Chapter 13 Study Guide
Solvents as catalysts

Literature does not usually consider solvents to be catalysts but I think of them as catalysts. Solvents work the same as catalysts

- Solvents can initiate reactions
- Solvents stabilize intermediates
- Solvents stabilize transition states and thereby modify the intrinsic barriers to reactions
- Solvents act as efficient means for energy transfer
- Solvents can donate or accept electrons
- Mass transfer limitations are more important when solvents are present.

$$H_2 + Br_2 \Rightarrow 2\ HBr$$
(12.39)

$$
\begin{aligned}
&Br_2 \rightarrow 2Br \\
&Br + H_2 \rightarrow HBr + H \\
&H + Br_2 \rightarrow HBr + Br \\
&2\,Br \rightarrow Br_2
\end{aligned}
\tag{12.40}
$$

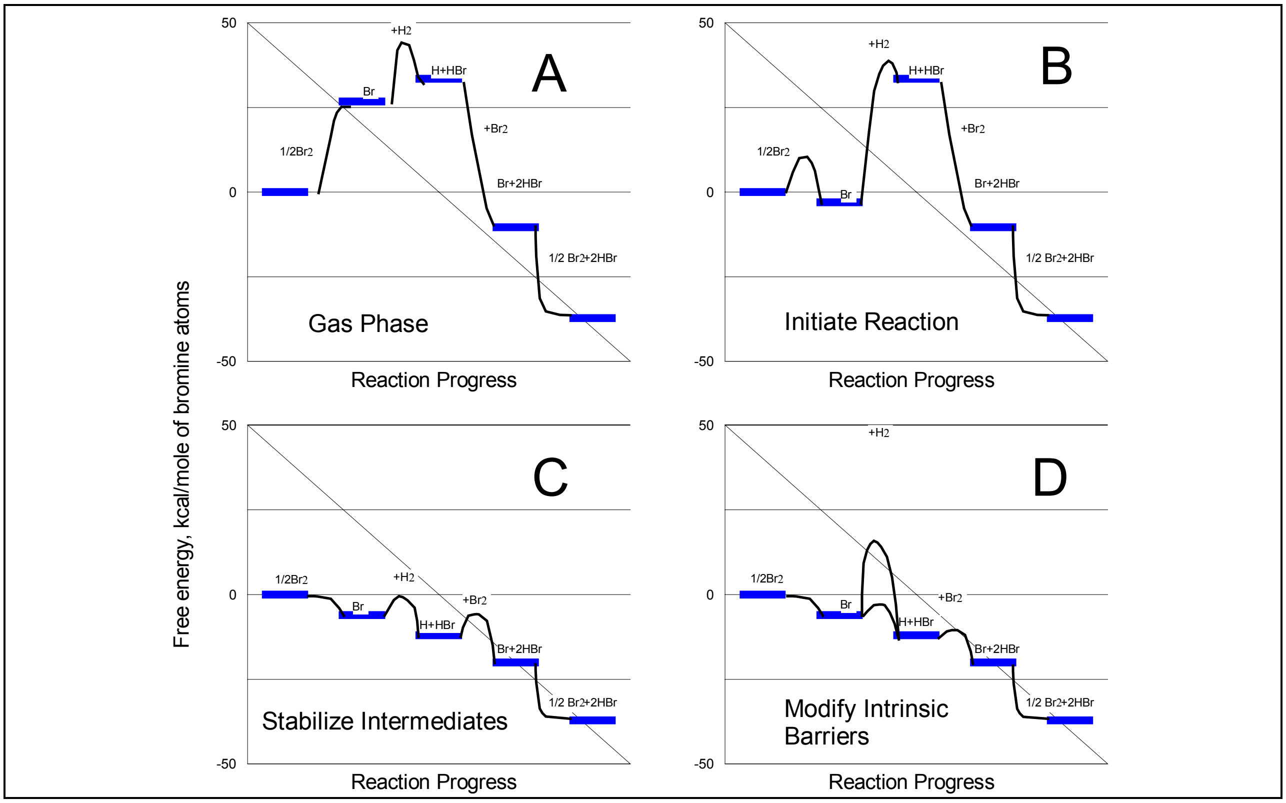


Figure 13.1 An illustration of some of the ways a solvent can affect the free energy changes during the reaction. $H_2 + Br_2 \Rightarrow 2\,HBr$

Examples of the role of solvents

Table 13.1 The rate of the Deils Alder reaction (2 cyclopentadiene → cyclopentadiene dimer) at 300 K. Data of A. Wasserman, Montash Chem, 83 (1952) 543.

Solvent	Rate constant, lit/mole-sec	Solvent	Rate constant, lit/mole-sec
gas phase	6.9×10^{-7}	carbon disulfide	9.3×10^{-7}
ethanol	19×10^{-7}	tetrachloromethane	7.9×10^{-7}
nitrobenzene	13×10^{-7}	benzene	6.6×10^{-7}
paraffin oil	9.8×10^{-7}	"neat liquid"	5.2×10^{-7}

Effect small for non-ionic reactions

Table 13.2 The rate of the S_N2 reaction $NaCl + CH_3I \rightarrow CH_3Cl + NaI$ at 350 K. Data from A. J. Parker, Chem Rev 69 (1969) 1. The gas phase rate in the table is estimated from the abinitio calculations of Glukhovsten et al

Solvent	Rate constant, lit/mole-sec	Solvent	Rate constant, lit/mole-sec
gas phase	about 10^{-45}		
Water	3.5×10^{-6}	methyl cyanide	0.13
Methanol	3.1×10^{-6}	dimethyl formamide (DMF)	2.5

Big effect for ionic reactions

Table 13.3 The rate of some association reactions in various solvents. Data from, Menschutkin, Z. Phys Chem, 6 (1890) 41 and Laidler, Chemical Kinetics (1965)

Solvent	dielectric constant	Rate of the reaction $(C_2H_5)_3N + CH_3I \rightarrow [(C_2H_5)_3NCH_3]^+ + [I]^-$ at 100 C, lit/mole-sec	Rate of the reaction $CH_3COOCOCH_3 + 2\ C_2H_5OH \rightarrow 2\ CH_3COOC_2H_5$ at 50 C, lit/mole-sec
hexane	1.89	0.5×10^{-5}	0.0119
benzene	2.28	39×10^{-5}	0.0053
chlorobenzene	5.62	160×10^{-5}	0.0046
methoxy benzene	9	400×10^{-5}	0.0029
acetone	20.7	265×10^{-5}	
nitrobenzene	35	1383×10^{-5}	0.0024

Intermediate effect when Ions form during reaction

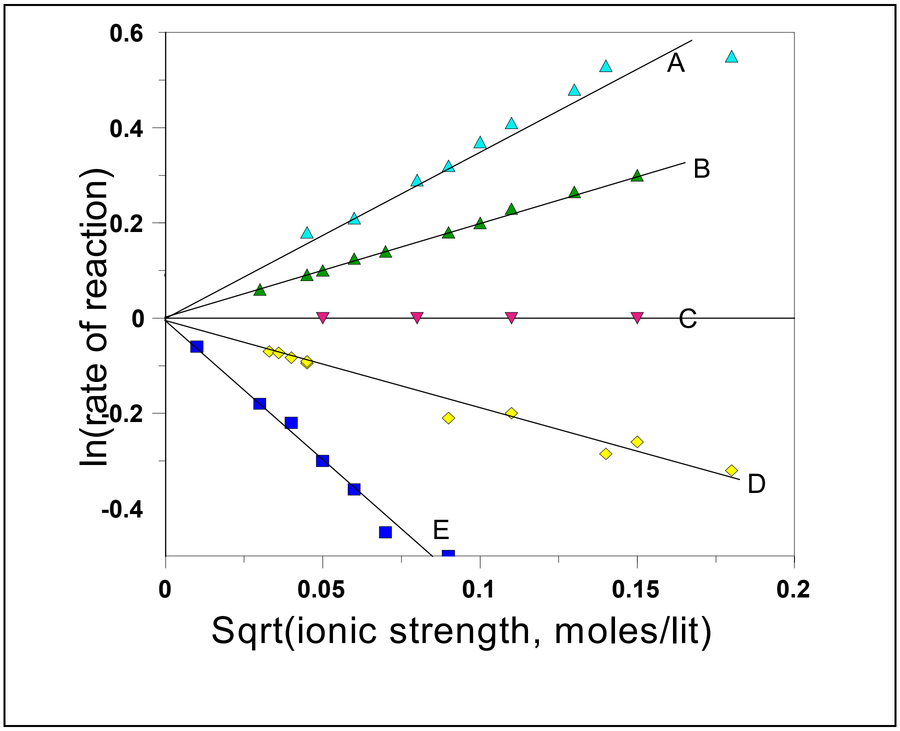


Figure 13.2 The effect of ion strength on a number of reactions after Laidler (1987). The points are data. The lines are predictions of equation (13.39).

A. $Co\,(NH_3)_5\,Br^{2+} + Hg^{2+} \rightarrow$

B. $S_2O_8^{2-} + I^- \rightarrow$

C. $[(Cr(urea)_6]^{3+} + H_2O \rightarrow$

D. $Co(NH_3)_5\,Br^{2+} + OH^- \rightarrow$ products

E. $Fe^{2+} + Co\,(C_2\,O_4)^{3-} \rightarrow$ products

Ionic strength also affects rate

Why do solvents change rates?

- Solvents stabilize intermediates
- Solvents can initiate reactions
- Solvents stabilize transition states and thereby modify the intrinsic barriers to reactions
- Solvents act as efficient means for energy transfer
- Solvents can donate or accept electrons
- Mass transfer limitations are more important when solvents are present.

Solvation of intermediates

$$\mathrm{CH_3I + NaCl \rightarrow CH_3I + NaI}$$

(13.1)

$$\mathrm{Cl^- + CH_3I \rightarrow ClCH_3 + I^-}$$

(13.2)

$$\mathrm{Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-}$$

(13.3)

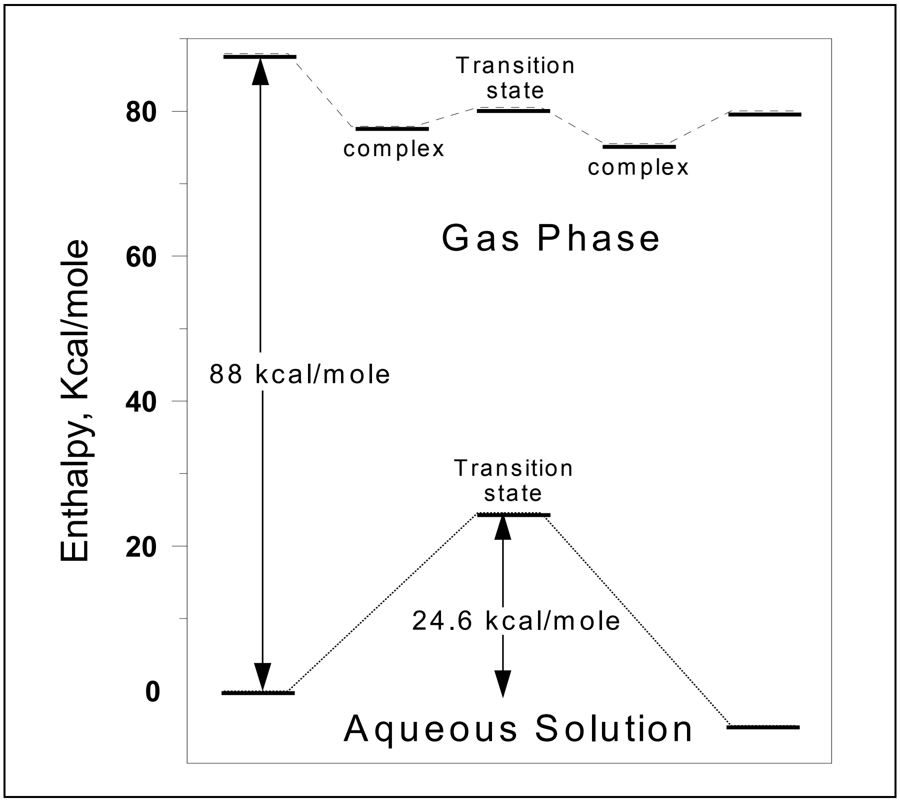


Figure 13.3 A comparison of the free energy changes during the reaction $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$. Data from p131 in Reichardt[1988]

Table 13.2 The rate of the S_N2 reaction $NaCl + CH_3I \rightarrow CH_3Cl + NaI$ at 350 K. Data from A. J. Parker, Chem Rev 69 (1969) 1. The gas phase rate in the table is estimated from the abinitio calculations of Glukhovsten et al

Solvent	Rate constant, lit/mole-sec	Solvent	Rate constant, lit/mole-sec
gas phase	about 10^{-45}		
water	3.5×10^{-6}	methyl cyanide	0.13
methanol	3.1×10^{-6}	dimethyl formamide (DMF)	2.5

Literature discussed this differently:

Concentration of intermediates go up, but reactivity goes down.

Table 13.4 The rate of the S_N2 reaction $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$ at 298 K. Data from p 130 of Reichart[1988].

Solvent	Rate constant, lit/mole-sec	Solvent	Rate constant, lit/mole-sec
gas phase	2.1×10^{-11}		
acetone	5.5×10^{-21}	methanol	1.0×10^{-26}
DMF	9.3×10^{-22}	water	8.3×10^{-27}

Table 13.5 The rate constant a prototypical S_N1 reaction: the solvolysis of p-methoxyneophyl-tolunesulfonate in a number of solvents at 75 C. Data of Smith, Fainberg and Winstein JACS 83 618 (1961)

Solvent	k, min^{-1}	Solvent	k, min^{-1}
formic acid	7.1	methyl cyanide	3.6×10^{-3}
water	4.0	DMF	3.0×10^{-3}
acetic acid	0.19	acetic anhydride	2.0×10^{-3}
methanol	0.1	pyridine	1.3×10^{-3}
ethanol	3.8×10^{-2}	acetone	5.1×10^{-4}
$C_7H_{15}COOH$	4.4×10^{-3}	ethyl acetate	6.8×10^{-5}
DMSO	1.1×10^{-2}	dioxane	5.1×10^{-5}
nitro methane	7.2×10^{-3}	diethyl ether	$\sim3\times10^{-6}$

Table 13.6 Some examples of protic and aprotic solvents

Protic solvents: good for S_N1 reactions of anions water, ethanol, methanol, acetic acid, formic acid, ammonia, ethane thiol
Polar Aprotic solvents: good for S_N2 reactions of anions acetone, dimethyl sulfoxide (DMSO) $[(CH_3)_2S{=}O]$, dichloromethane, ethers, Dimethylformamide (DMF) $[(CH_3)_2NCHO]$, cyclohexanone, acetaldehyde
Non-polar Aprotic solvents: good for radical reactions ethylene, benzene

Solvents can initiate reactions

tbutyl-peroxide -> tbutyl-O radicals
rare effect

Solvents stabilize intermediates
key effect

Table 13.2 The rate of the S_N2 reaction $NaCl + CH_3I \rightarrow CH_3Cl + NaI$ at 350 K. Data from A. J. Parker, Chem Rev 69 (1969) 1. The gas phase rate in the table is estimated from the abinitio calculations of Glukhovsten et al

Solvent	Rate constant, lit/mole-sec	Solvent	Rate constant, lit/mole-sec
gas phase	about 10^{-45}		
water	3.5×10^{-6}	methyl cyanide	0.13
methanol	3.1×10^{-6}	dimethyl formamide	2.5

Quantitative trends

Everything goes as the difference between the free energy of solvation of the TST and the reactants. Anything you do to stabilize the TST relative to the reactants speeds up the reaction.

Introduction to solvation:

solvation: The process of forming a solution with a dissolved species

- solute molecules must separate from each other and move into the solvent
- some solvent molecules must separate to make room for the solute
- solute and solvent must mix together

$$\boxed{\Delta G_{\text{solvation}} = \Delta G_{\text{solute}} + \Delta G_{\text{solvent}} + \Delta G_{\text{mix}}}$$

(13.12)

Let’s consider some examples

Table 13.7 Solubility of some alkyl halides in water		
salt	solubility, moles/liter	Lattice energy (ΔH_{solute}), kcal/mole
LiF	0.10	247
NaCl	6.11	188
KBr	4.49	167
CsI	1.69	144
LiI	12.32	174
CsF	24.16	177

- The hydrophobic interaction
- The electrostatic interaction
- Solvation forces

Analysis explains table 13.7

Hughes-Ingold rules

- If the transition state for a reaction has a larger charge than the reactants, then the rate of reaction will increase as the polarity of the solvent increases.
- If the transition state for a reaction has a smaller charge than the reactants, then the rate of reaction will decrease as the polarity of the solvent increases.
- If the net charge remains the same, but the charge is dispersed, then there will be a small decrease in rate as the polarity of the solvent increases.
- If the net charge remains the same, but the charge is localized, then there will be a small increase in rate as the polarity of the solvent increases.

Table 13.9 Implications of the Hughes-Ingold rules for SN type reactions

Mechanism	Reactants	Transition state	Change in charge in the transition state	Effect of increase in solvent polarity on rate
S_N2	$Y^- + RX$	$^{\delta-}Y\cdots R\cdots X^{\delta-}$	Dispersed	Small Decrease
S_N2	$Y + RX$	$^{\delta+}Y\cdots R\cdots X^{\delta-}$	Increased	Large Increase
S_N2	$Y^- + RX^+$	$^{\delta-}Y\cdots R\cdots X^{\delta+}$	Reduced	Large Decrease
S_N2	$Y + RX^+$	$^{\delta+}Y\cdots R\cdots X^{\delta-}$	Dispersed	Small Decrease
S_N1	RX	$^{\delta+}R\cdots X^{\delta-}$	Increased	Large increase
S_N1	RX^+	$^{\delta+}R\cdots X^{\delta+}$	Dispersed	Small decrease

Hydrophobic effects:

SN2 - TST larger than reactants (want aprotic solvent)

SN1 -TST smaller than reactants (want protic solvent)

Quantative models:

Double sphere model
Single sphere model
Debye-Huckel theory

> Assumes main effect of changing solvent is to change the electrostatic interactions between molecules

Regular solution theory

> Assumes main effect of changing solvent is to change the hydrophobic effect

Double sphere model
assumptions:

- solvents change electrostatic interaction between reactants
- energy is energy to bring reactants together

$$R_3C^+ + Y^- \rightarrow R_3CY$$

(13.25)

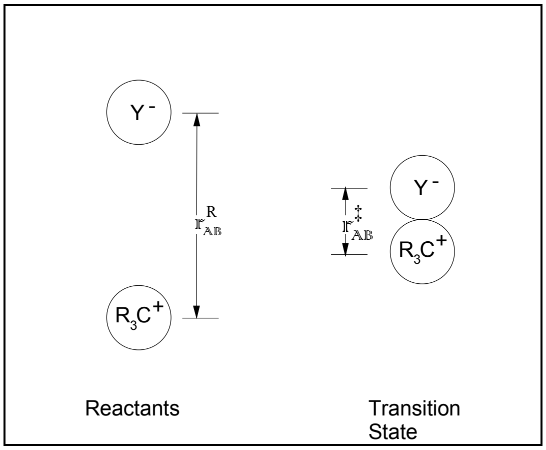


Figure 13.5 The double sphere model of a reaction.

$$\Delta G_S^{\ddagger} = \Delta G_\infty^{\ddagger} + \left(\Delta G_{\infty \rightarrow S}^{\ddagger} - \Delta G_{\infty \rightarrow S}^{R} \right)$$

(13.26)

$$\Delta G^{\ddagger}_{\infty \rightarrow s} = \frac{Z_A Z_B e^2}{\varepsilon r^{\ddagger}_{AB}}$$

(13.28)

$$\boxed{{}_{B}T \ln\left(\frac{k_S}{k_\infty}\right) = \Delta G^{\ddagger}_{\infty} + \frac{Z_A Z_B e^2}{\varepsilon r^{\ddagger}_{AB}}}$$

(13.29)

rate proportional to 1/ε

Single sphere model.

- solvents change electrostatic interaction
- energy is the change in the electrostatic interaction with the solvent as the reactants come together

$$\Delta G^{\ddagger}_{g\rightarrow S} = -\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)\frac{(Z_A)^2 e^2}{r_A}$$

(13.30)

$$\Delta G^{B}_{g\rightarrow S} = -\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)\frac{(Z_B)^2 e^2}{r_B}$$

(13.31)

$$\Delta G^{\ddagger}_{g\rightarrow S} == \left(\frac{\varepsilon-1}{2\varepsilon+1}\right)\frac{(Z_{\ddagger})^2 e^2}{r_{\ddagger}}$$

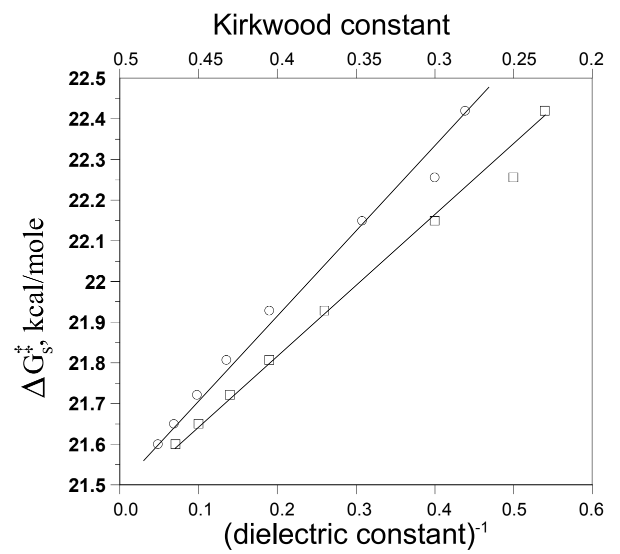
(13.32)

result

$$k_B T \ln\left(\frac{k_S}{k_g}\right) = \Delta G_S^{\ddagger} = \Delta G_g^{\ddagger} + \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) \left(\frac{(Z_A)^2 e^2}{r_A} + \frac{(Z_B)^2 e^2}{r_B} - \frac{(Z_{\ddagger})^2 e^2}{r_{\ddagger}}\right)$$

(13.33)

rate proportional to Kirkwood constant (ε-1)/(2ε+1)



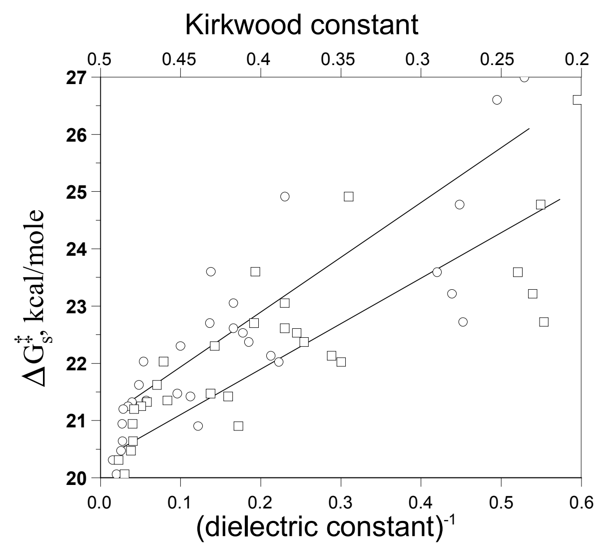


Figure 13.6 A plot of $\Delta G_s^\ddagger$ for reaction (13.36) in a series of dioxane acetone mixtures.

(○) data plotted against $1/\varepsilon$

(□) data plotted against $(\varepsilon-1)/(2\varepsilon+1)$

Figure 13.7 A plot of $\Delta G_s^\ddagger$ for reaction (13.36) in a series of different solvents.

(○) data plotted versus $1/\varepsilon$

(□) data plotted versus $(\varepsilon-1)/(2\varepsilon+1)$

Debye huckel theory - how does addition of salt affect rates?

Idea the ions in salt can screen dielectric charges. reduces electrostatic effects.

$$\ln\left(\frac{k_S}{k_\infty}\right)=\left(\frac{G^{\ddagger}_{S\rightarrow\infty}-G^{R}_{S\rightarrow\infty}}{{}_{B}T}\right)=\left(\frac{Z_A Z_B e^2}{\varepsilon r_{AB}}\right)$$

$$-2Z_A Z_B Q_D\sqrt{I}$$

(13.39)

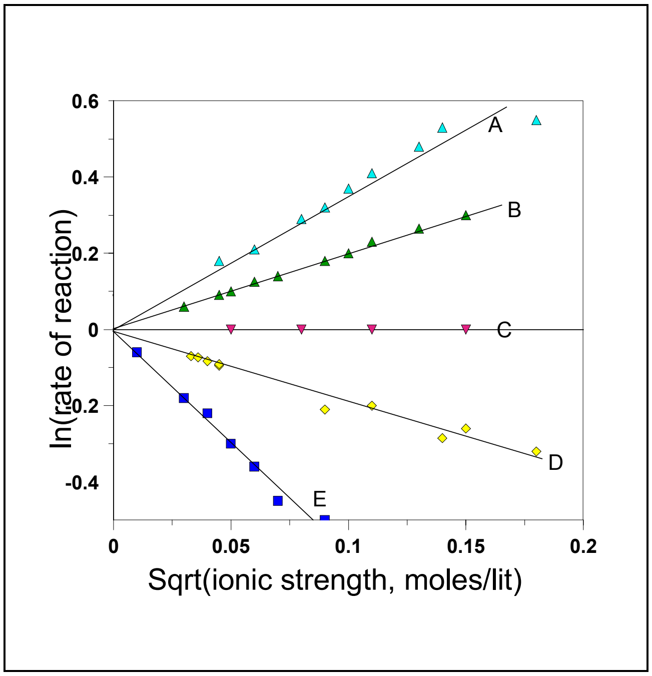


Figure 13.2 **The effect of ion strength on a number of reactions after Laidler (1987). The points are data. The lines are predictions of equation (13.39).**

A. $Co(NH_3)_5Br^{2+} + Hg^{2+} \rightarrow$
B. $S_2O_8^{2-} + I^- \rightarrow$
C. $[(Cr(urea)_6]^{3+} + H_2O \rightarrow$
D. $Co(NH_3)_5Br^{2+} + OH^- \rightarrow$ products
E. $Fe^{2+} + Co(C_2O_4)^{3-} \rightarrow$ products

Regular solution theory:

- Assumes hydrophobic interaction controls changes in rate with changing solvent.

Assume a bubble has to form to hold solute.

$$E_{cavity} = V_A \times (\text{CEDs})$$

(13.40)

CED=heat of vaporization per mole/molar volume

$$\delta_A = (\text{CED}_A)^{1/2}$$

(13.44)

$$\delta_S = (\text{CED}_S)^{1/2}$$

(13.45)

$$\boxed{\Delta G^{A}_{A\to S} = V_A \times (\delta_A - \delta_S)^2}$$

(13.48)

$$\Delta G_S^{\ddagger}=\Delta G_{ideal}^{\ddagger}+\left(\begin{array}{l}V_{\ddagger}\left(\delta_{\ddagger}-\delta_S\right)^2-V_A\left(\delta_A-\delta_S\right)^2\\-V_B\left(\delta_B-\delta_S\right)^2\end{array}\right)$$

(13.49)

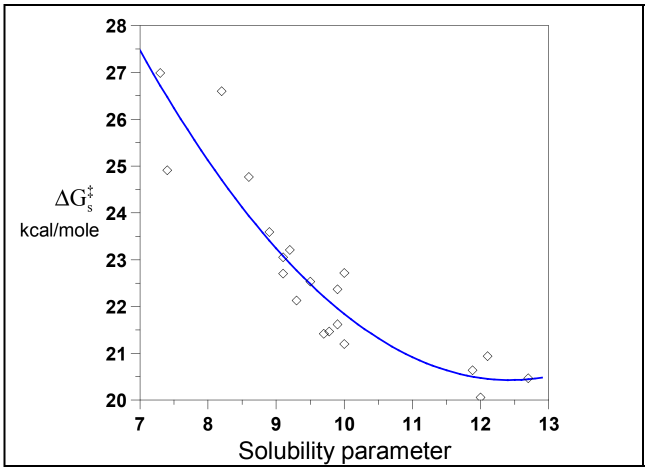


Figure13.8 A plot of $\Delta G_s^{\ddagger}$ for reaction (13.36) in a series of different solvents as a function of the solubility parameter of the solvent.

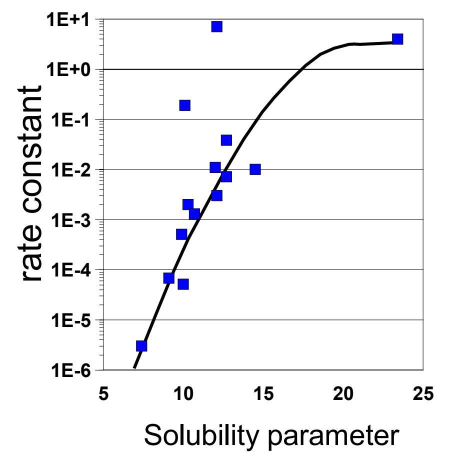


Figure 13.9 A plot of the rate constant for the reaction in Table **13.5 in a series of different solvents as a function of the solubility parameter of the solvent.**

Summary

- Solvents can initiate reactions
- Solvents stabilize intermediates
- Solvents stabilize transition states and thereby modify the intrinsic barriers to reactions

Double Sphere model

- solvents change electrostatic interaction between reactants
- energy is energy to bring reactants together

Single sphere model

- solvents change electrostatic interaction
- energy is the change in the electrostatic interaction with the solvent as the reactants come together

Debye-Huckel theory - how does addition of salt affect rates?
Idea the ions in salt can screen dielectric charges. Reduces electrostatic effects.

Regular solution theory

- Assumes hydrophobic interaction controls changes in rate with changing solvent.

- Next discuss Mass transfer limitations are more important when solvents are present.

- Mass transfer limitations change the nature of the collision process between molecules in solution. The correct first term in equation (13.4) might not be the gas phase value $ķ_B T/h_p$.
- There are dynamic corrections in solution which are different than those in the gas phase. Those dynamic corrections are not properly accounted for in equation (13.4).

Derivation of diffusion equ

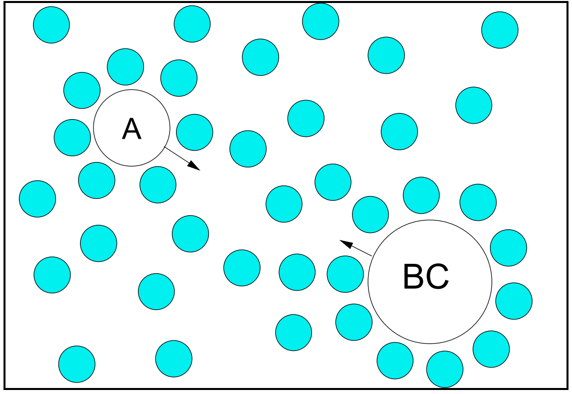


Figure 13.10 The diffusion of an ion A toward BC

$$J_{A\to BC}=-\left(D_A+D_{BC}\right)\left[\left(\frac{\partial C_A}{\partial \mathbb{r}}\right)+\left(\frac{C_A}{k_B T}\right)\left(\frac{\partial V(\mathbb{r})}{\partial \mathbb{r}}\right)\right]$$

(13.50)

$$k_D=\frac{4\pi\left(D_A+D_{BC}\right)I_{ABC}\mathbb{N}_A}{1+\dfrac{4\pi\left(D_A+D_{BC}\right)I_{ABC}\mathbb{N}_A}{k_1\left(\exp\left(-V(d_{coll})\right)/k_B T\right)\right)}}$$

(13.52)

fast diffusion limit

$$-k_B T\ln\left(\frac{k_1}{k_1^o}\right)=\Delta G_S^{\ddagger}=\Delta G_\infty^{\ddagger}+\frac{Z_A Z_{BC}e^2}{\varepsilon \mathbb{R}}$$

(13.56)

(equation from before)

Slow diffusion limit:

$$k_D=4\pi\left(D_A+D_{BC}\right)I_{ABC}\mathbb{N}_A$$

(13.57)

Almost all real data on small molecules taken in fast diffusion regieme.

Table 13.10 The value of the right hand side of equation 13.60 for some typical sets of parameters for diffusion of small molecules in water. Diffusion rate.

E_a, kcal/mole	T, K	RHS	E_a	T, K	RHS
0	300	0.1	5	300	453
1	300	0.54	10	300	2×10^{6}
2	300	2.9	15	300	1×10^{10}
3	300	15.6	20	300	4×10^{13}
4	300	85	25	300	2×10^{17}

Important to biological molecules (small diffusivities)
Important to photolysis reactions:

$$CH_2CO + h\nu \rightarrow CH_2 + CO$$

(13.64)

In chapter 9 we found that the ketene (CH_2CO) is excited by a photon, Then in the gas phase, the products form over the next 10^{-10} seconds. Now consider what would happen in a viscous solution, We would still excite the ketene, but the products might not diffuse away. That could lead to a diffusion limitation.

Friction effects - molecules may not stay hot long enough to react

Folker Plank equ:

$$CH_2CO + h\nu \rightarrow CH_2 + CO$$

(13.64)

- A low friction regime where the reactants are not strongly coupled to the solvent. In this case the rate of reaction looks like that expected from RRKM theory or the equivalent.
- A medium friction regime where the coupling with the solvent is stronger. In this case the solvent is an effective collision partner for the reactants, so the rate looks like that from transition state theory.
- A high friction regime where molecules have so many collisions with the solvent that hot molecules are de-excited before they have a chance to go over the barrier

in the potential energy surface. In this case the rate of reaction is less than that expected from transition state theory.

a) Summary

In summary then, in this chapter we discussed how solvents affect rates of reactions. Generally we found that solvents act just like catalysts:

- Solvents stabilize intermediates
- Solvents stabilize transition states
- Solvents act as efficient means for energy transfer
- Mass transfer limitations are more important when solvents are present.

The effects are huge. Rates in solution can be a factor of 10^{40} higher than in the gas phase, and can vary by a factor of 10^{6} from one solvent to the next.

Key qualitative findings are that aprotic solvents are best for S_N1 reactions, polar protic solvents are best for S_N2 reactions while non-polar solvents are best for radical reactions. There are also the Hughes Ingold rules to see how solvent polarity affects rates.

Unfortunately, though, when this book was being written, people did not have good models to understand the variations. In this chapter we mentioned the single sphere model, the double sphere model and regular solution theory. All three models could explain the qualitative variations in rate with changing solvent. However, the quantitative agreement is not as good. Errors as large as a factor of 100 in rate are seen. There are no better models at present, although molecular dynamics calculations are beginning to give useful insights.