

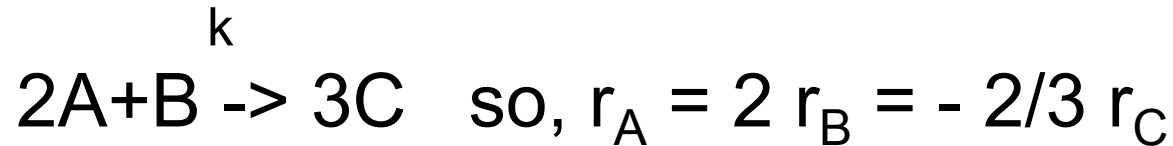
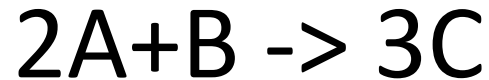
# 1<sup>st</sup> order reaction

$$-r_i = k * C_i$$

$$-r_i = k * C_{i0} * (1-X)$$

$$-r_i = k * (C_{i0} + v_i \xi / V) \quad (V = \text{volume of reaction mixture})$$

# Irreversible elementary rxn



Assume  $r_A = -2 \text{ mol/cm}^3/\text{sec}$ , so

$$r_B = ?$$

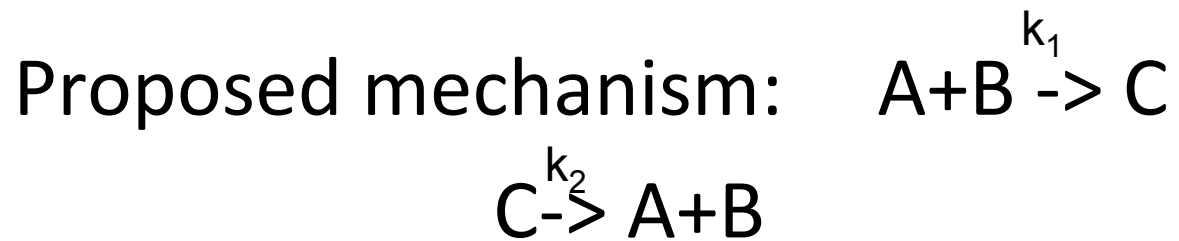
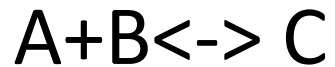
$$r_C = ?$$

The rate equations must also be consistent, so  
assuming  $r_A = -k[A]^2[B]$ , then

$$r_B = ?$$

$$r_C = ?$$

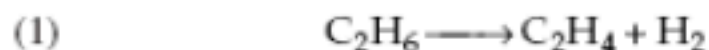
# Reversible elementary rxn



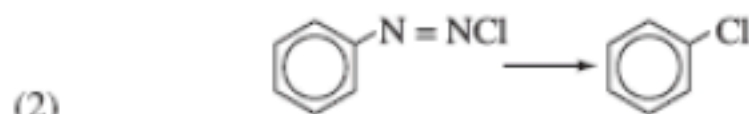
Note that stoichiometry is correct

$r_A, r_B, r_C?$

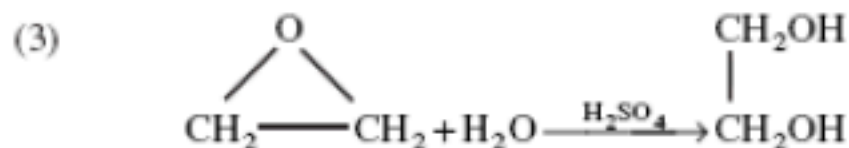
## A. First-Order Rate Laws



$$-r_A = kC_{\text{C}_2\text{H}_6}$$



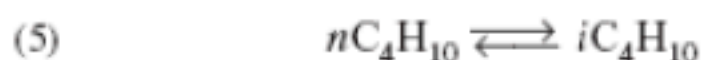
$$-r_A = kC_{\phi\text{N}-\text{NO}_2}$$



$$-r_A = kC_{\text{CH}_2\text{OCH}_2}$$

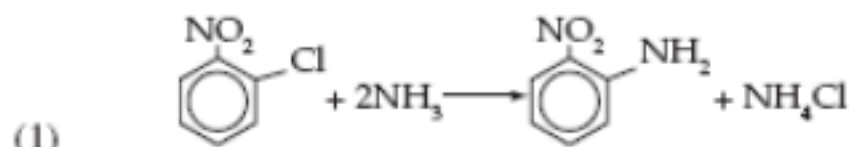


$$-r_A = kC_{\text{CH}_3\text{COCH}_3}$$

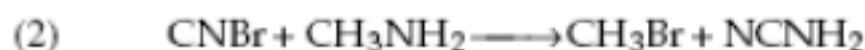


$$-r_n = k[C_{nC_4} - C_{iC_4}/K_C]$$

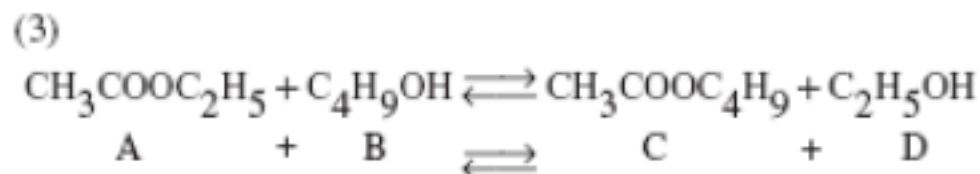
## B. Second-Order Rate Laws



$$-r_A = k_{\text{ONCB}} C_{\text{ONCB}} C_{\text{NH}_3}^{\dagger}$$



$$-r_A = kC_{\text{CNBr}} C_{\text{CH}_3\text{NH}_2}$$



$$-r_A = k[C_A C_B - C_C C_D / K_C]$$

# Arrhenius' Law

For many reactions, and particularly elementary reactions, the rate expression can be written as a product of a temperature-dependent term and a composition-dependent term, or

$$\begin{aligned}r_i &= f_1(\text{temperature}) \cdot f_2(\text{composition}) \\ &= k \cdot f_2(\text{composition})\end{aligned}\tag{33}$$

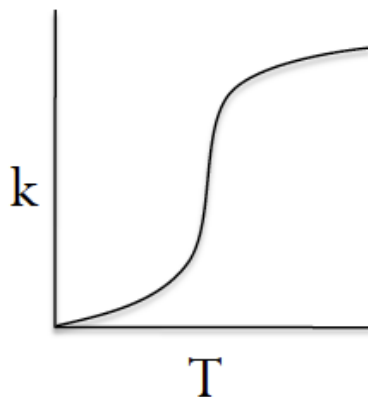
Why do reaction rates depend on temperature, pressure and concentration? (molecular behaviors)

# Arrhenius' Law

For such reactions the temperature-dependent term, the reaction rate constant, has been found in practically all cases to be well represented by Arrhenius' law:

$$k = k_0 e^{-E/RT} \quad (34)$$

where  $k_0$  is called the frequency or pre-exponential factor and  $E$  is called the activation energy of the reaction.\* This expression fits experiment well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency.



## Reaction rate modeling

### Temperature dependence of collision and transition theories

Using the reaction scheme  $A + B \xrightleftharpoons[k_2]{k_1} AB^* \xrightarrow{k_3} C$

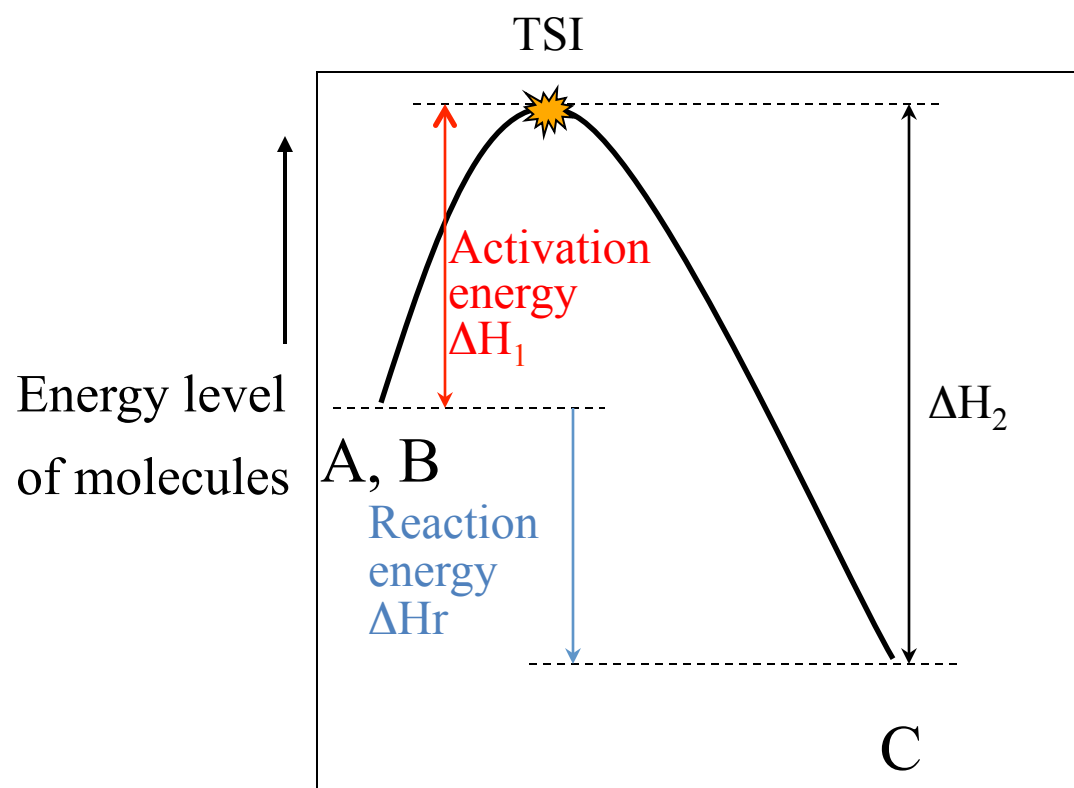
$-r_A = (\% \text{ collisions with } E \text{ [sufficient energy to react]})$   
(collision rate)

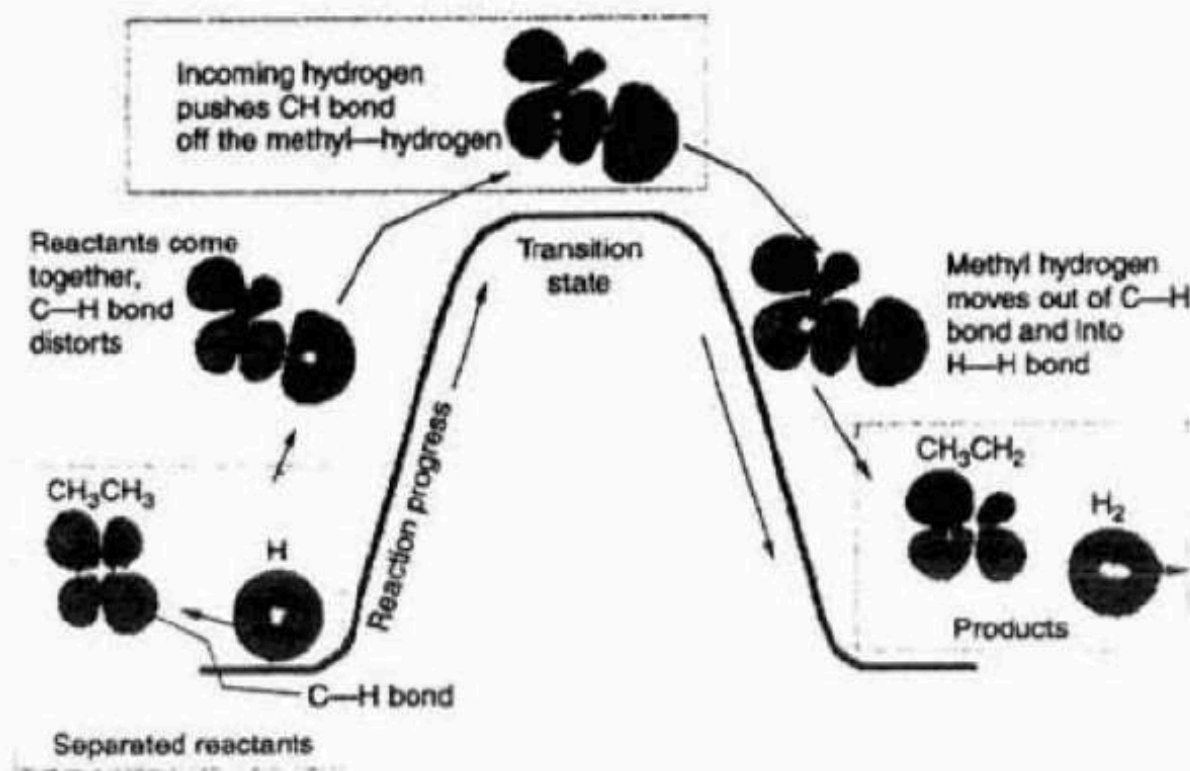
$$= k C_A C_B$$

$k$  is proportional to  $e^{-E/RT}$ , i.e.  $k = k_0 * e^{-E/RT}$

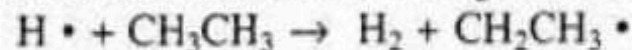


For the reaction to occur, the reactants must overcome an energy barrier (activation energy)





**Figure 3-2** A diagram of the orbital distortions during the reaction



The diagram shows only the interaction with the energy state of ethane (the C-H bond). Other molecular orbitals of the ethane also distort. [Courtesy of R. Masel, *Chemical Kinetics* (McGraw Hill, 2002), p. 594.]

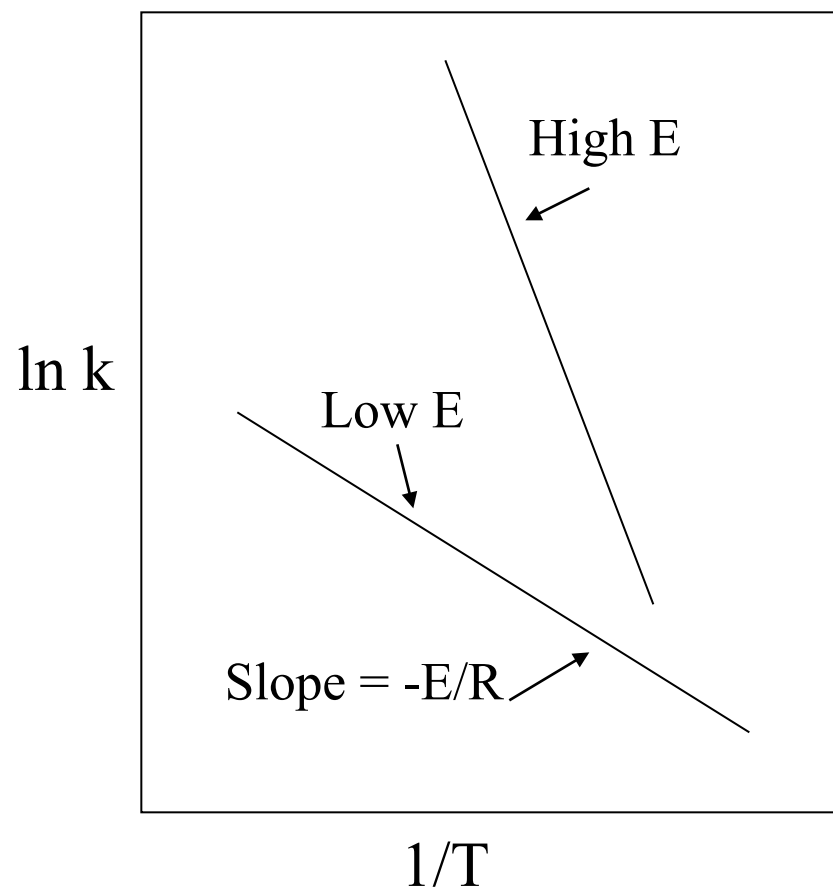
## Temperature dependence of collision and transition theories

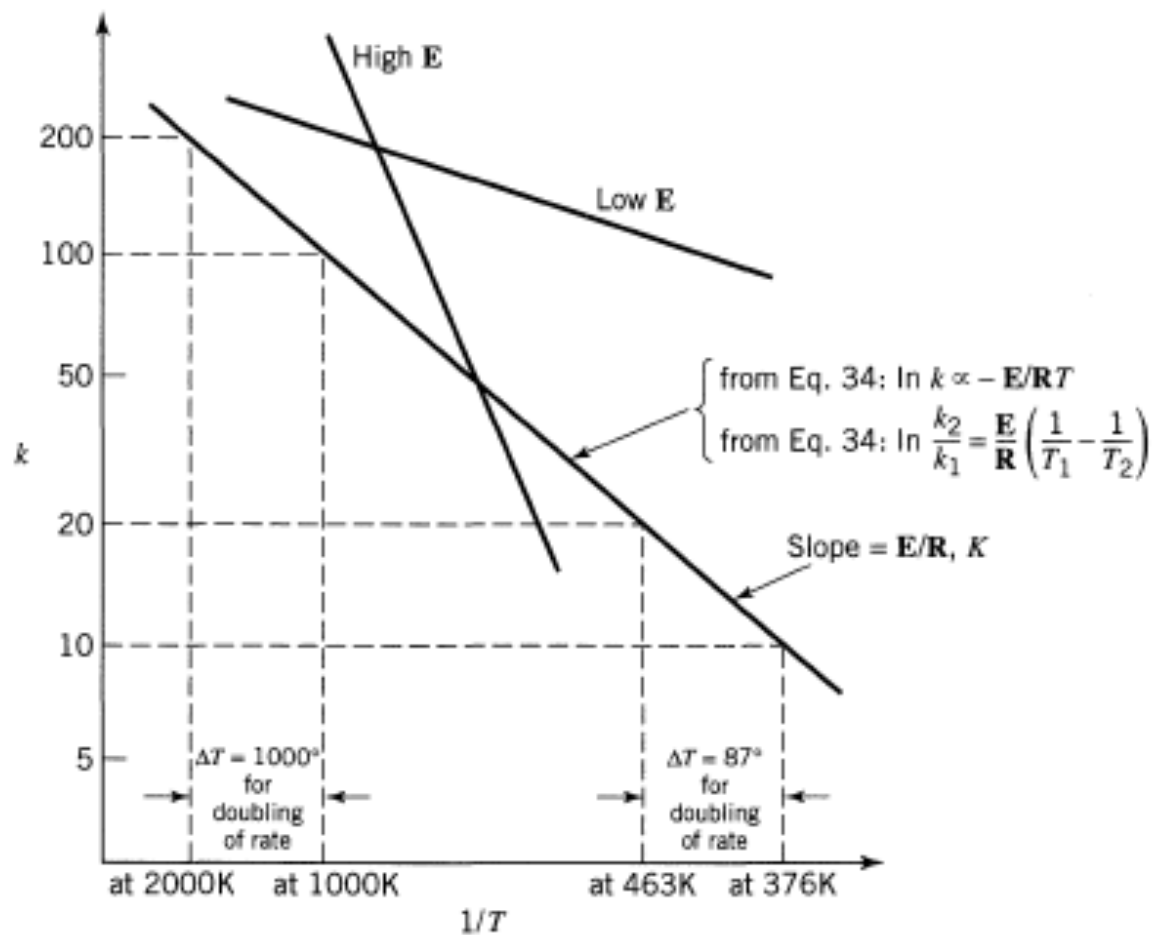
This simplified dependence on temperature allows us to plot  $\ln k$  vs.  $T$  (absolute temp) and obtain estimates of the energy of activation of the reaction

Note that due to the log scale, reactions are more sensitive to changes at low  $T$  vs. high  $T$

$$\ln(r_2/r_1) = E/R (1/T_1 - 1/T_2)$$

provided  $E$  stays constant





Reactions with high activation energies are very temperature-sensitive

**Table 2.1** Temperature Rise Needed to Double the Rate of Reaction for Activation Energies and Average Temperatures Shown<sup>a</sup>

Average Temperature	Activation Energy <b>E</b>			
	40 kJ/mol	160 kJ/mol	280 kJ/mol	400 kJ/mol
0°C	11°C	2.7°C	1.5°C	1.1°C
400°C	65	16	9.3	6.5
1000°C	233	58	33	23
2000°C	744	185	106	74

<sup>a</sup> Shows temperature sensitivity of reactions.

# Example

Milk is pasteurized if it is heated to  $63^{\circ}\text{C}$  for 30 min, but if it is heated to  $74^{\circ}\text{C}$  it only needs 15 s for the same result. Find the activation energy of this sterilization process.

To ask for the activation energy of a process means assuming an Arrhenius temperature dependency for the process. Here we are told that

$$t_1 = 30 \text{ min} \quad \text{at a} \quad T_1 = 336 \text{ K}$$

$$t_2 = 15 \text{ sec} \quad \text{at a} \quad T_2 = 347 \text{ K}$$