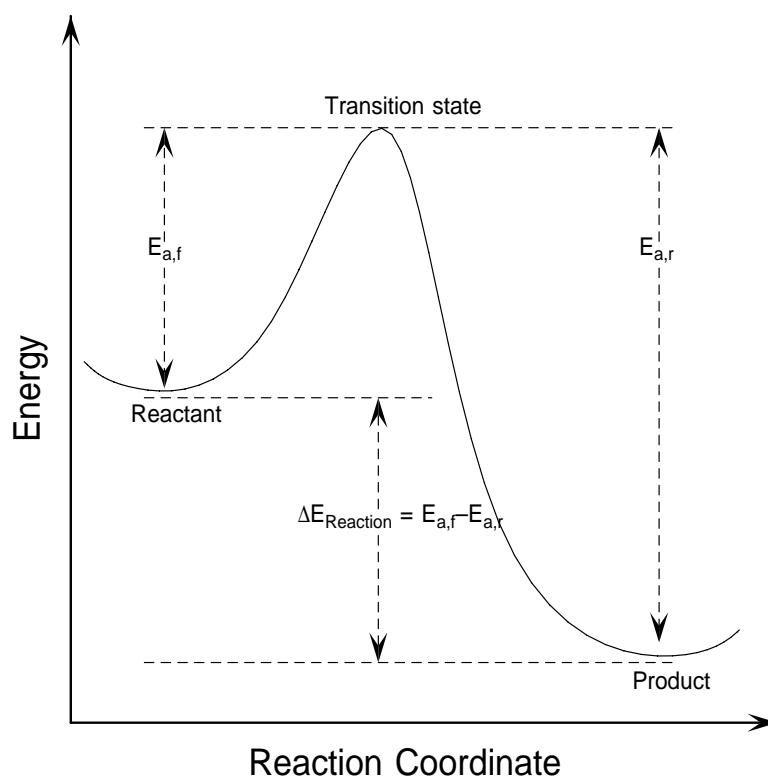


# Thermodynamics vs Kinetics

## Overview

A general **Reaction Coordinate Diagram** relating the energy of a system to its geometry along one possible reaction pathway is given in the figure below. In the figure below, the **Activation Energy,  $E_a$**  is that critical minimum energy in a chemical reaction required by reactants to be converted into products. the quantities,  $E_{a,f}$  and  $E_{a,r}$  are the activation energies for the forward and reverse reactions respectively. The **Transition State** is that point on the energy surface where the **Activated Complex**, an unstable species having the highest energy, crosses over from reactants to products.



The rate constant  $k$  in a chemical reaction is a kinetic quantity related to the activation energy through the **Arrhenius Equation**,  $k = Ae^{-E_a/RT}$ .

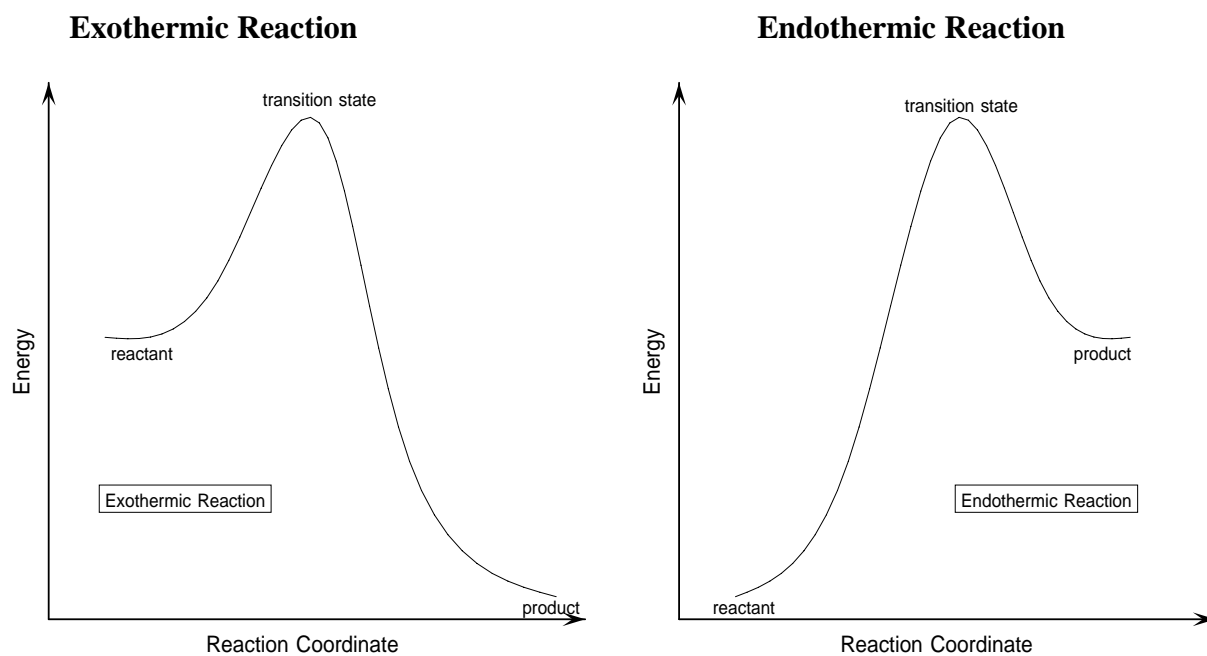
The energy difference,  $\Delta E_{\text{Reaction}} = E_{a,f} - E_{a,r}$ , is a thermodynamic quantity related to the **Free Energy ( $\Delta G$ )**, for a chemical reaction:

$$\Delta G = \Delta E_{\text{Reaction}} = E_{a,f} - E_{a,r}$$

# Interpretation of Reaction Coordinate Diagram

The simple reaction coordinate diagram given on the previous page contains a great deal of useful information:

- It defines the geometries of reactants, transition state, and products along the reaction coordinate.
- It provides insight regarding the thermochemistry of the overall chemical reactions. For example, in the figure below on the left, the products are *lower* in energy than the reactants leading to an **exothermic** reaction ( $\Delta H < 0$ ). On the other hand, if the reaction were **endothermic** ( $\Delta H > 0$ ) as in the figure below on the right, the products would be *higher* in energy than the reactants.



- Finally, the diagram gives information about the rate of a reaction. The higher the energy of the transition state (corresponding to an increase in activation energy  $E_a$ ) the slower the reaction is likely to proceed.

## **The Importance of Computational Chemistry**

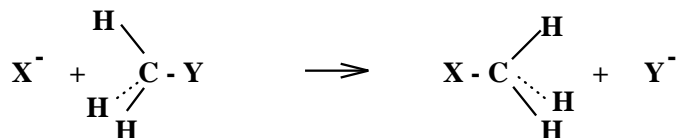
Calculation can provide a direct handle on all the important components of reaction surfaces including the geometries and energies of reactants and products as well as reactive intermediates and transition states which are difficult and even impossible to determine experimentally.

The idea in the following exercises is to compute a reaction coordinate for chemical reactions not only by determining the structures and energies of both reactants and products but also in obtaining information about the elusive transition state structures along the reaction pathway. This is one example of the power and usefulness of Computational Chemistry.

## S<sub>N</sub>2 Reactions

An S<sub>N</sub>2 reaction involves the attack of a nucleophile X<sup>-</sup> (e.g. F<sup>-</sup>, Cl<sup>-</sup>, OH<sup>-</sup>) at a tetrahedral carbon site opposite a leaving group Y<sup>-</sup> which leads to *inversion* at the carbon center, similar to an umbrella that flips inside out as a result of a strong wind. A nucleophile is any species with a large concentration of electron density (e.g. a negatively charged ion) which has a strong affinity for a positively charged center.

For example, the **carbon-chlorine** bond in H<sub>3</sub>C – Cl is polarized (C<sup>δ+</sup> – Cl<sup>δ-</sup>) which leads the nucleophile X<sup>-</sup> to attack at the positively charged carbon atom: X<sup>-</sup> ∼ C<sup>δ+</sup> – Cl<sup>δ-</sup>.



The S<sub>N</sub>2 reaction in which the attacking nucleophile and leaving group are both Cl<sup>-</sup> can be written as:



This is known as a **symmetrical** or **identity** reaction since both the reactants (Cl<sup>-</sup> + CH<sub>3</sub>Cl) and products (CH<sub>3</sub>Cl + Cl<sup>-</sup>) are identical. However, more general reactions involving different attacking and leaving groups form the basis of this reaction.

The restriction of having identical attacking and leaving groups was purposefully chosen for one component of the present exercise in order to allow an easier analysis without any loss of the concepts inherent in more general S<sub>N</sub>2 reactions.

In this exercise we will examine both an **identity** S<sub>N</sub>2 reaction as well as a more general S<sub>N</sub>2 reaction.

In the reaction above the two species: Cl<sup>-</sup> ⋯ CH<sub>3</sub>Cl, ClCH<sub>3</sub> ⋯ Cl<sup>-</sup> are called **ion-molecule complexes**. They are formed when the anion and the molecule approach each other at distances (≈ 2.5 – 3.5 Å) where they can interact to produce a stable, weakly-bound aggregate, **ion-molecule** complex. The forces holding this complex together are mostly coulombic and are very similar to the **ionic** forces you have discussed in lecture. The geometry of the methyl chloride group in these complexes is similar to that of isolated methyl chloride, and though too weakly interacting to persist in solution, they do exist in the gas phase.

The complex [Cl – ⋯ – CH<sub>3</sub> – ⋯ – Cl]<sup>-‡</sup> is defined as the **transition state structure**, the highest energy structure on the reaction energy surface, and has a trigonal-bipyramidal geometry similar to Cl – PH<sub>3</sub> – Cl. Of course, the transition state structure,

[Cl – ⋯ – CH<sub>3</sub> – ⋯ – Cl]<sup>-‡</sup>, is much more unstable than Cl – PH<sub>3</sub> – Cl because the carbon atom has **five bonds** (two weak C-Cl bonds and three C-H bonds), but carbon likes to form **four bonds**. On the other hand, the phosphorus atom is capable of forming stable structures containing **five bonds**.

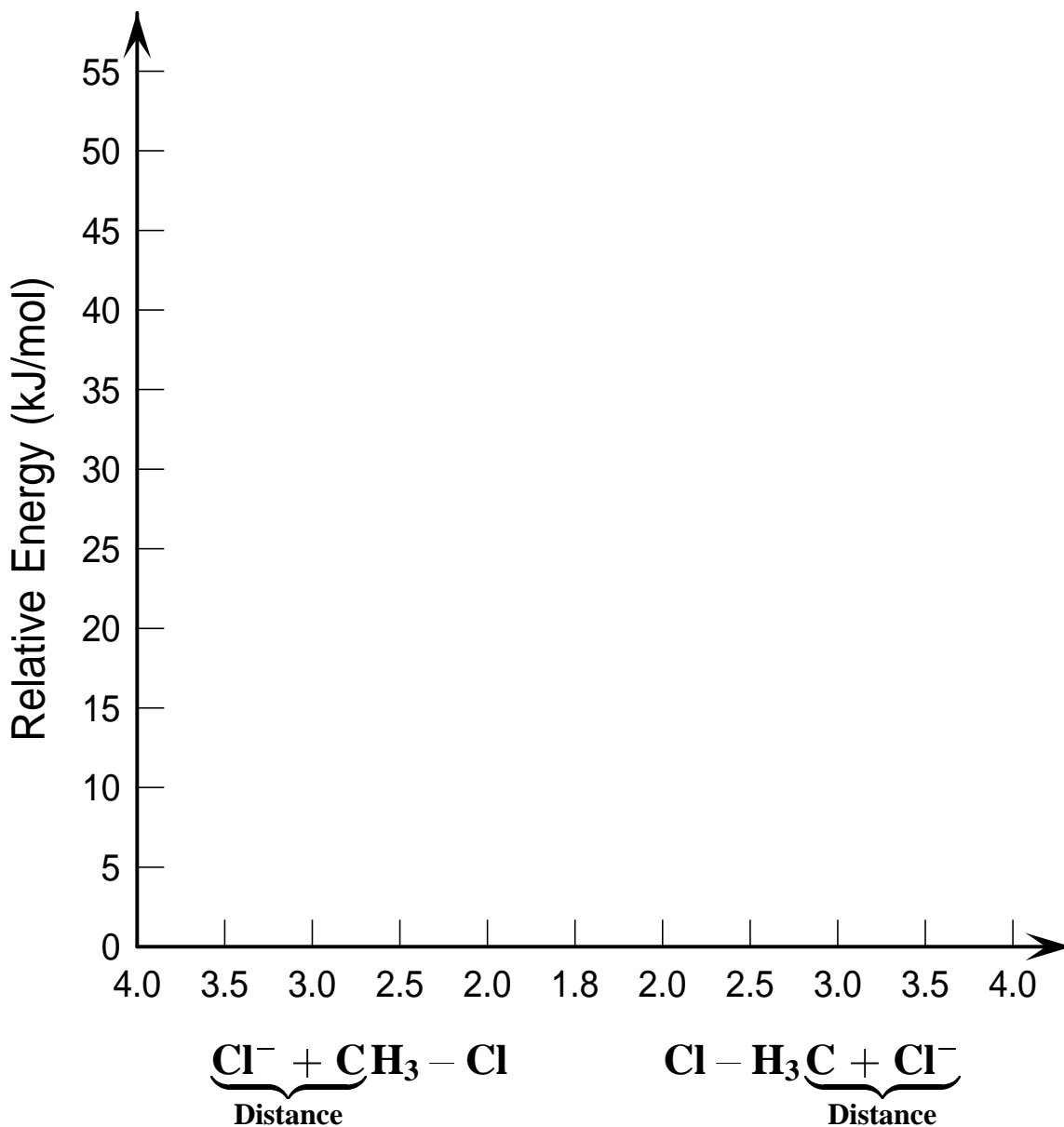
## Reaction Profile for the $\text{Cl}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

Initially, we will focus our attention on the **symmetric** or **identity** reaction discussed previously:



Construct the gas phase **Reaction Coordinate Diagram** for the  $\text{Cl}^- + \text{CH}_3\text{Cl}$   $\text{S}_{\text{N}}2$  reaction by plotting the relative energy in  $\text{kJ mol}^{-1}$  versus  $\underbrace{\text{Cl}^- + \text{CH}_3 - \text{Cl}}_{\text{Distance}}$ . Place the **Reaction Coordinate**

**Diagram** on the graph provided below and plot the energies on a relative energy scale. Label the various species along the reaction pathway.



## Structure and Bonding in the $\text{Cl}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

Examine the geometries of the reacting species for the symmetric  $\text{Cl}^- + \text{CH}_3\text{Cl}$   $\text{S}_{\text{N}}2$  reaction, and enter the observed geometries in the table below.

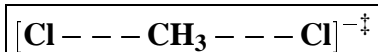
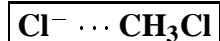
**Geometries of Reacting Species**

Species	Distances			Angles	
	$r_{\text{C-H}}$	$r_{\text{C-Cl}}$	$r_{\text{Cl}\cdots\text{C}}$	$\angle \text{H-C-Cl}$	$\angle \text{H-C-H}$
$\text{Cl}^- + \text{CH}_3 - \text{Cl}^a)$					
$\text{Cl}^- \cdots \text{CH}_3 - \text{Cl}^b)$					
$[\text{Cl} \cdots \text{CH}_3 \cdots \text{Cl}]^{-\ddagger}$					

- a) The entry  $\{\text{Cl}^- + \text{CH}_3 - \text{Cl}\}$  is taken to mean an isolated  $\text{Cl}^-$  ion “plus” an isolated  $\text{CH}_3\text{Cl}$  molecule. Consequently, choose a point on the graph where the distance between the  $\text{Cl}^-$  ion and  $\text{C}$  atom is largest. The  $\text{Cl} \cdots \text{C}$  distance is not significant.
- b) The entry  $\{\text{Cl}^- \cdots \text{CH}_3 - \text{Cl}\}$  corresponds the ion-molecule complex so the  $\text{Cl} \cdots \text{C}$  distance is significant in this case.

### Sketches of Reacting Species

- Sketch structures of the reactants, ion-molecule complex, transition state species, and products. Indicate important structural parameters including bond distances and bond angles on each sketch.



## Structure and Bonding in the $\text{Cl}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

### Questions

- Obtain values of charges for all the atoms in the ion-molecule species  $\text{Cl}^- \cdots \text{CH}_3\text{Cl}$  and place them on the corresponding sketch given previously. Discuss the forces holding together this weak complex. Compare the  $\text{C} \cdots \text{Cl}^-$  bond distance with  $\text{C-Cl}$  bond distance in  $\text{CH}_3 - \text{Cl}$ , and comment on the relative strength of these two bonds.

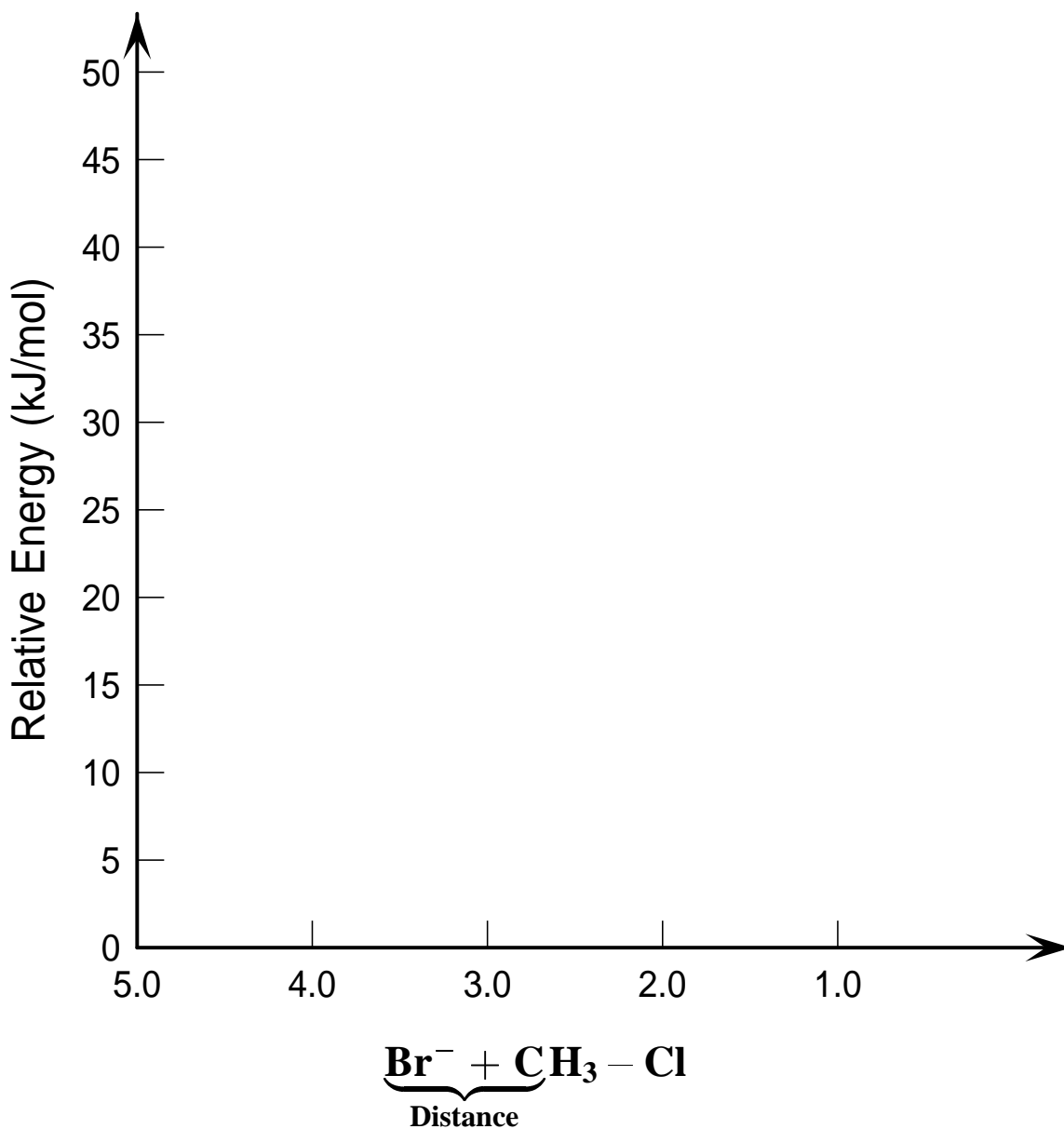
- Discuss the bonding around the central **C** atom in the  $[\text{Cl} - - - \text{CH}_3 - - - \text{Cl}]^{-\ddagger}$  transition state. Does the **carbon** atom prefer to have four or five bonds attached to it? Why doesn't the **carbon** atom easily undergo **valence-shell expansion** similar to the **P** atom in  $\text{PCl}_5$ ? Predict the structure of the  $[\text{Cl} - - - \text{CH}_3 - - - \text{Cl}]^{-\ddagger}$  transition state from **VSEPR** theory and give the **Structure Number (SN)** about the **C** atom.

## Reaction Profiles for the $\text{Br}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

The following exercises now focus on a more general  $\text{S}_{\text{N}}2$  reaction in which the attacking group ( $\text{Br}^-$ ) differs from the leaving group ( $\text{Cl}^-$ ):



Construct both gas and solution phase **Reaction Coordinate Diagrams** for the  $\text{Br}^- + \text{CH}_3\text{Cl}$   $\text{S}_{\text{N}}2$  reaction by plotting the relative energy in  $\text{kJ mol}^{-1}$  versus  $\underbrace{\text{Br}^- + \text{CH}_3 - \text{Cl}}_{\text{Distance}}$ . Place both reaction profiles on the same graph provided below, and plot the energies on a relative energy scale. Please be sure to label the various species along the reaction pathway.





## Structure and Energetics of the $\text{Br}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

Examine the geometries of the reacting species for the symmetric  $\text{Br}^- + \text{CH}_3\text{Cl}$   $\text{S}_{\text{N}}2$  reaction, and enter the observed geometries in the table below.

**Geometries of Reacting Species**

Species	Distances			Angles	
	$r_{\text{C-H}}$	$r_{\text{C-X}}$	$r_{\text{X}\cdots\text{C}}$	$\angle\text{H-C-X}$	$\angle\text{H-C-H}$
$\text{Br}^- + \text{CH}_3 - \text{Cl}$					
$[\text{Br} \cdots \cdots \text{CH}_3 \cdots \cdots \text{Cl}]^{-\ddagger}$					
$\text{Br} - \text{CH}_3 + \text{Cl}^-$					

Examine the energies of the reacting species for the symmetric  $\text{Br}^- + \text{CH}_3\text{Cl}$   $\text{S}_{\text{N}}2$  reaction in both the gaseous and aqueous phases, and enter the observed energies in the table below. These values are the calculated heats of formation ( $\Delta\text{H}_{\text{f}}^{\circ}$ ).

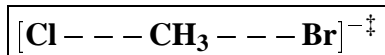
**Gas and Aqueous Phase Energies (kJ/mol) for Reacting Species**

Species	Gas Phase	Aqueous Phase	Solvation Energy <sup>a)</sup>
$\text{Br}^- + \text{CH}_3 - \text{Cl}$			
$\text{Br}^- \cdots \text{CH}_3 - \text{Cl}$			
$[\text{Br} \cdots \cdots \text{CH}_3 \cdots \cdots \text{Cl}]^{-\ddagger}$			
$\text{Br} - \text{CH}_3 \cdots \text{Cl}^-$			
$\text{Br} - \text{CH}_3 + \text{Cl}^-$			

a) Solvation Energy =  $\Delta\text{H}_{\text{f}}^{\circ}(\text{aqueous}) - \Delta\text{H}_{\text{f}}^{\circ}(\text{gas})$

## Analysis of the $\text{Br}^- + \text{CH}_3\text{ClS}_\text{N}2$ Reaction

- Sketch the structure of the transition state species below providing geometrical parameters including bond distances and bond angles.



How does the above structure compare to the transition state structure for the **identity** or **symmetric**  $\text{Cl}^- + \text{CH}_3\text{ClS}_\text{N}2$  reaction:  $[\text{Cl} \cdots \text{CH}_3 \cdots \text{Cl}]^{-\ddagger}$ ?

Which structure corresponds more closely to the idealized trigonal bipyramid structure with a carbon atom at the center?

- View the animation of the **electrostatic potential map** for the  $\text{Br}^- + \text{CH}_3\text{ClS}_\text{N}2$  reaction by stepping through each frame. Specifically, observe the changes which occur in the electrostatic potential map of the iso-density surface from frame to frame and interpret the color shifts.

Recall that colors toward **red** represent excess **negative** charge while colors toward **blue** represent excess **positive** charge. Describe your observations.

## Analysis of the $\text{Br}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

- View the animation of the imaginary frequency for the  $[\text{Cl} \cdots \text{C} \cdots \text{Br}]^{-\ddagger}$  transition state structure. Make a sketch of the movement of each atom by sketching the structure below and draw small vectors next to each atom to designate the direction of movement.
  
  
  
  
  
  
  
  
  
  
- View the animation of the **bond density** for the  $\text{Br}^- + \text{CH}_3\text{Cl}$  reaction by stepping through each frame. Observe what electron density shifts are taking place, and describe your findings.
  
  
  
  
  
  
  
  
  
  
- From the above observations provide a description of the chemical transformation taking place as the  $\text{Br}^-$  ion approaches the  $\text{CH}_3\text{Cl}$  molecule.

## Analysis of the $\text{Br}^- + \text{CH}_3\text{ClS}_{\text{N}}2$ Reaction

- Observe the trend for changes in charges on nucleophile ( $\text{Br}^-$ ) and leaving group ( $\text{Cl}^-$ ) as the  $\text{Br}^- + \text{CH}_3\text{ClS}_{\text{N}}2$  reaction proceeds. Describe your findings.
  
  
  
  
  
  
  
  
  
  
- Explain how the presence of a solvent modifies the gas-phase reaction profile. Does the solvent affect the barrier height? Does the solvent affect the reaction exothermicity? To answer this question, observe how the solvent affects the reactants and products, and contrast this observation with its effect on the transition state.

## Thermodynamics and Kinetics of the $\text{Br}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

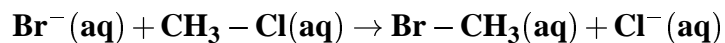
The equilibrium constant ( $\mathbf{K} = \frac{[\text{products}]}{[\text{reactants}]}$ ) can be related to the **Free Energy** ( $\Delta\mathbf{G}$ ) between reactants and products by the equation:

$$\Delta\mathbf{G}^0 = -\mathbf{R}\mathbf{T}\ln\mathbf{K}$$

where  $\mathbf{R}$  is the gas constant ( $8.31451\text{ J mol}^{-1}\text{ K}^{-1}$ ), and  $\mathbf{T}$  is the temperature in degrees Kelvin. As was noted earlier, the **Free Energy** change for a reaction can be given by

$$\Delta\mathbf{G} = \Delta\mathbf{E}_{\text{Reaction}} = \mathbf{E}_{\text{a,f}} - \mathbf{E}_{\text{a,r}}$$

- Calculate the equilibrium constant,  $\mathbf{K}$  for the  $\text{S}_{\text{N}}2$  reaction:

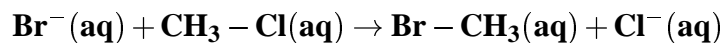


at  $25\text{ }^{\circ}\text{C}$  and  $60\text{ }^{\circ}\text{C}$

- Is the trend in  $\mathbf{K}$  derived from your calculations above consistent with what should occur as the temperature is increased? Explain.

## Thermodynamics and Kinetics of the $\text{Br}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

The rate can be expressed as a second order equation for the  $\text{S}_{\text{N}}2$  reaction:



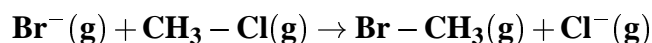
$$\text{rate} = k [\text{Br}^-] [\text{CH}_3 - \text{Cl}]$$

where the rate constant,  $k$  at  $60^\circ\text{C}$  is  $6.2 \times 10^{-4} \text{ L}^{-1} \text{ mol}^{-1} \text{ s}^{-1}$ .

- Calculate the rate constant at  $25^\circ\text{C}$  using the equation

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

For the  $\text{S}_{\text{N}}2$  reaction in the gas phase



the identical second order rate law given above is followed. However the rate constant  $k$  is several orders of magnitude larger giving rise to significantly faster rates for the gas phase.

- Give possible reasons why the gas phase reaction rate is faster than that for the solution phase.

**Last Revised: 02/02/98**