

# Lecture 15

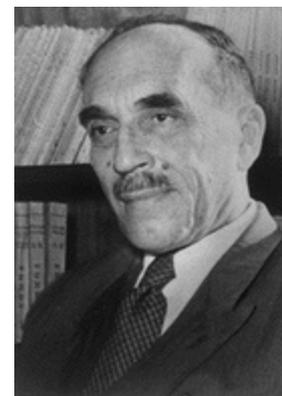
## Unimolecular reactions

How do they occur?

Look at the following reaction.



Sir Cyril Hinshelwood  
1897-1967, Nobel 1956



Nikolai Nikolaevic Semenov  
1896-1986, Nobel 1956



These are unimolecular reactions.

The reactant molecules somehow have enough energy to react by themselves. How can energy transfer occur without collisions?

The first successful explanation of unimolecular reactions is by Frederick Lindemann in 1921 and elaborated later by Cyril Hinshelwood. This mechanism is called as Lindemann- Hinshelwood mechanism.

The generalised explanation is as follows.

The reactant molecule A gets activated by collisions with another molecule.



Collisions with other molecule can result in loss of this energy.



Some activated molecules may form products.



In case the unimolecular decay is slow, the net reaction is first order.

This can be demonstrated by applying steady state for the formation of  $A^*$ .

$$d[A^*]/dt = k_a[A]^2 - k'_a[A][A^*] - k_b[A^*] \approx 0$$

Solution is,

$$[A^*] = k_a[A]^2 / \{k_b + k'_a[A]\}$$

The rate law for the formation of P is,

$$d[P]/dt = k_b[A^*] = k_a k_b [A]^2 / \{k_b + k'_a [A]\}$$

As can be seen, the rate law is not first order.

The important aspect is that rate of deactivation of  $A^*$  by collisions with A is much larger than the rate of unimolecular decay.

$$k'_a [A^*][A] \gg k_b [A^*] \text{ or } k'_a [A] \gg k_b$$

Thus we can neglect  $k_b$  in the denominator and write,

$$d[P]/dt \approx k[A] \quad \text{where} \quad k = k_a k_b / k'_a$$

This is a first order rate law.

The rate expression also shows that when the concentration (partial pressure) of A is small, then  $k'_a [A] \ll k_b$ , we get

$$d[P]/dt \approx k_a [A]^2$$

If we write the rate expression as,

$$d[P]/dt = k[A]$$

where

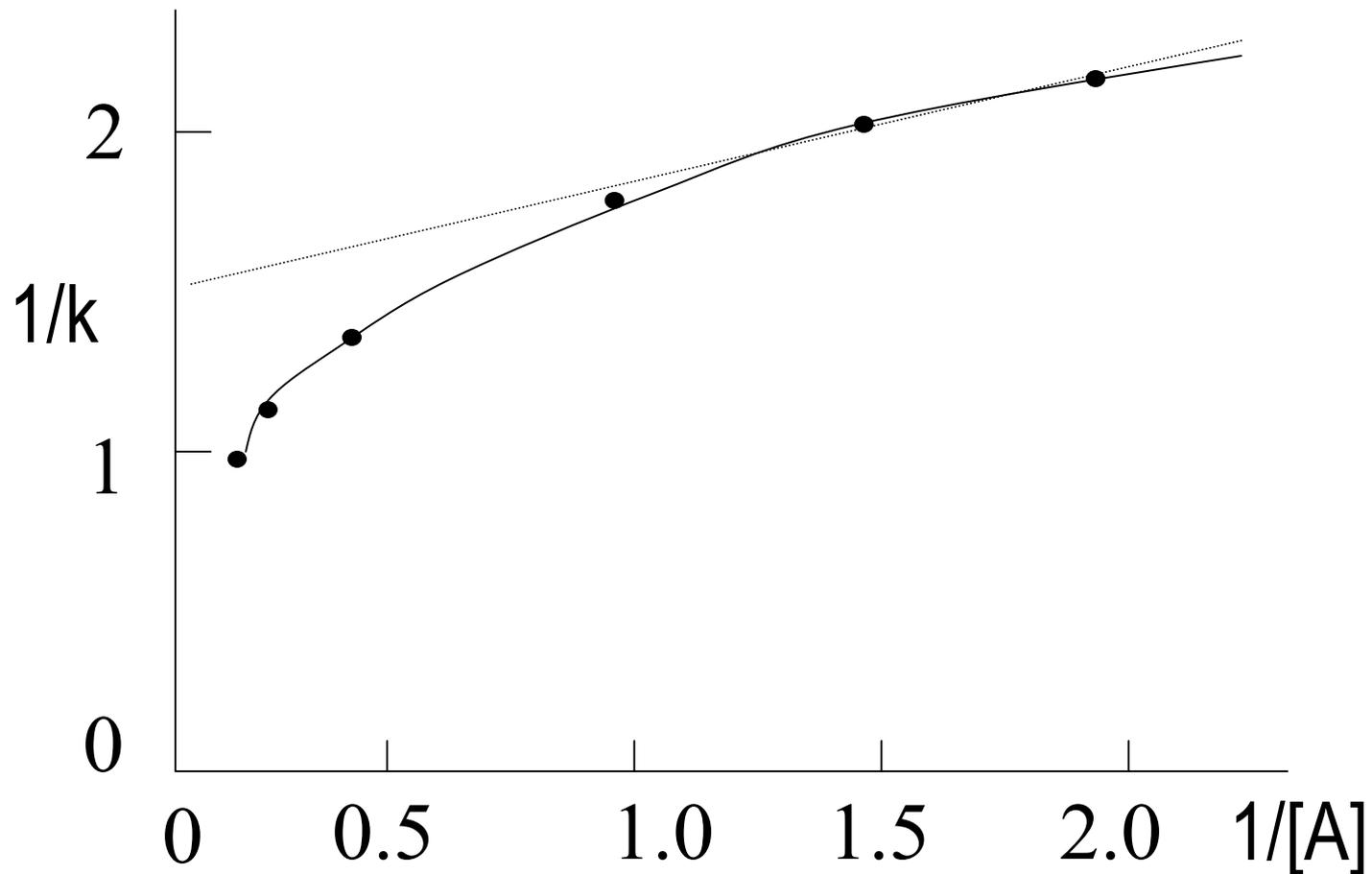
$$k = k_a k_b [A] / \{k_b + k'_a [A]\}$$

The effective rate constant is,

$$1/k = k'_a / (k_a k_b) + 1/k_a [A]$$

The test for the theory is to get a straight line for  $1/k$  vs.  $1/[A]$  plot.

A typical plot is seen below.



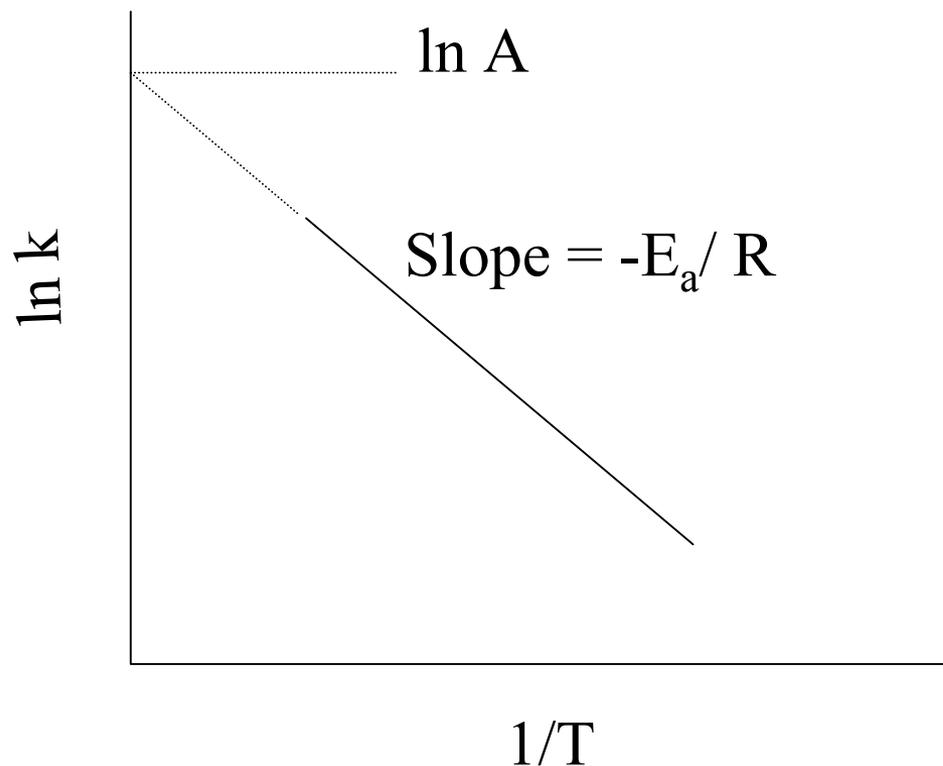
The behaviour is in gross agreement with the theory. At high pressures (lower  $1/[A]$ ) the value of  $k$  is higher (lower  $1/k$ ) than expected from a linear behaviour. The reaction studied is the unimolecular isomerization of trans-CHD=CHD. The Lindemann-Hinshelwood mechanism is the straight line, extrapolation from lower pressure (larger  $1/[A]$ ) to higher pressure (smaller  $1/[A]$ ).

# Temperature dependence of reaction rate

The reaction rates generally increase many fold by increasing temperature by 10 C. In a number of cases, it doubles. The behaviour is quantitatively represented by an equation called, Arrhenius equation.

$$\ln k = \ln A - E_a/RT$$

or  $k = Ae(-E_a/RT)$



A is called the pre-exponential factor or the frequency factor. The slope of the line is  $-E_a/R$ .  $E_a$  is called the activation energy. Both these quantities collectively are called Arrhenius parameters.

In several cases this behaviour is found to hold good. There are also cases where Arrhenius behaviour, in the sense that linear graph of  $\ln k$  vs.  $1/T$ , is not seen. Yet it is possible to define an activation energy for such cases as,  $E_a = RT^2(d\ln k/dT)$ . This equation is the same as the previous one, just that  $E_a$  is not a constant. Here  $E_a$  has to be defined at a specific temperature.

# The activation energy of a composite reaction

Rates of reactions increase with temperature for positive  $E_a$ . Rate of each step may increase with temperature. But how about the rate of a composite reaction?

In the L-H mechanism above, consider the composite rate constant  $k$ .

$$k = k_a k_b / k'_a = (A(a)e^{-E_a(a)/RT}) (A(b)e^{-E_a(b)/RT}) / (A'(a)e^{-E'_a(a)/RT}) \\ = \{A(a)A(b)/A'(a)\} \{e^{-\{E_a(a)+E_a(b)-E'_a(a)\}/RT}\}$$

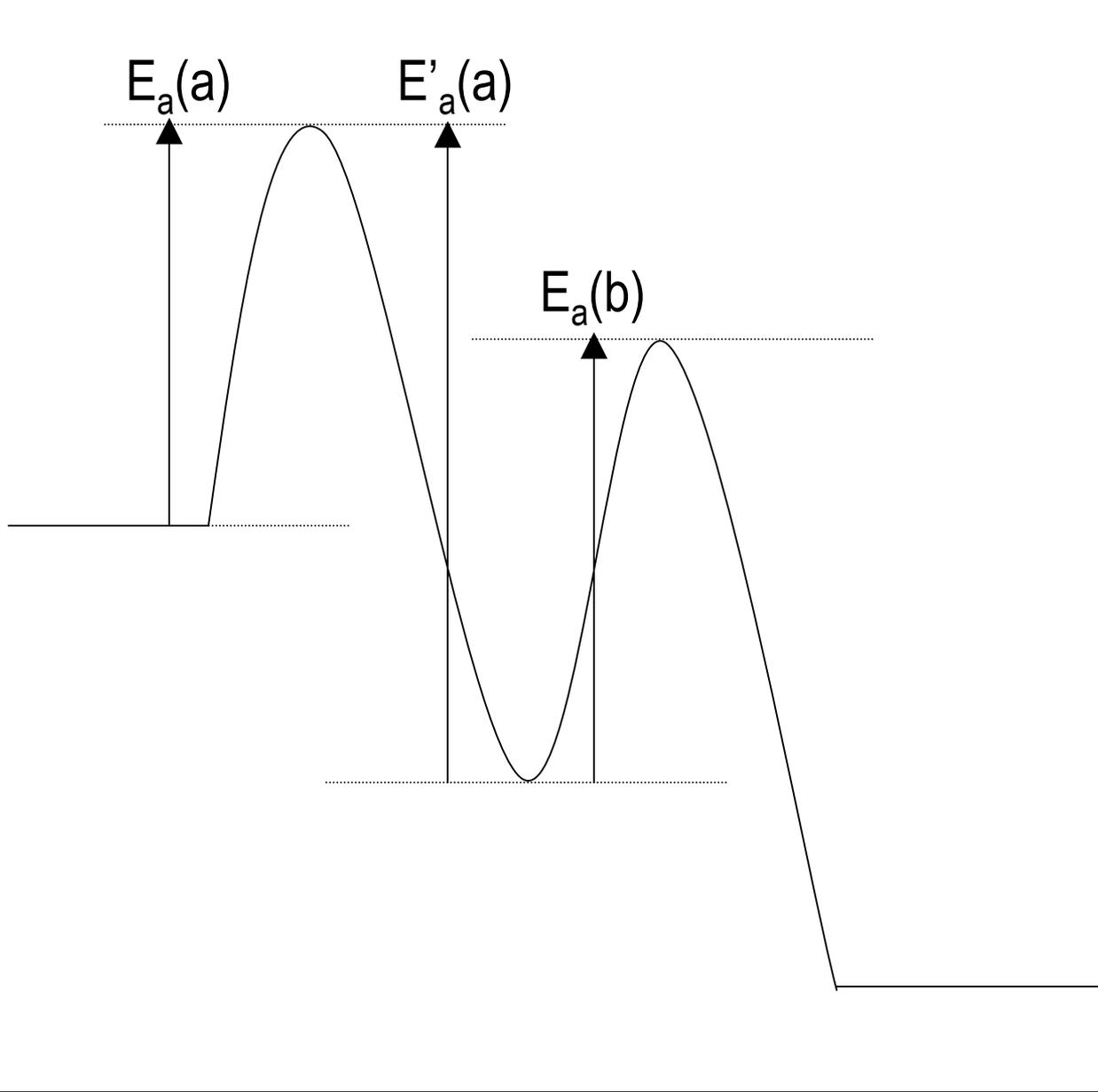
Composite rate constant  $k$  has an activation energy,

$$E_a = E_a(a) + E_a(b) - E'_a(a)$$

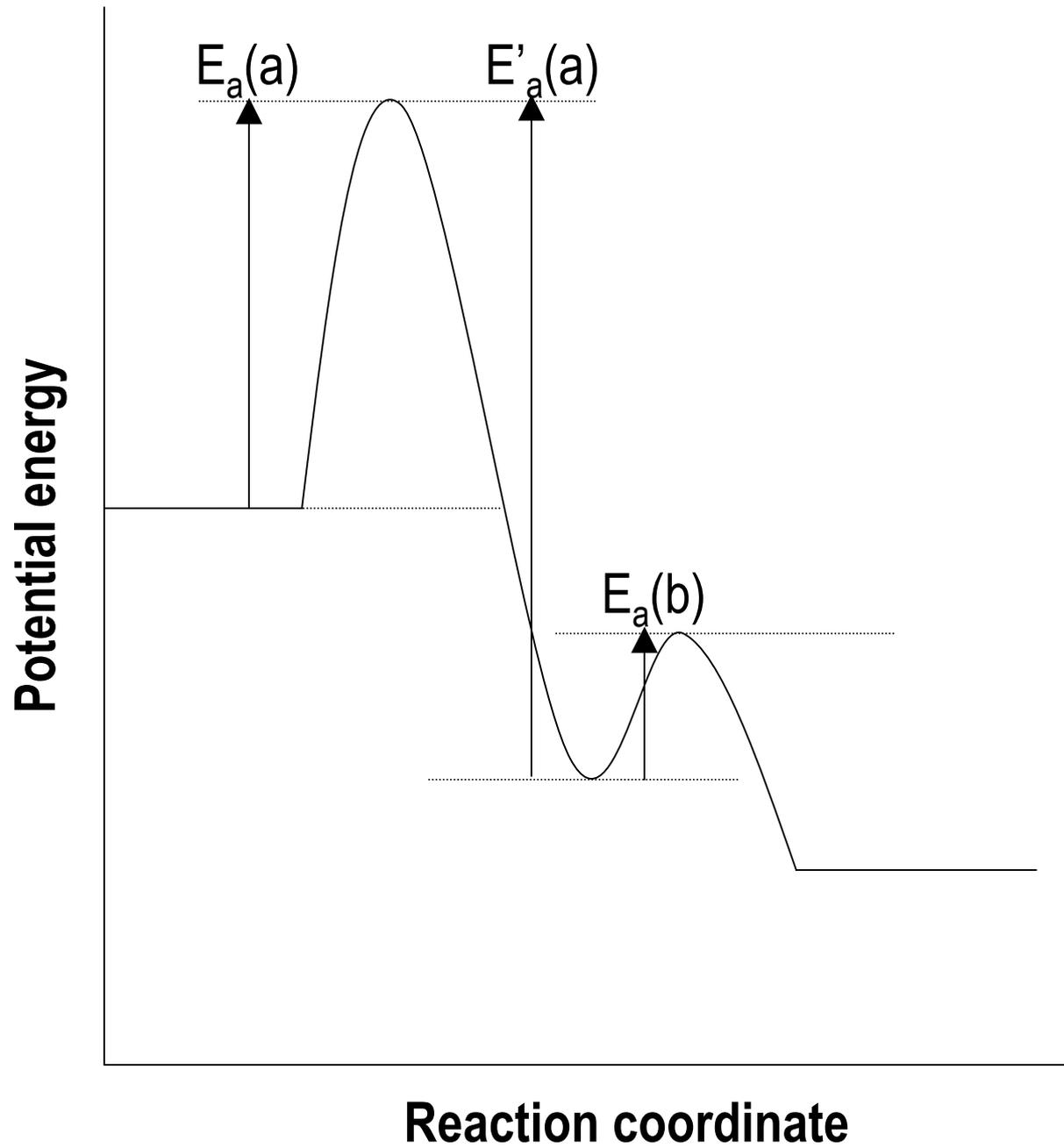
If  $E_a(a) + E_a(b) > E'_a(a)$ , the activation energy is positive.

In the opposite case the activation energy is negative and the rate will decrease with temperature. The cases with overall positive and negative activation energies are depicted below.

Potential energy



Reaction coordinate



## Concept of reaction coordinate

$A + B \longrightarrow C$  what is the reaction coordinate?

Reaction occurs along a path

This path can be simplified to a molecular coordinate

The variation in the energy of the system is due to this change in coordinate

