

# Foundations of Chemical Kinetics Lecture 19: Transition-state theory in the solution phase

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## Transition-state theory in solution

- We revisit our original derivation of the thermodynamic formalism of transition-state theory.
- We decompose the reaction  $A + B \xrightarrow{k} \text{products}$  into



- For this representation,  $v = k^\ddagger[\text{TS}]$ .
- The equilibrium constant  $K^\ddagger$  is related to the activities of the transition state and reactants by

$$\begin{aligned} K^\ddagger &= \frac{a_{\text{TS}}}{a_{\text{A}} a_{\text{B}}} \\ &= \frac{\gamma_{\text{TS}}}{\gamma_{\text{A}} \gamma_{\text{B}}} \frac{[\text{TS}]c^\circ}{[\text{A}][\text{B}]} \end{aligned}$$

## Transition-state theory in solution (continued)

- The derivation is completed as follows:

$$[\text{TS}] = \frac{K^\ddagger}{c^\circ} \frac{\gamma_A \gamma_B}{\gamma_{\text{TS}}} [\text{A}][\text{B}]$$

$$\therefore v = k^\ddagger [\text{TS}] = k^\ddagger \frac{K^\ddagger}{c^\circ} \frac{\gamma_A \gamma_B}{\gamma_{\text{TS}}} [\text{A}][\text{B}]$$

$$\therefore k = k^\ddagger \frac{K^\ddagger}{c^\circ} \frac{\gamma_A \gamma_B}{\gamma_{\text{TS}}}$$

- For an ideal solution, all the activity coefficients are equal to unity, and we get the limiting value

$$k_0 = k^\ddagger \frac{K^\ddagger}{c^\circ}$$

- Therefore

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma_{\text{TS}}}$$

# Transition-state theory in solution

## First-order rate constants

- If we repeat the above derivation for a first-order reaction  $R \rightarrow \text{product(s)}$ , we get

$$k = k_0 \frac{\gamma_R}{\gamma_{TS}}$$

- In a unimolecular reaction, the reactant and transition state are often similar, the difference between the two involving small changes in charge distribution and/or geometry.
- Accordingly,  $\gamma_R \approx \gamma_{TS}$ , so various factors that affect the activity coefficients (e.g. pressure, ionic strength) will typically have little effect on the rate constant.

## Transition-state theory in solution

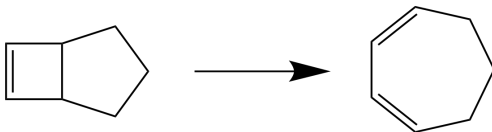
### Constancy of first-order rate constants (continued)

- Now imagine slowly decreasing the density of the solvent.
- In the limit, this operation converts a reaction in solution to one in the gas phase.
- By the argument above, the ratio of activity coefficients shouldn't change much, so the rate constant should be more-or-less constant throughout this operation.
- This explains the experimental observation that, for first-order reactions,  $k$  is often roughly the same whether the reaction occurs in the gas phase or in solution.

# Transition-state theory in solution

## Gas vs solution phase example

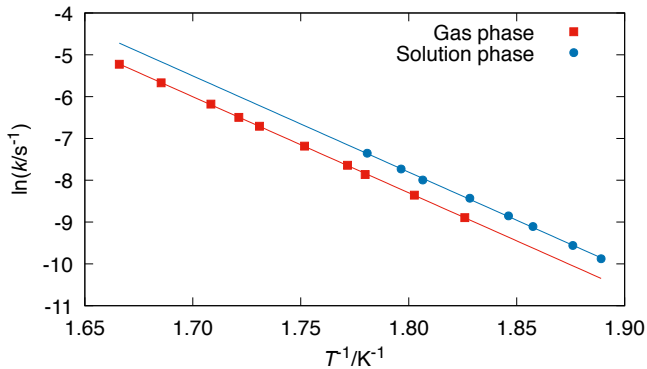
Branton et al. [*Trans. Faraday Soc.* **62**, 659 (1966)] studied the reaction



in both gas- and solution-phase.

# Transition-state theory in solution

## Gas vs solution phase example



# Transition-state theory in solution

## Gas vs solution phase example

	$E_a/\text{kJ mol}^{-1}$	$A/10^{14}\text{s}^{-1}$	$\Delta^\ddagger S^\circ/\text{JK}^{-1}\text{mol}^{-1}$
Gas	$191.1 \pm 0.6$	$2.28 \pm 0.30$	$16.55 \pm 0.13$
Solution	$191.3 \pm 2.0$	$4.0 \pm 1.8$	$21.2 \pm 0.5$

- The barrier height is unaffected.
- The pre-exponential factor is slightly larger in solution.
- Since

$$A = \frac{k_B T}{h} e^{1 + \Delta^\ddagger S^\circ / R}$$

for a first-order reaction, this is an entropic effect, but not a large one.

(Entropies of activation calculated at 550 K)



## Variation of rate constant with pressure

- We return to the ideal solution case.  
In the thermodynamic formulation of transition-state theory, we have, for second-order reactions,

$$k_0 = \frac{k_B T}{c^\circ h} \exp\left(-\frac{\Delta^\ddagger G^\circ}{RT}\right)$$

- Recall that

$$dG = V dp - S dT$$

or, for a reaction,

$$d\Delta G = \Delta V dp - \Delta S dT$$

so that

$$\left.\frac{\partial \Delta G}{\partial p}\right|_T = \Delta V$$

## Variation of rate constant with pressure (continued)

- For  $k_0$ , we have

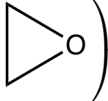
$$\ln k_0 = \ln \left( \frac{k_B T}{c^\circ h} \right) - \frac{\Delta^\ddagger G^\circ}{RT}$$
$$\therefore \left. \frac{\partial}{\partial p} \ln k_0 \right|_T = -\frac{1}{RT} \left. \frac{\partial \Delta^\ddagger G^\circ}{\partial p} \right|_T = -\frac{\Delta^\ddagger V^\circ}{RT}$$


where  $\Delta^\ddagger V^\circ$  is the change in the molar volume (change in volume of solution per mole of reaction) on accessing the transition state.

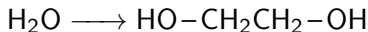
- If  $\Delta^\ddagger V^\circ > 0$ , the rate constant decreases as  $p$  increases. The reverse is true if  $\Delta^\ddagger V^\circ < 0$ .

## Variation of rate constant with pressure

Example: Acid-catalyzed hydrolysis of ethylene oxide

- In the presence of acid, ethylene oxide (oxirane, )

hydrolyzes to ethylene glycol:  +



- The rate law for this reaction is

$$v = k[\text{H}^+][\text{C}_2\text{H}_4\text{O}]$$

- Data from Baliga et al., *Trans. Faraday Soc.* **61**, 517 (1965) at 25.00 °C in the solvent water:

$p/\text{bar}$	1	500	1000	2000	3000
$k/10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$	9.30	10.9	12.7	16.9	20.4

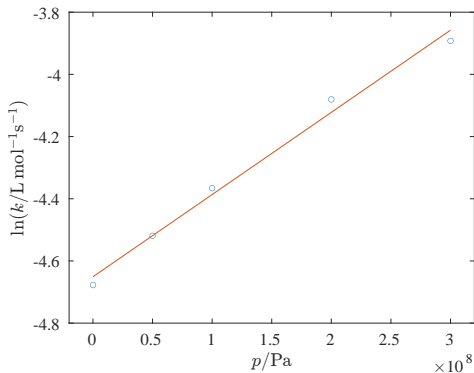
## Variation of rate constant with pressure

Example: Acid-catalyzed hydrolysis of ethylene oxide

- To avoid unit problems, convert  $p$  to Pa.

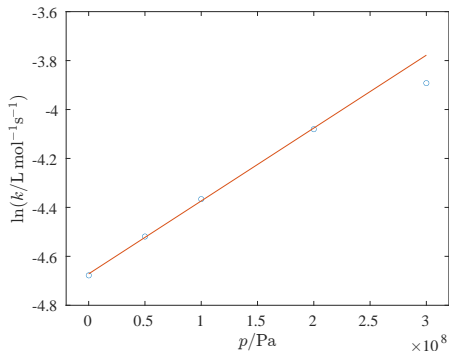
Why don't we need to convert  $k$  to SI units of  $\text{m}^3\text{mol}^{-1}\text{s}^{-1}$ ?

- Graph  $\ln k$  vs  $p$ . The slope should be  $-\Delta^\ddagger V^\circ/RT$ .
- First attempt:



# Variation of rate constant with pressure

Example: Acid-catalyzed hydrolysis of ethylene oxide



$$\text{slope} = 2.98 \times 10^{-9} \text{ Pa}^{-1}$$

$$\therefore \Delta^\ddagger V^\circ = -7.38 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$\equiv -7.38 \text{ cm}^3 \text{ mol}^{-1}$$

## Gas-phase vs solution-phase rate constants

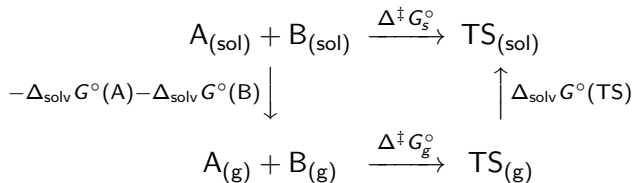
- We now consider the thermodynamic formulation of transition-state theory, which gives, for second-order reactions,

$$k_0 = \frac{k_B T}{c^\circ h} \exp\left(-\frac{\Delta^\ddagger G^\circ}{RT}\right)$$

- The above equation should apply both in solution ( $k_{0,s} \leftrightarrow \Delta^\ddagger G_s^\circ$ ) and in the gas phase ( $k_{0,g} \leftrightarrow \Delta^\ddagger G_g^\circ$ ).
- We want to figure out how the two rate constants are related.

## Gas-phase vs solution-phase rate constants (continued)

- Now consider the following thermodynamic cycle:



where  $\Delta_{\text{solv}} G^\circ$  is the standard free energy of solvation.

- Reading off the cycle, we have

$$\begin{aligned}
 \Delta^\ddagger G_s^\circ &= \Delta^\ddagger G_g^\circ + \Delta_{\text{solv}} G^\circ(\text{TS}) - [\Delta_{\text{solv}} G^\circ(\text{A}) + \Delta_{\text{solv}} G^\circ(\text{B})] \\
 &= \Delta^\ddagger G_g^\circ + \Delta^\ddagger \Delta_{\text{solv}} G^\circ
 \end{aligned}$$

## Gas-phase vs solution-phase rate constants (continued)

- From

$$k_{0,s} = \frac{k_B T}{c^\circ h} \exp\left(-\frac{\Delta^\ddagger G_s^\circ}{RT}\right)$$

and

$$\Delta^\ddagger G_s^\circ = \Delta^\ddagger G_g^\circ + \Delta^\ddagger \Delta_{\text{solv}} G^\circ$$

we get

$$\begin{aligned} k_{0,s} &= \frac{k_B T}{c^\circ h} \exp\left(-\frac{\Delta^\ddagger G_g^\circ}{RT}\right) \exp\left(-\frac{\Delta^\ddagger \Delta_{\text{solv}} G^\circ}{RT}\right) \\ &= k_{0,g} \exp\left(-\frac{\Delta^\ddagger \Delta_{\text{solv}} G^\circ}{RT}\right) \end{aligned}$$



## Gas-phase vs solution-phase rate constants (continued)

$$k_{0,s} = k_{0,g} \exp\left(-\frac{\Delta^\ddagger \Delta_{\text{solv}} G^\circ}{RT}\right)$$

TS better solvated than reactants:  $\Delta^\ddagger \Delta_{\text{solv}} G^\circ < 0$

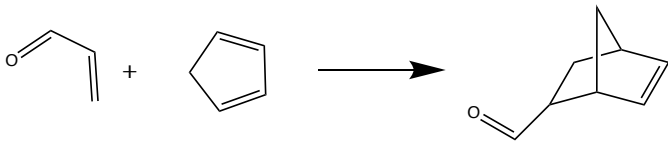
In this case, the argument of the exponential involving this solvation term is positive and  $k_{0,s} > k_{0,g}$ .

Reactants better solvated than TS:  $\Delta^\ddagger \Delta_{\text{solv}} G^\circ > 0$

We then have the exponential of a negative value, so  $k_{0,s} < k_{0,g}$ .

## Gas-phase vs solution-phase rate constants

Example: Reaction of acrolein with cyclopentadiene



- Measured kinetic parameters [Wassermann, *Trans. Faraday Soc.* **34**, 128 (1938)]:

In benzene:  $A = (1.3 \pm 0.9) \times 10^6 \text{ L mol}^{-1}\text{s}^{-1}$ ,  
 $E_a = 57.3 \pm 2.1 \text{ kJ mol}^{-1}$

In the gas phase:

$A = (1.6 \pm 1.8) \times 10^6 \text{ L mol}^{-1}\text{s}^{-1}$ ,  
 $E_a = 64 \pm 4 \text{ kJ mol}^{-1}$

## Gas-phase vs solution-phase rate constants

Example: Reaction of acrolein with cyclopentadiene (continued)

- We want to use these data to learn something about the relative solvation of the transition state.
- We need to choose a temperature to do the calculation. Let's use the boiling point of benzene (353.2 K), which is the highest temperature at which the experiment could be done in the solvent without increasing the pressure.

$$k_{0,s} = 4.4 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$k_{0,g} = 5.5 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$$

## Gas-phase vs solution-phase rate constants

Example: Reaction of acrolein with cyclopentadiene (continued)

$$\begin{aligned}\Delta^\ddagger \Delta G^\circ &= RT \ln(k_{0,g}/k_{0,s}) \\ &= (8.314\,463\text{ J K}^{-1}\text{ mol}^{-1})(353.2\text{ K}) \ln \left( \frac{5.5 \times 10^{-4}\text{ L mol}^{-1}\text{ s}^{-1}}{4.4 \times 10^{-3}\text{ L mol}^{-1}\text{ s}^{-1}} \right) \\ &= -6.1\text{ kJ mol}^{-1}\end{aligned}$$

- The negative sign means that the transition state is better solvated than the reactants, which is why the reaction is faster in solution.
- Note that in this case, the difference is almost entirely due to the activation energy, i.e. to the difference in enthalpy of solvation between the reactants and transition state.

## Rethinking second-order reactions

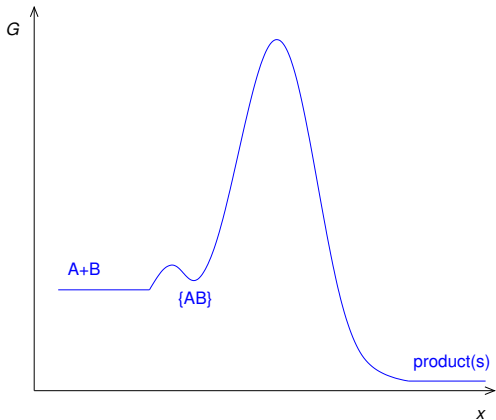
- In the foregoing, we have applied transition-state theory to second-order reactions without thinking too hard about whether this is entirely sensible.
- Thinking back to the theory of diffusion-influenced reactions, we decomposed a second-order process into




- The encounter pair is held together (briefly) by a solvent cage. There is a barrier to forming this species and to breaking it up due to the necessary rearrangement of the solvent around A and B.

# Rethinking second-order reactions

## Free energy profile



# Rethinking second-order reactions

Free energy profile 

- Because transition-state theory is an **equilibrium theory**, we can apply it to the formation of the transition state without worrying about details of how we get there **provided** there isn't another deep minimum that significantly perturbs the overall equilibrium distribution.
- The free energy barrier for formation of the encounter pair will generally be much smaller than the free energy barrier for reaction.
- This allows us to apply transition-state thinking to a second-order reaction without separating the encounter pair formation from the reactive event.

## Dealing with solvation computationally

- We have seen that solvation can have a significant effect on reaction rates.
- It is possible to approximate the effect of solvation using polarized continuum models (PCM).
- PCM methods treat the solvent as a continuum made of a polarizable dielectric material.
- The solute is placed in a cavity within the polarizable dielectric, and the mutual effects of the molecule's and the dielectric's electric fields on each other are computed.



## Dealing with solvation computationally (continued)

- To calculate a rate constant by transition-state theory, we need, as usual, the energies and partition functions of reactants and products.
- To calculate properties in a solvent, in the solvation tab of GaussView, select a solvation model and a solvent.
- The IEFPCM model is generally recommended **unless** you specifically want to calculate solvation free energies, in which case you should choose SMD.

## The reaction of $\text{H}_2$ with $\bullet\text{OH}$

- The reaction  $\text{H}_2 + \bullet\text{OH} \longrightarrow \bullet\text{H} + \text{H}_2\text{O}$  is observed following the photolysis of water.
- Calculation methods used:
  - Job type: For  $\text{H}_2$  and  $\bullet\text{OH}$ , optimization + frequency.  
For the optimization to a TS, calculate force constants at all points.
  - Method: DFT ( $\omega\text{B97X-D}$ ), unrestricted wavefunction, 6-31G++(d,p) basis set.
  - Solvation: IEFPCM, solvent water
  - Additionally: pressure = 0.986 923 atm (1 bar)

# The reaction of $\text{H}_2$ with $\bullet\text{OH}$

## Results

	$\epsilon/\text{hartree}$	$\hat{q}$ (bottom)
$\text{H}_2$	-1.175 435	4.298
$\bullet\text{OH}$	-75.717 467	$6.727 \times 10^3$
Transition state	-76.888 087	2.236



# The reaction of $\text{H}_2$ with $\bullet\text{OH}$

Calculation of rate constant at  $25^\circ\text{C}$

$$\Delta^\ddagger\epsilon = 4.815 \times 10^{-3} \text{ hartree} \equiv 12.64 \text{ kJ mol}^{-1}$$

$$\begin{aligned} k &= \frac{k_B T}{hc^\circ} \frac{\hat{q}^\ddagger}{\hat{q}_{\text{H}_2} \hat{q}_{\text{OH}}} e^{-\Delta^\ddagger\epsilon/RT} \\ &= 2.9 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \equiv 2.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

Experimental value:  $4.2 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$

Likeliest source of trouble: Maybe “simple” TST is missing something...