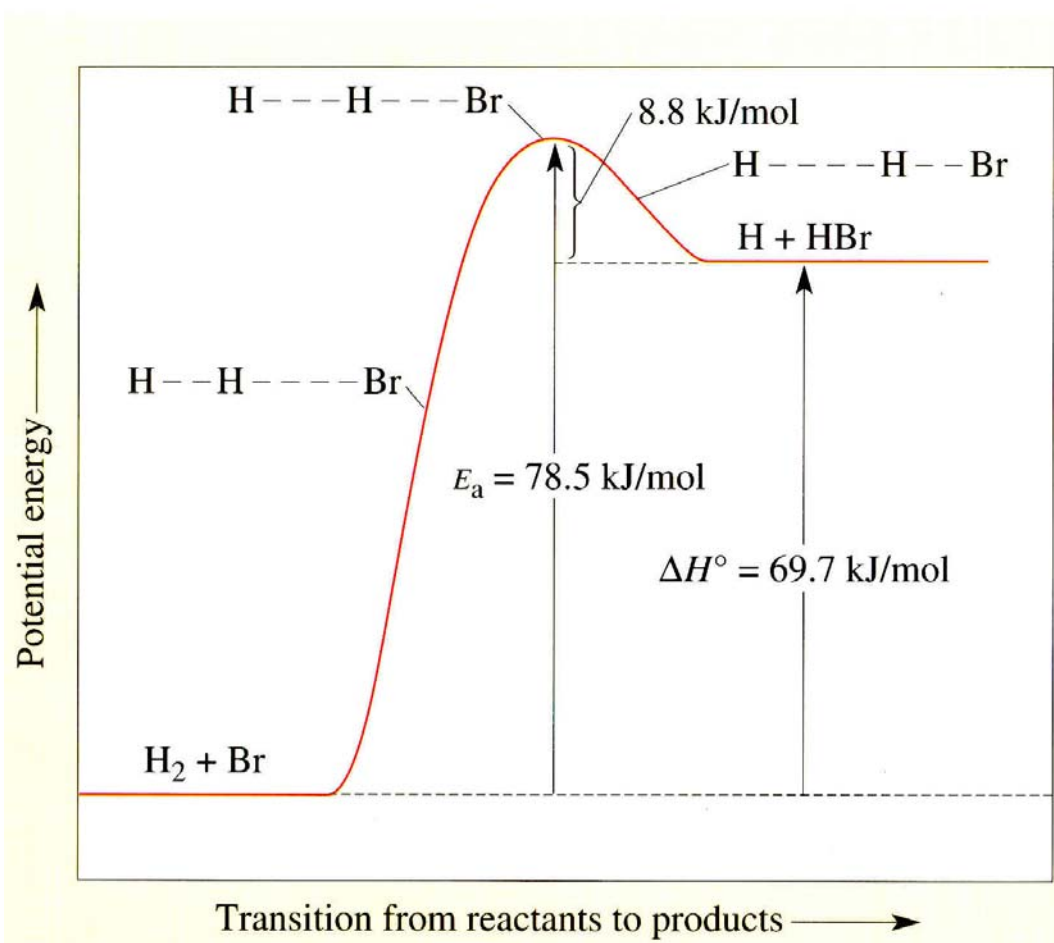
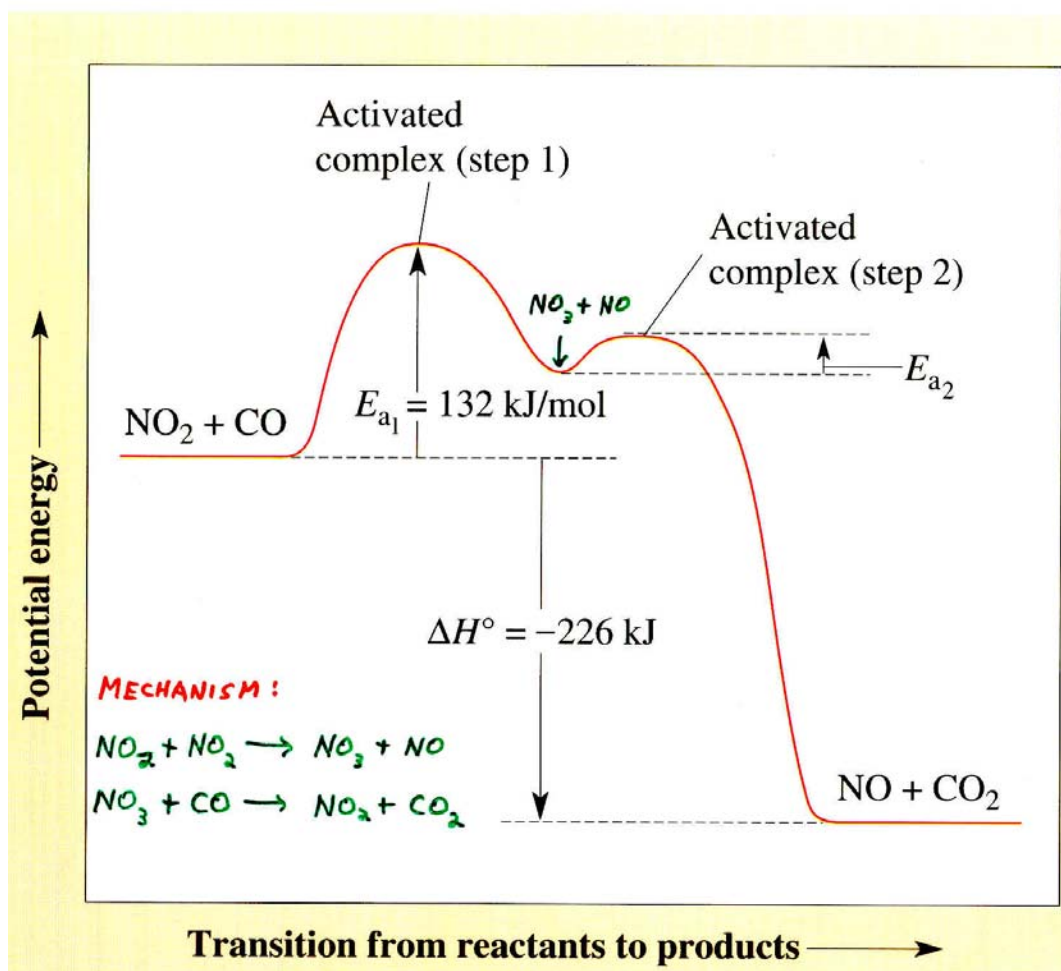


Fig. 19.10. (a) When two slow-moving molecules collide, their electron clouds cannot interpenetrate much and they just bounce off each other, chemically unchanged. (b) When fast-moving molecules collide, atoms approach each other much more closely as their electron clouds interpenetrate. This can lead to bond making and bond breaking. The net change here is $AB + C \rightarrow A + BC$.

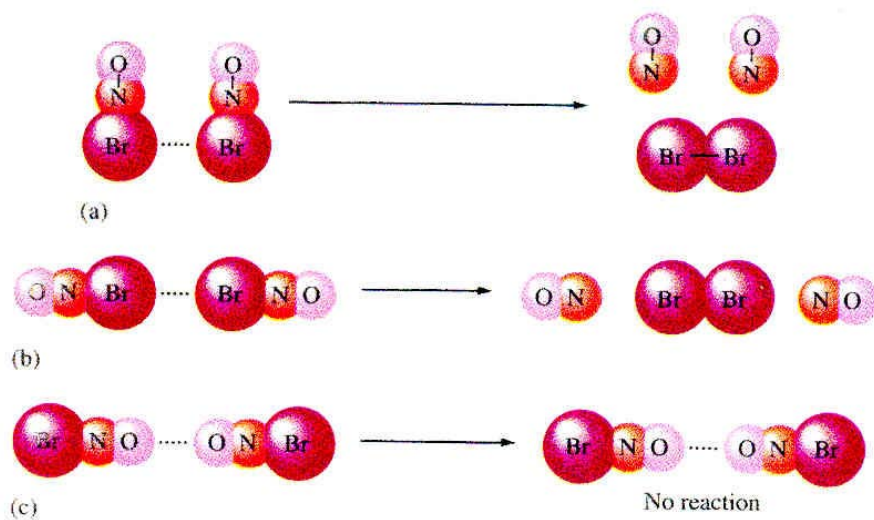
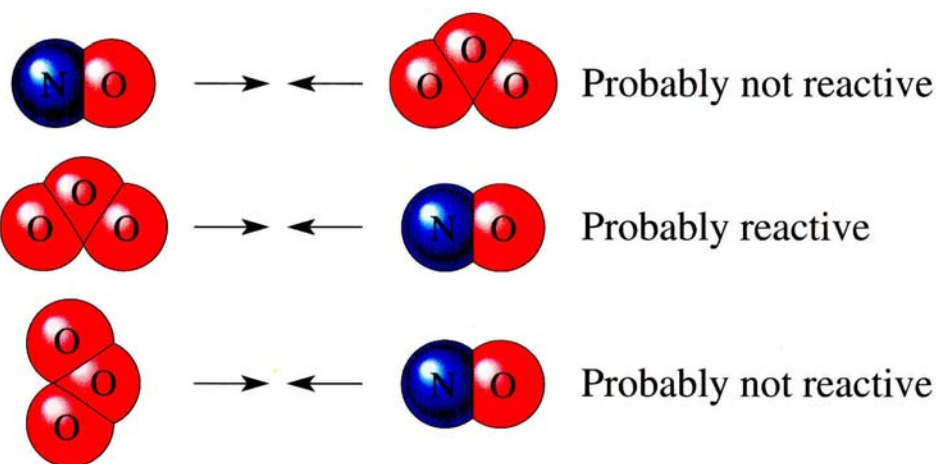
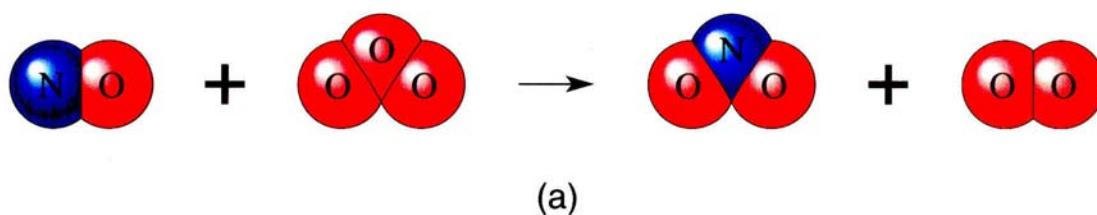
Potential energy Profile for an Exothermic Reaction

Potential Energy Profile for an Endothermic Reaction

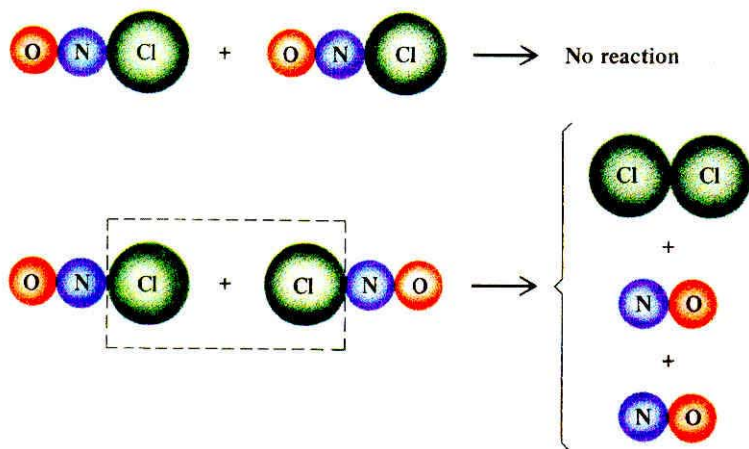
Potential Energy Profile for a Two-Step Reaction



Reactive and Non-reactive Collisions

**Figure 15.11**

Several possible orientations for a collision between two BrNO molecules. Orientations (a) and (b) can lead to a reaction, but orientation (c) cannot.

**Figure 11-12**

The steric effect on the probability of a reaction. The two NOCl molecules must approach each other in such a way that the two chlorine atoms are close together, if the encounter is to produce Cl₂(g) and NO(g).

Table 11-1 Steric Factors for Gas-Phase Reactions

Reaction	Steric Factor P
$2 \text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2$	0.16
$2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$	5.0×10^{-2}
$2 \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	2.5×10^{-3}
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	1.7×10^{-6}
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	4.0

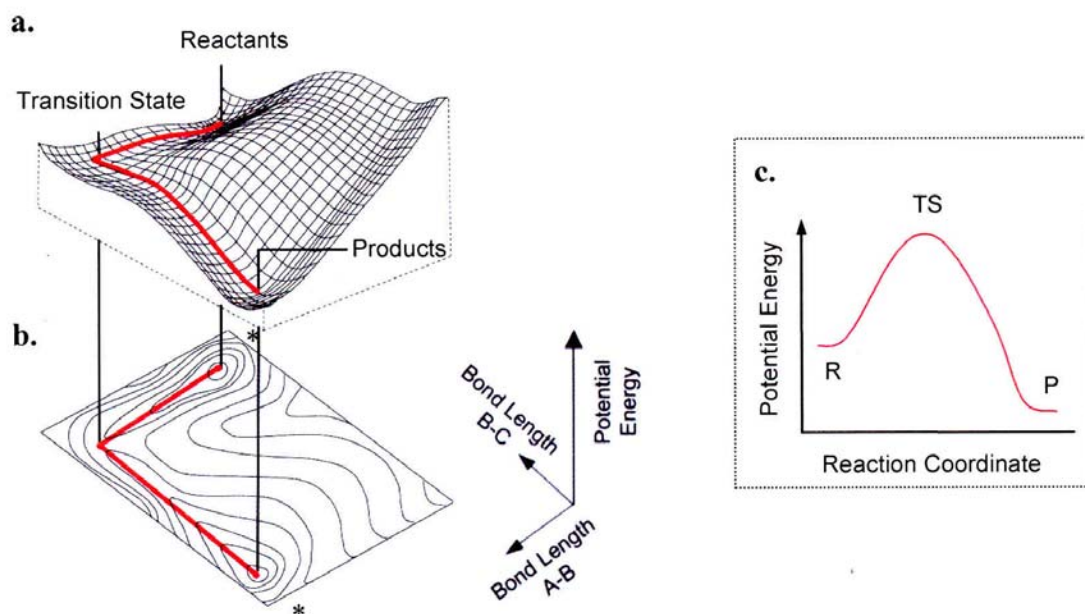


Figure 1.3. (a.) Cartoon of the three-dimensional potential energy surface for the reaction $A-B + C \rightarrow A + B-C$. The reactants and products are found in potential energy wells and the reaction pathway (red line) follows a minimum energy route. The transition state occupies a saddle point on the reaction pathway which means that the activated complex has only two paths in which it can obtain lower potential energy, by returning to the reactant formation or continuing on to form products. (b.) The same potential energy surface projected into two dimensions for easier interpretation. The topographical lines represent regions of degenerate energy and the asterisks (*) mark the equilibrium bond length for A-B and B-C. (c.) The reaction coordinate diagram distills the reaction information from figures like A and B, which contain unique variables for characterizing a particular reaction, to a set of uniform variables, potential energy and reaction coordinate. The diagram comes from the cross section of (a.) and (b.) through the red line and reflects potential energy changes as the reaction progresses. (R = reactants, TS = transition state, P = products)

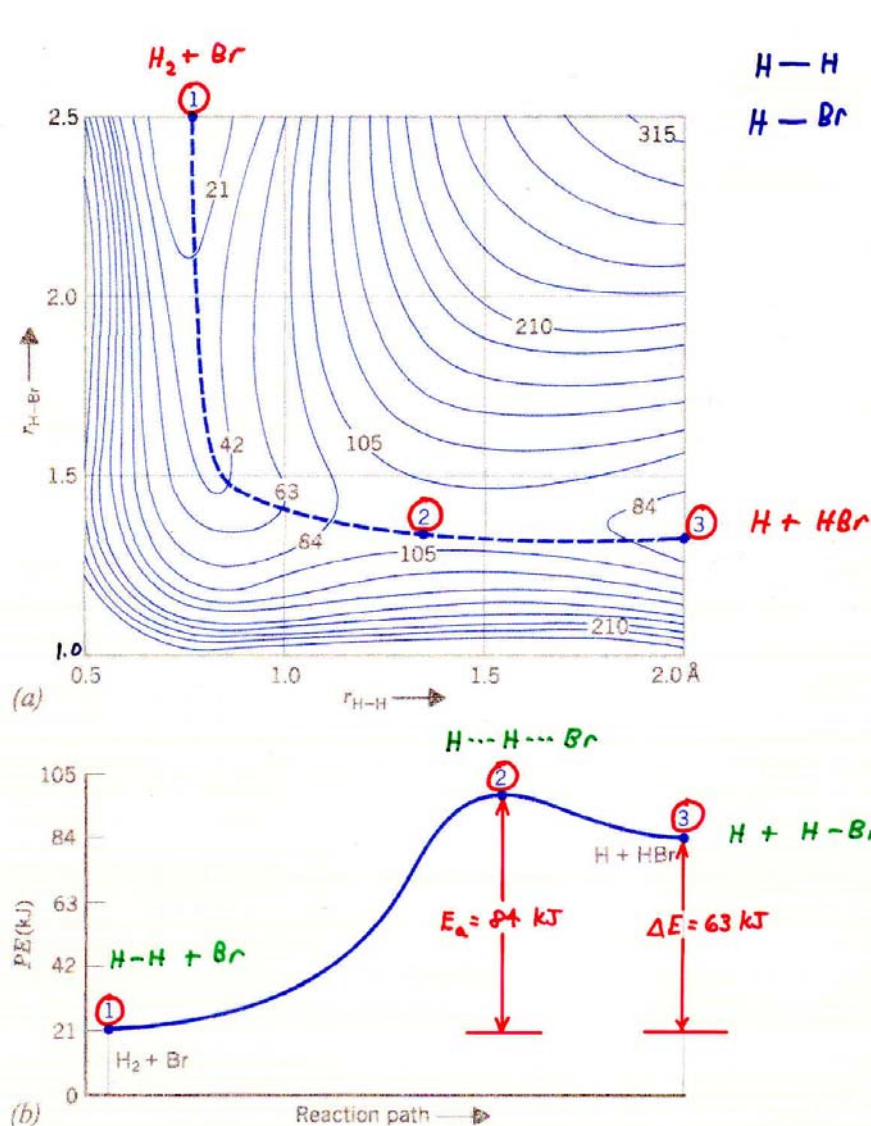
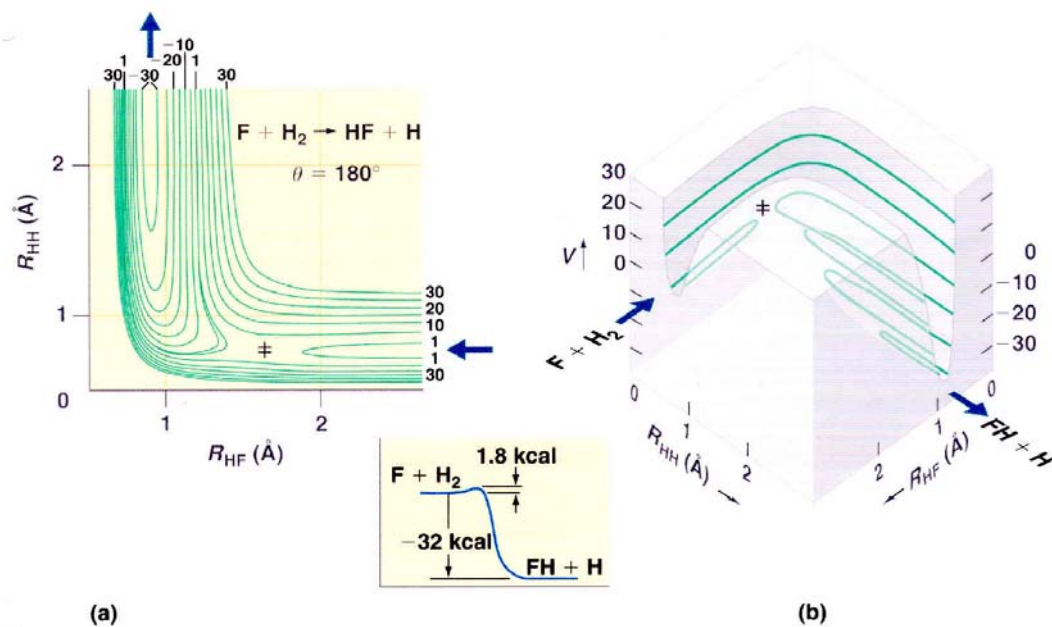


Fig. 19.14. (a) Contour diagram of the potential energy surface for the reaction $H_2 + Br \rightarrow H + HBr$ as a function of the internuclear distances r_{H-Br} and r_{H-H} in angstroms. All three atoms are assumed to be collinear throughout the reaction. Contours of equal potential energy are marked in kilojoules per mole. Point 1 is the initial state, with a Br atom far from an H_2 molecule. Point 3 is the final state, with an H atom far from an HBr molecule. The reaction pathway is indicated by the dashed colored line, which is the path that requires crossing the lowest possible potential energy contours between points 1 and 3. Point 2 is the activated complex, the state of highest potential energy along the reaction pathway. (b) A potential energy profile of the reaction pathway. Points 1–3 represent the same states as points 1–3 on the contour diagram. Note that this is an endothermic reaction, as the products are at a higher energy than the reactants.

**Figure 15.12**

Depictions of the potential energy surface for the reaction $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ based on a recent highly accurate molecular orbital calculation (Stark & Werner, *J. Chem. Phys.*, 1996). **(a)** Potential energy contour map for collinear $\text{F} \cdots \text{H} \cdots \text{H}$ geometry ($\theta = 180^\circ$ is the bond angle). Contours are drawn every 5 kcal/mol for +30 to -30 kcal, with one extra contour added for $V = 1$ kcal in order to delineate the activation barrier, whose location is indicated by ‡. Reagents enter from the lower right, where R_{HF} is large and R_{HH} is at equilibrium for H_2 at the lowest point, and products emerge at

the upper left, where R_{HH} is large and R_{HF} is now at equilibrium. The difference in energy between these extremes is 31.8 kcal/mol, which is the exothermicity of the reaction; the barrier height is 1.8 kcal, in good agreement with E_a from Table 15.4. **(b)** This surface is shown as a groove cut into a transparent block; for clarity, only half of the contours are drawn, with the positive-energy ones on the large- R edge of the groove omitted. It is more easily seen here than in (a) that the extremes represent bond potential energy curves for the two diatomics. The inset shows the corresponding energy profile.