

# Low Temperature Extrapolations; Methods of Estimation

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# ISSI Meeting: Questions to be addressed

- Assumption: emphasis mainly on chemistry in 'cold cores' of dense ISC's
- Errors in rate coefficients measured at low temperatures
- Estimates of rate coefficients at low temperatures from data at higher temperatures
- Estimates where there are no measurements of rate coefficients
- Products of reactions?

# Categories of Reaction

- **Ion-Molecule Reactions**
  - (a) ions + non-polar molecules
  - (b) ions + polar molecules
- **Neutral-Neutral Reactions**
  - (a) radicals + molecules
  - (b) radicals + radicals
- **Radiative Association**  
**{electron-molecule processes} X**

# Caveats and Acknowledgements

- Kinetic experiments measure rate coefficients but rarely products or branching ratios – which are equally important in models
- Reactants for reactions in ISM may not be in LTE – local thermodynamic equilibrium
- This presentation leans heavily on articles by Canosa *et al* and by Gerlich in

*Low Temperatures and Cold Molecules*

ed. IWMS to be published by World Scientific in 2008

# Reactions of Ions with Non-Polar Molecules

- 'Langevin model' assumes central potential (in cgs):

$$V(R_{AB}) = -\alpha q^2 / 2 R_{AB}^4$$

- Leads to

$$k(T) = 2\pi q (\alpha/\mu)^{1/2}$$

- Model predictions borne out by experiment

- 
- No apparent influence of quadrupole or non-spherical polarisability
  - Possible effects of fine-structure (spin-orbit) states

Rate Coefficients /  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Reactants	T = 8 K	T = 20 K	T = 30 K	Langevin
He <sup>+</sup> + N <sub>2</sub>	1.2	1.3	1.3	1.7
He <sup>+</sup> + O <sub>2</sub>	1.0	0.85		1.6
He <sup>+</sup> + CO	1.5	1.4		1.8
N <sup>+</sup> + O <sub>2</sub>	0.55			0.95
N <sup>+</sup> + CH <sub>4</sub>	0.82			1.4
N <sup>+</sup> + CO	1.1			1.1
H <sub>3</sub> <sup>+</sup> + CO			1.7	2.0
H <sub>3</sub> <sup>+</sup> + N <sub>2</sub>			1.3	1.9
H <sub>3</sub> <sup>+</sup> + CH <sub>4</sub>			1.9	2.4

# Comparison of $T$ -dependence: non-polar *versus* polar molecules

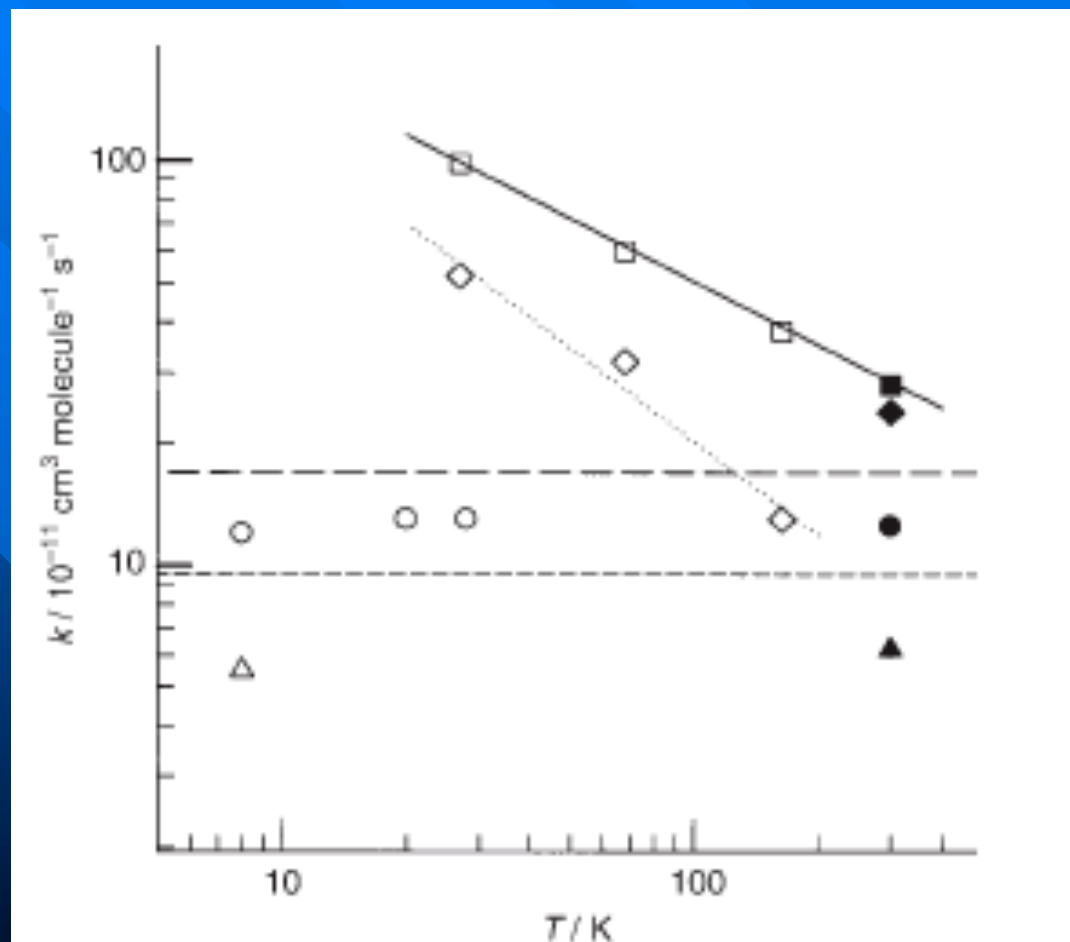
$\triangle, \blacktriangle$ :  $\text{N}^+ + \text{O}_2$

$\circ, \bullet$ :  $\text{He}^+ + \text{N}_2$

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$\square, \blacksquare$ :  $\text{N}^+ + \text{H}_2\text{O}$

$\diamond, \blacklozenge$ :  $\text{N}^+ + \text{NH}_3$



# Reactions of Ions with Polar Molecules

- Potential now depends on orientation:

$$V(R_{AB}) = -\alpha q^2 / 2 R_{AB}^4 - q \mu_D \cos\theta / 2 R_{AB}^2$$

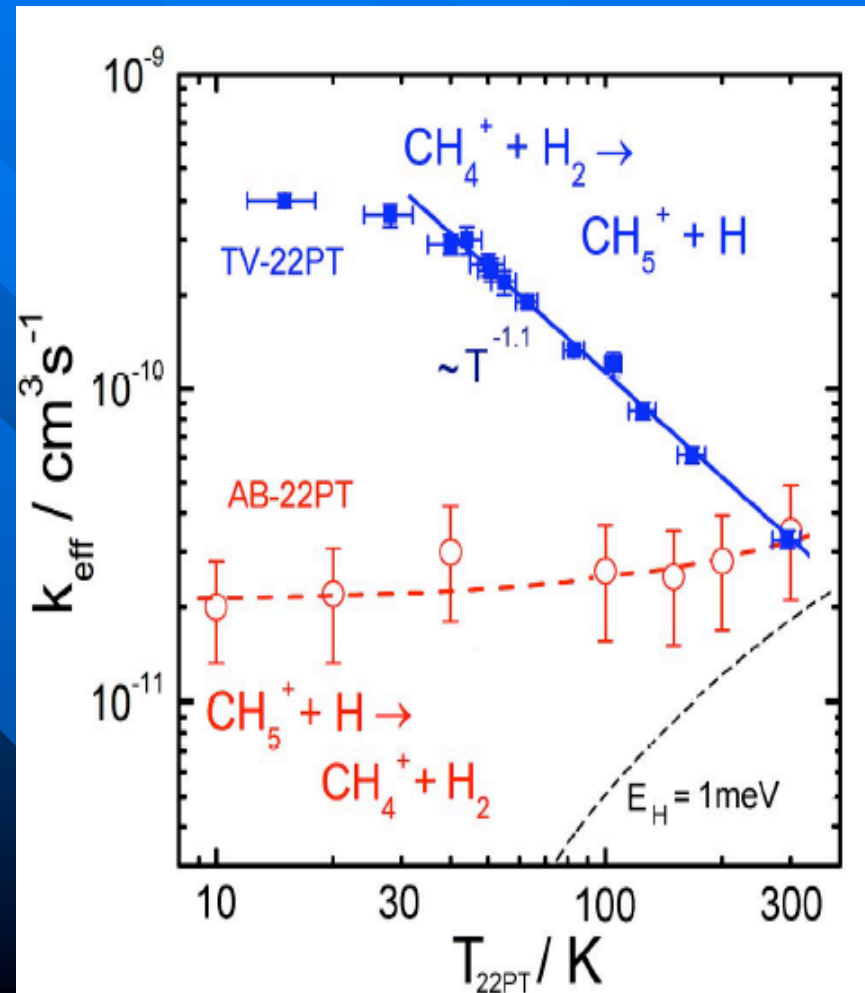
- Theory (Bowers, Troe, Clary, etc) based on 'capture' – suggests  $k(T)$  depends on rotational state of reactants

Rate Coefficients ( $\propto T^n$ ) /  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Reactants	T = 27 K	T = 68 K	$n$
He <sup>+</sup> + HCl	11.0	4.6	-0.94
He <sup>+</sup> + SO <sub>2</sub>	8.2	6.5	-0.25
He <sup>+</sup> + H <sub>2</sub> S	5.5	4.6	-0.19
He <sup>+</sup> + NH <sub>3</sub>	4.5	3.0	-0.44
He <sup>+</sup> + H <sub>2</sub> O	4.3	1.8	-0.94
C <sup>+</sup> + HCl	3.8	1.9	-0.75
C <sup>+</sup> + SO <sub>2</sub>	5.7	4.1	-0.36
C <sup>+</sup> + H <sub>2</sub> S	4.8	3.0	-0.51
C <sup>+</sup> + NH <sub>3</sub>	4.6	3.2	-0.39
C <sup>+</sup> + H <sub>2</sub> O	12.0	5.2	-0.91
N <sup>+</sup> + NH <sub>3</sub>	5.2	3.2	-0.53
N <sup>+</sup> + H <sub>2</sub> O	9.9	6.0	-0.54

# Ion-Molecule Reactions: Summary and Exceptions

- Where for  $A^+ + B$ :  
 $k(298 \text{ K}) > 10^{-9} \text{ cm}^3 \text{ s}^{-1}$   
if B is *non-polar*,  
assume  $k(T) = k(298 \text{ K})$   
if B is *polar*,  
assume  $k(T) \propto T^{-0.5}$
- If  $k(298 \text{ K}) < 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ,  
?? e.g.  $\text{CH}_4^+ + \text{O}_2$ ,  
examples in figure  
(Gerlich)



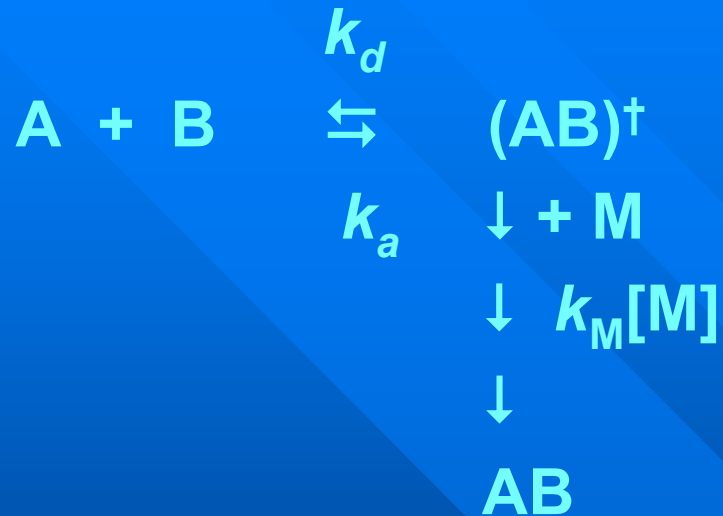


# Categories of Reaction

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- **Radiative Association**  
**{electron-molecule processes} X**

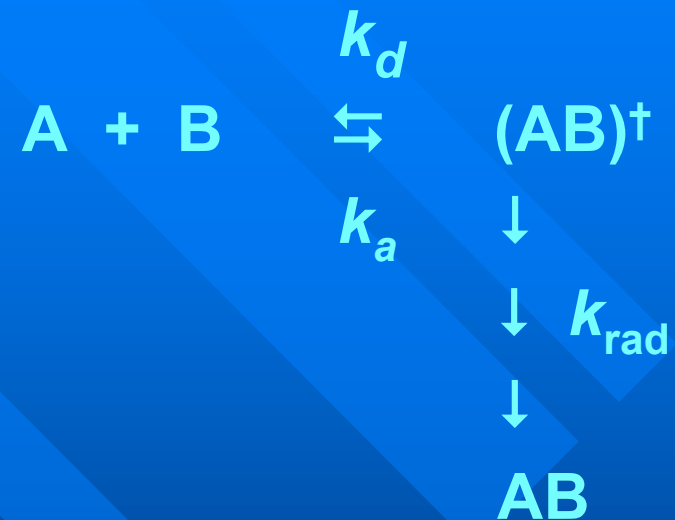
# Collisional and Radiative Association

'low pressure conditions':



$$k_M^\circ = k_M[M] (k_a / k_d)$$

'very low pressure conditions':



$$k_{\text{RA}}^\circ = k_{\text{rad}} (k_a / k_d)$$

$$k_{\text{RA}}^\circ = (k_M^\circ / [M]) (k_{\text{rad}} / k_M)$$

**T-dependence: of  $(k_{\text{rad}} / k_M)$  slight; of  $k_{\text{RA}}^\circ$  and  $(k_M^\circ / [M])$  similar**

# Rate Coefficients and $T$ -dependence for Collisional Association

Rate Coefficients ( $\propto T^n$ ) /  $10^{-27}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>

Reaction	15 K	~20 K	~50 K	~70 K	~150 K	$n$
$\text{N}_2^+ + \text{N}_2 + \text{N}_2$			1.5	1		
$\text{O}_2^+ + \text{O}_2 + \text{O}_2$		>1	>0.3	0.2		
$\text{CH}_3^+ + \text{H}_2 + \text{He}$		3.4		1.9		
$\text{CH}_3^+ + \text{CO} + \text{He}$		85		34		-1.1
$\text{CH}_3^+ + \text{N}_2 + \text{He}$		12		1.5		-1.7
$\text{CH}_3^+ + \text{H}_2\text{O} + \text{He}$		>70		>40		
$\text{C}^+ + \text{H}_2 + \text{He}$		< 0.1				
$\text{Ar}^+ + \text{Ar} + \text{Ar}$		~0.005	~0.001			
$\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{He}$		27	8.7		2.1	-1.3
$\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{N}_2$			17	10		
$\text{NH}_4^+ + \text{NH}_3 + \text{He}$	93	51	17		2.3	-1.6
$\text{NH}_4^+ + \text{NH}_3 + \text{Ar}$			29			
$\text{NH}_4^+ + \text{NH}_3 + \text{N}_2$			124	50	8.7	-2.4

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$\text{Ar}^+ + \text{Ar} + \text{Ar}$		~0.005	~0.001			
$\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{He}$		27	8.7		2.1	- 1.3
$\text{O}^+ + \text{H}_2\text{O} + \text{N}_2$			17	10		
$\text{I}_4^+ + \text{NH}_3 + \text{He}$	93	51	17		2.3	- 1.6
$\text{I}_4^+ + \text{NH}_3 + \text{Ar}$			29			
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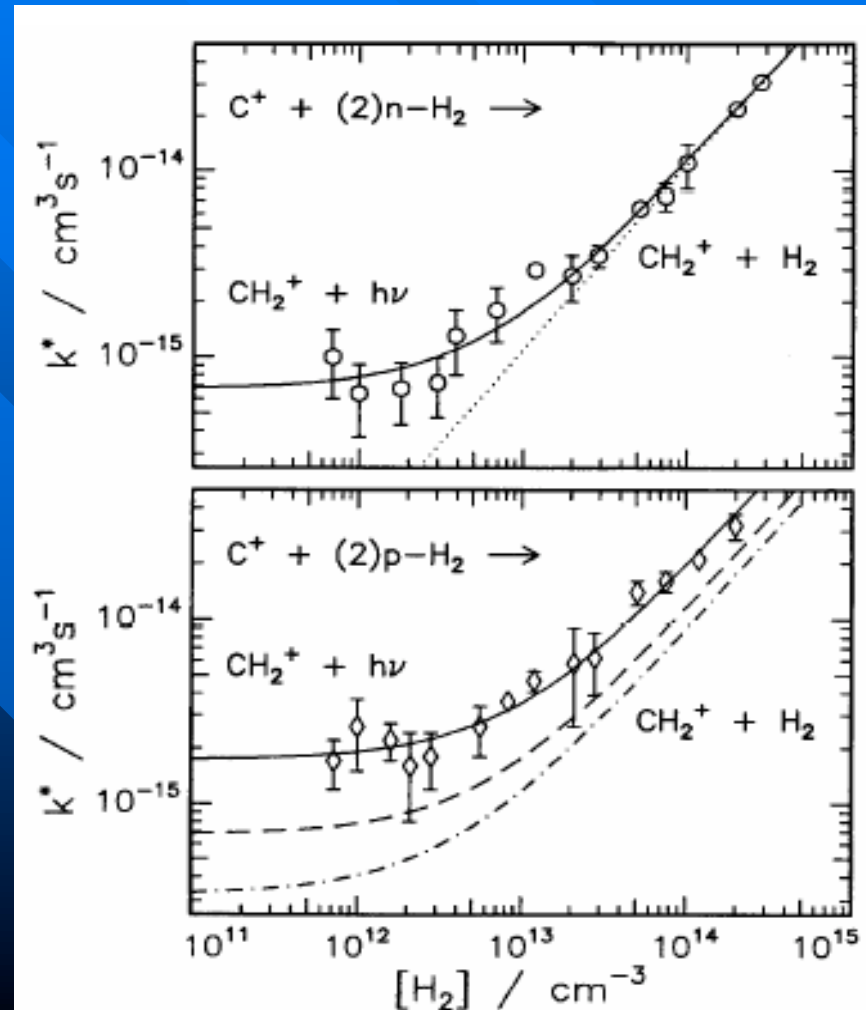
Rate Coefficients ( $\propto T^n$ ) /  $10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$

Reactants	298 K	Range of ( $T/K$ )	$n$
$\text{CH} + \text{N}_2 + \text{Ar}$	0.16	53 – 584	- 2.2
$\text{CH} + \text{CO} + \text{Ar}$	4.1	53 – 584	- 2.1
$\text{CH} + \text{H}_2 + \text{Ar}$	5.2	13 – 744	- 1.6
$\text{CN} + \text{NO} + \text{Ar}$	2.6	99 – 450	- 2.1
$\text{OH} + \text{NO} + \text{Ar}$	0.45	23 – 298	-2.6
$\text{OH} + \text{NO}_2 +$			
$\text{OH} + \text{butenes} +$	data at high-p limit only		

# Radiative Association and the ISM

*ca. 10 K (Gerlich)*

- Important processes either (a) involve  $\text{H}_2$  or (b) large species
- e.g.  $\text{C}^+ + \text{H}_2$  and  $\text{CH}_2^+ + \text{H}_2$  – rate coefficients measured in ion traps
- problems if excited electronic states might be involved: e.g.  $\text{C} + \text{C}_n$



# Categories of Reaction

- Ion-Molecule Reactions
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  - (b) radicals + radicals
- Radiative Association
  - {electron-molecule processes} **X**

# Neutral-Neutral Reactions: Summary of Experiments

- Canosa *et al.* list 93 reactions: 73 studied in continuous CRESU (Rennes, Birmingham, Bordeaux); 20 in pulsed CRESU (Arizona, Berkeley, Göttingen)
- Continuous CRESU reach as low as 13 K; pulsed CRESU to 53 K
- **Radicals:** B( $^2P_J$ ), C ( $^3P_J$ ), O ( $^3P_J$ ), Al ( $^2P_J$ ), and Si ( $^3P_J$ )  
CN, OH, CH, NH, C<sub>2</sub>(X), C<sub>2</sub>(a), C<sub>2</sub>H, C<sub>4</sub>H
- **Molecules:** alkenes/alkynes (52); saturated molecules (19); radicals (15); aromatics (2); others (5)

# T-dependence of rate coefficients

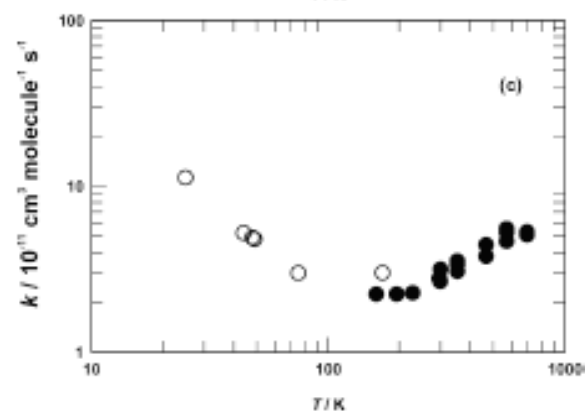
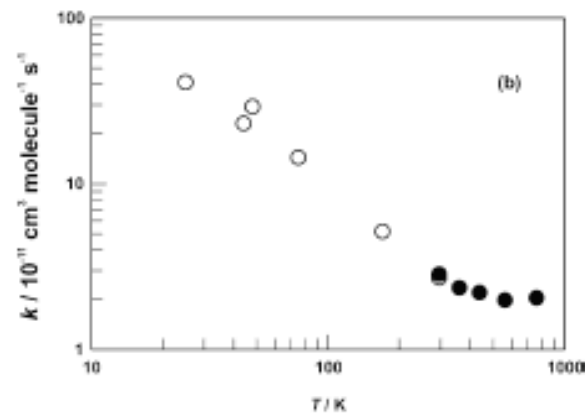
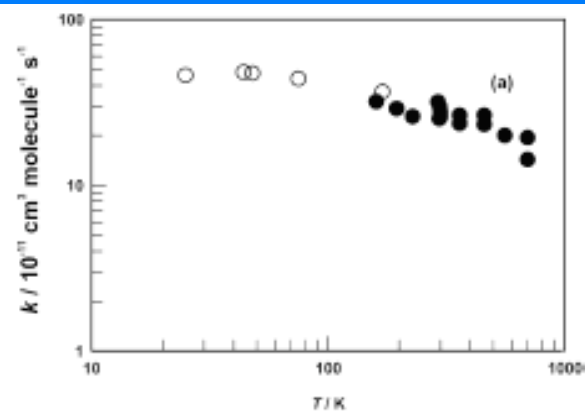
- 'all' fast low temperature reactions have  $k(298\text{ K}) > 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$



- the rate coefficients increase at lower temperatures – but form of  $k(T)$  versus  $T$  varies



- For nearly all reactions  $k(10\text{-}20\text{ K})$  are  $1 - 4 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$



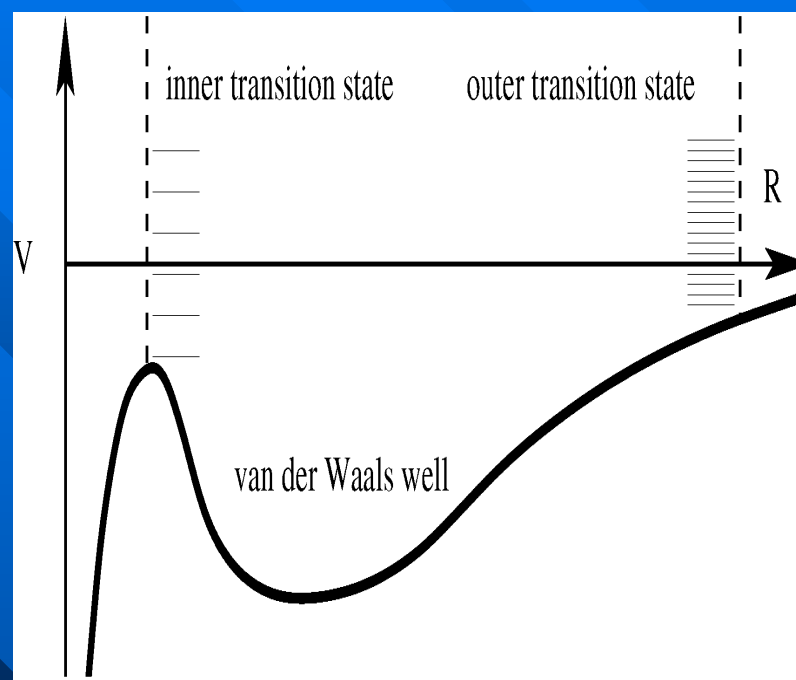


# Neutral-Neutral Reactions: Capture Theories

- Capture theories have been applied by Troe, Clary, Stoecklin, Klippenstein and others
- In contrast to ion-molecule reactions, the long-range attraction is much weaker so that maxima in effective potentials are at smaller separations
- Georgievskii and Klippenstein examined 26 neutral-neutral reactions by long-range TST (including all terms in long-range potential)
- They found that for 18 reactions  $k_{\text{calc}} > 1.5 \times k_{\text{expt}}$

# Two transition state model (Klippenstein)

- Rate coefficient may be limited by 'inner' transition state – which may have higher or lower value of  $V(R_{AB})$  but will have lower entropy
- Quantitative application requires:
  - (a) accurate long/medium range potential
  - (b)  $\mu J$  application of TST



# Two transition state model: CN + C<sub>2</sub>H<sub>6</sub>

Comparison between  
experimental and  $\mu J$ -TST  
calculations for



?? Can results be  
generalised ??

