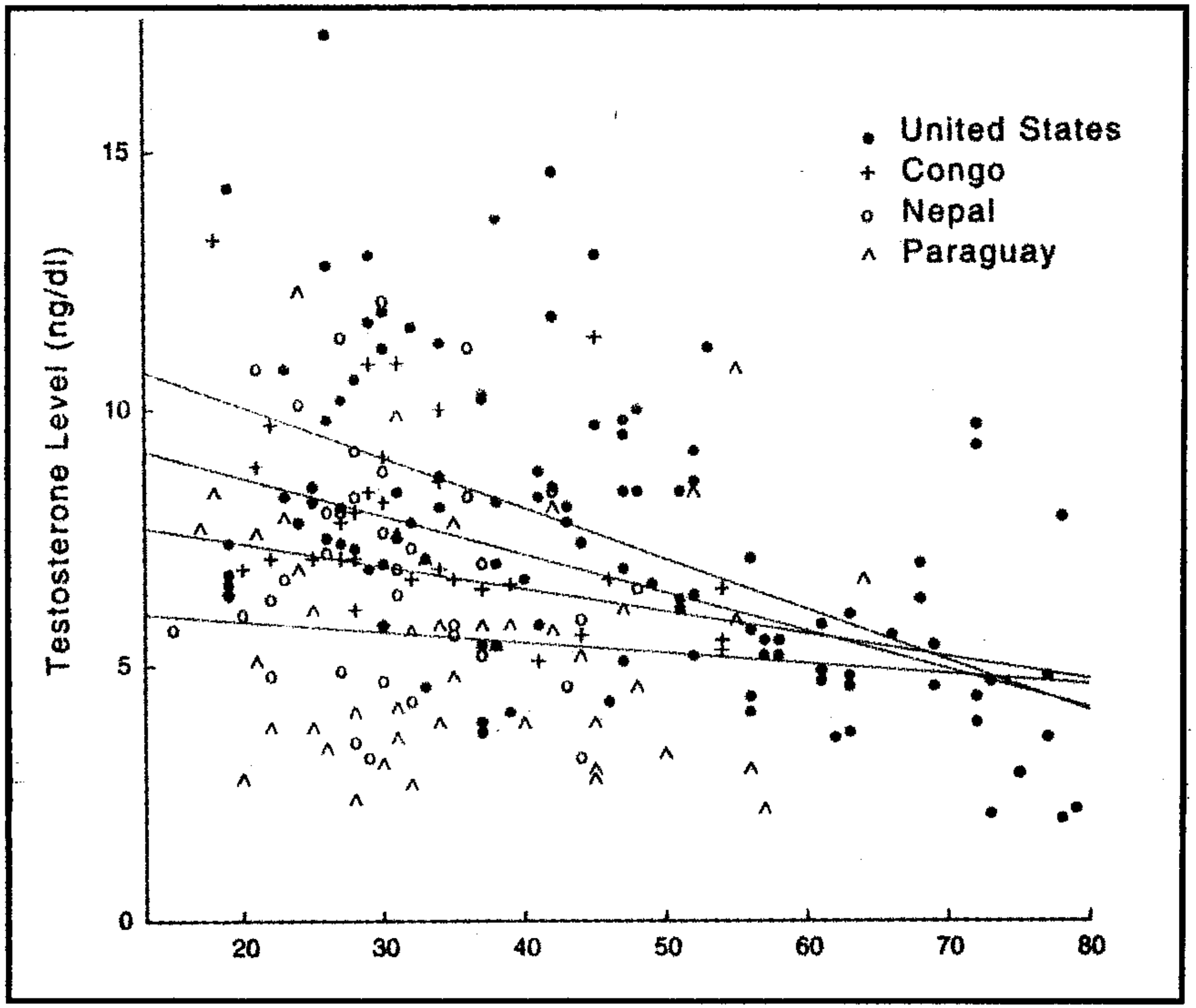
LECTURE 34/36 DEC-2-02

— ARRHENIUS EQ.

— THEORY

FIREFLY RXN

tant functions in both men and women. Among other things, it signals the body to build muscle, make new red blood cells, and release neurotransmitters in the brain, where it exerts a powerful influence on our perceptions of ourselves and the world around us.



Decline in testosterone levels across the life span in different populations.

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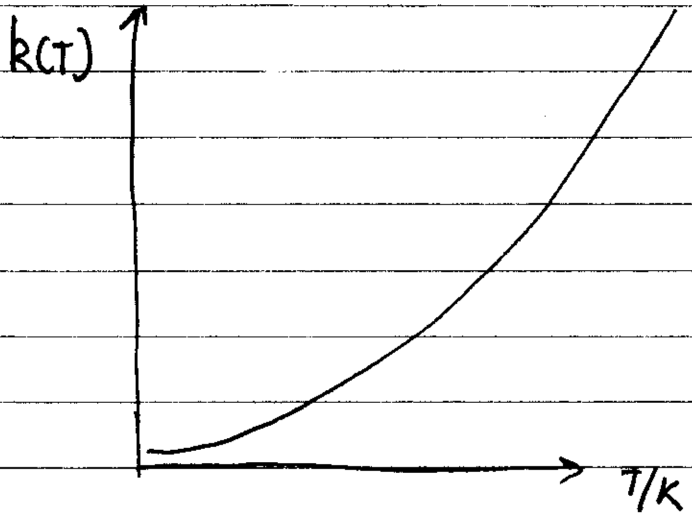
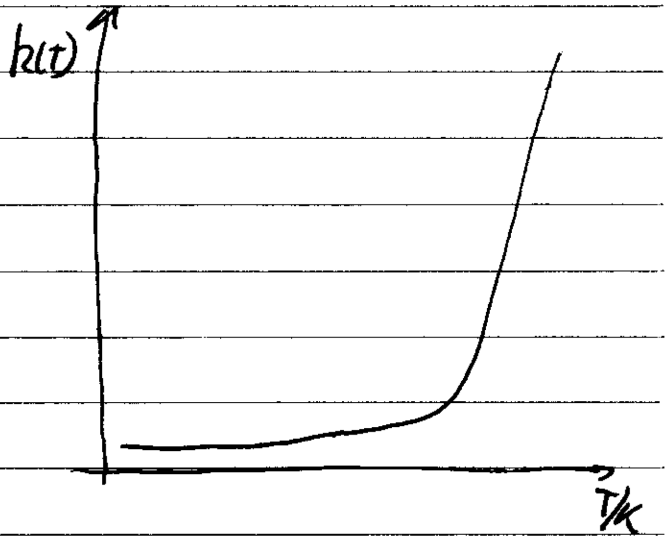
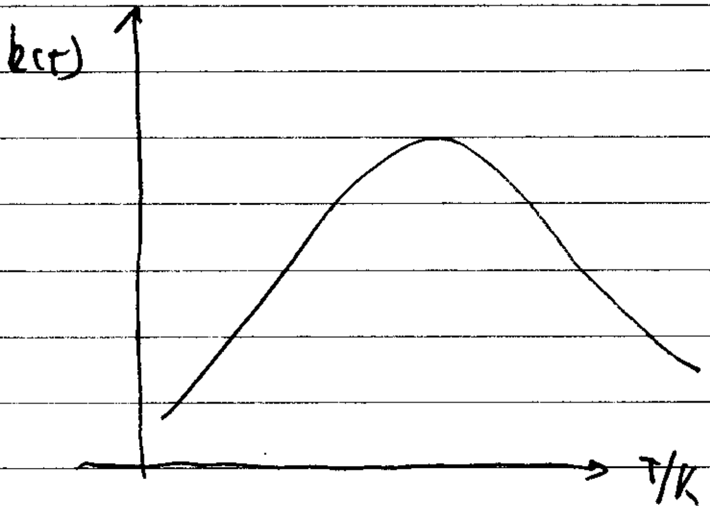
RATE CONSTANT ARE TEMPERATURE DEPENDENT.



USUAL



EXPLOSION



ENZYMATIC RXN

ARRHENIUS EQ. FOR THE FORWARD OR BACKWARDS RATE CONSTANTS

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$$

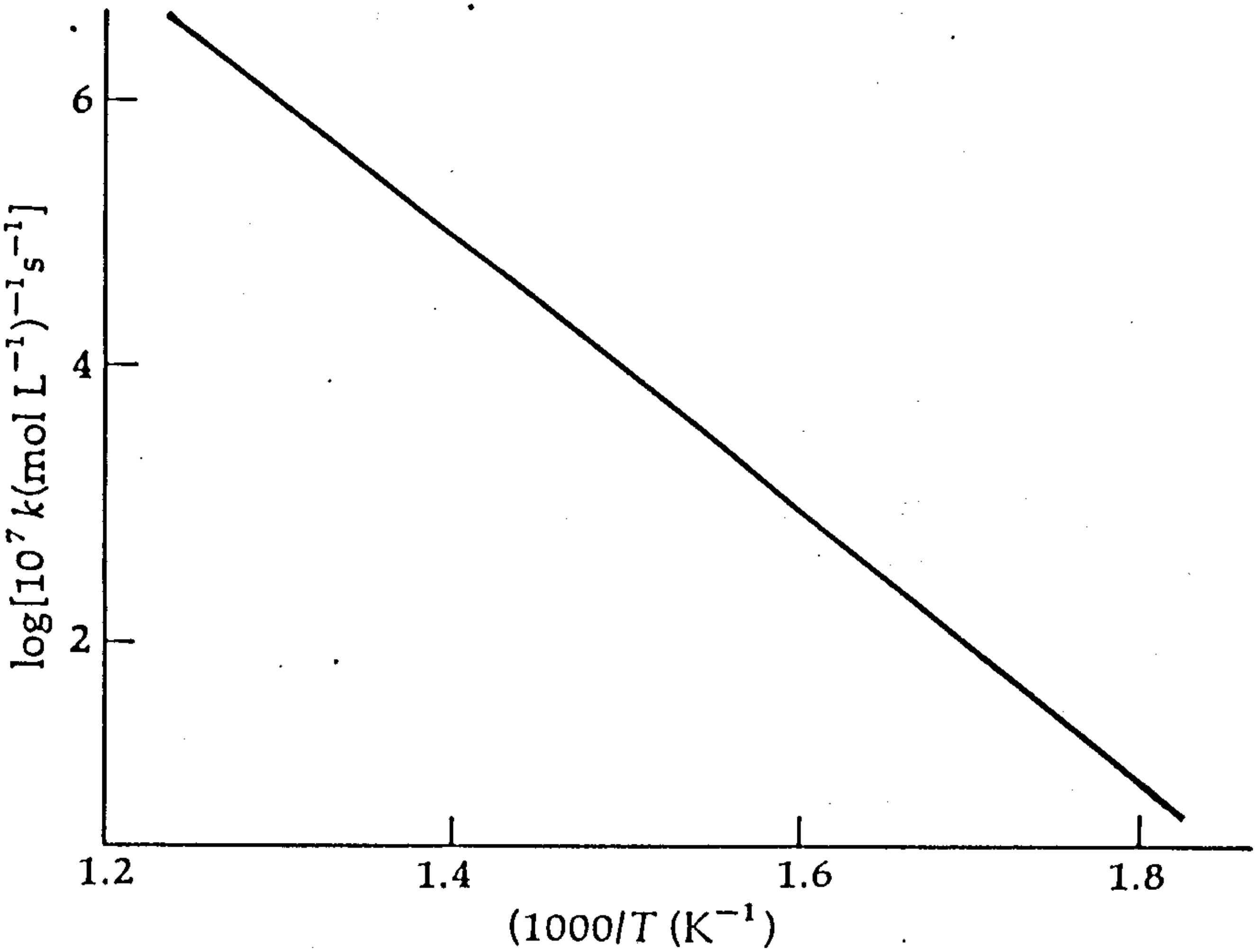


FIGURE 14.8
Arrhenius plot of the temperature dependence of the rate constant of the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$. When log k is plotted versus $1/T$, the slope of the line is equal to $-E_a/2.303R$, and the intercept is equal to log A.

SVANTE ARRHENIUS

EMPIRICAL EQ.

$$\frac{d}{dT} \ln k = \frac{E_a}{RT^2}$$

WHERE T IS THE ABSOLUTE TEMP AND E_a IS THE ACTIVATION ENERGY.

IF WE INTEGRATE WE GET

$$\ln k = \ln A - \frac{E_a}{RT}$$

OR

$$k(T) = A e^{-\frac{E_a}{R}\frac{1}{T}}$$

IF WE

FOR EXAMPLE CONSIDER

$$2\,HI(g) \longrightarrow H_2(g) + I_2(g)$$

WE FIND

$$E_a = 184 \frac{kJ}{mol}$$

AND

$$A = 7.94 \times 10^{10}\ M^{-1} s^{-1}.$$

TYPICALLY WE DETERMINE THE RATE CONSTANT AT TWO DIFFERENT TEMP TO ESTIMATE THE ACTIVATION ENERGY

$$k(T_1) = A\,e^{-\frac{E_a}{RT_1}}$$

$$k(T_2) = A\,e^{-\frac{E_a}{RT_2}}$$

OR

$$\frac{k(T_1)}{k(T_2)} = e^{-\frac{E_a}{RT_1} + \frac{E_a}{RT_2}}$$

$$\boxed{\ln\left[\frac{k(T_1)}{k(T_2)}\right] = -\frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

FOR SOME RXN THE PLOT $\ln k$ VS $1/T$ IS NOT LINEAR BUT

$$k(T) = aT^m e^{-\frac{E_a}{RT}}$$

WHERE a AND E_a ARE TEMPERATURE INDEPENDENT CONSTANT. THE VALUE OF m IS HARD TO DETERMINE DUE TO THE LOG COMPRESSION $\ln T$, AND THE EXPONETIAL DEPENDENCE.

$$\ln k = \ln a + m \ln T - \frac{E_a}{RT}$$

THE ARRHENIUS EQUATION APPLIES TO MANY PROCCESSES OFTEN CALLED THERMALLY ACTIVATED PROCESSES

IF WE CONSIDER THE ADSORPTION OF PARTICLES ON A SURFACE, THE 2-D DIFFUSION PROCESS IS THERMALLY ACTIVATED

$$D = D_0 e^{-\frac{E_a}{RT}}.$$

MOREOVER, DEPENDING ON THE VALUE OF E_a WE CAN CLASSIFY THE ADSORPTION AS PHYSISORPTION OR CHEMISORPTION, WHERE $E_a^{PS} < E_a^{CS}$. IN THIS CASE DIFFUSION IS VIEW AS A HOPPING PROCESS.

CRICKETS CHIRP AT A RATE

$$r = r_0 e^{-\frac{E_a}{RT}}.$$

THUS THE CHIRPING RATE CAN GIVE US AN ESTIMATE OF THE TEMPERATURE.

THERMALLY ACTIVATED PROCESSES

a) ETHANE HYDROGENOLYSIS ON SILICA-SUPPORTED METALS

21 ~ 58 kcal/mol

b) ELECTRON CONDUCTIVITY

OXIDE SEMICONDUCTORS 0.3 -0.5 eV/PART

$\frac{eV}{PART} \sim 23 \frac{kcal}{mol}$

$7 - 12 \frac{kcal}{mol}$

OXIDIZED CHOLESTEROL COMPLEXES

0.8 — 3.0 eV/PART

c) DEATH-RATE VS. TEMPERATURE

SOLUTION OF SINDIBIS VIRUS (COULD CHANGE
BACTERIA SOLUTE)
YEAST

d) DENATURATION OF PARTICLES

HEMOGLOBIN EGG ALBUMIN INVERTASE

BIO POLYMERS AT DIFFERENT pH

(CRICKETS) RATE OF CHIRPING	~ 12 Kcal/mol
(FIREELYES) RATE OF FLASHING	~ 17 Kcal/mol
FREQ. OF HUMAN α-BRAIN WAVES (BODY TEMP).	~ 7 Kcal/mol

LET US CONSIDER A BINARY REACTION

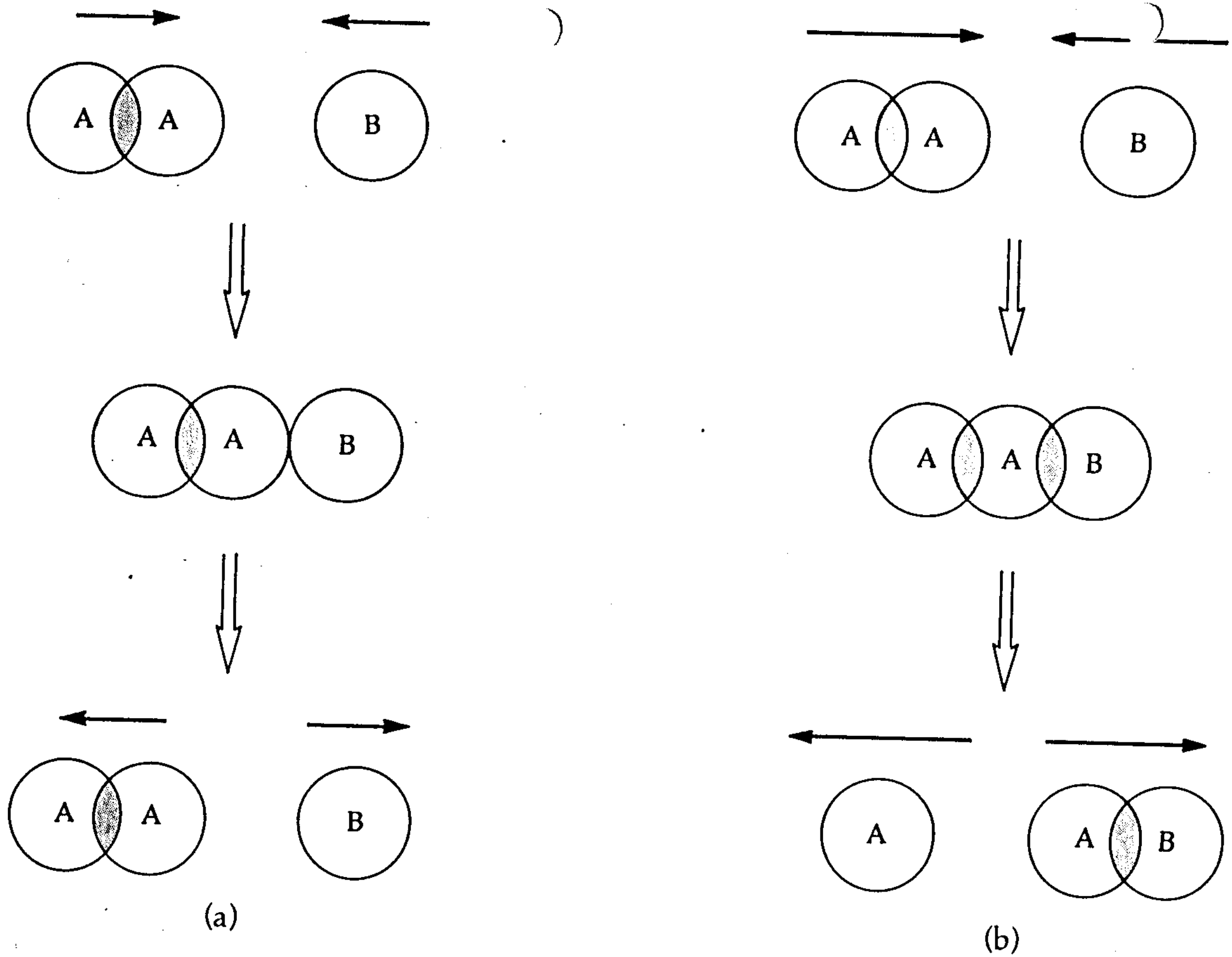
$$A + B \xrightarrow{k} C + D.$$

A MICROSCOPIC MODEL SHOULD ASSUMES THAT A BINARY REACTION IS RELATED TO A BINARY COLLISION. THUS WE SHOULD FIRST CALCULATE THE COLLISION FREQUENCY Z_{AB}.

FROM KINETIC THEORY

$$Z_{AB} = \sqrt{2}\,\pi d^2 \bar{v} [A][B]$$
$$\equiv k_{COLL} [A][B].$$

TYPICALLY $k_{COLL}(T) = 10^{11}\ M^{-1}S^{-1}$ AT 273 K. IF WE NOW COMPARE THIS VALUE WITH THE EXPERIMENTAL VALUES, WE CONCLUDE THAT k_{COLL} IS THE MAXIMUM POSSIBLE RATE.



(a)

(b)

FIGURE 14.11 Possible outcomes of the collision between two molecules. (a) The molecules collide with low relative velocity and bounce off before their electron clouds interpenetrate significantly. (b) The molecules collide with high relative velocity. The A—A bond is broken, and an A—B bond is formed. The reaction is $A_2 + B \rightarrow A + AB$.

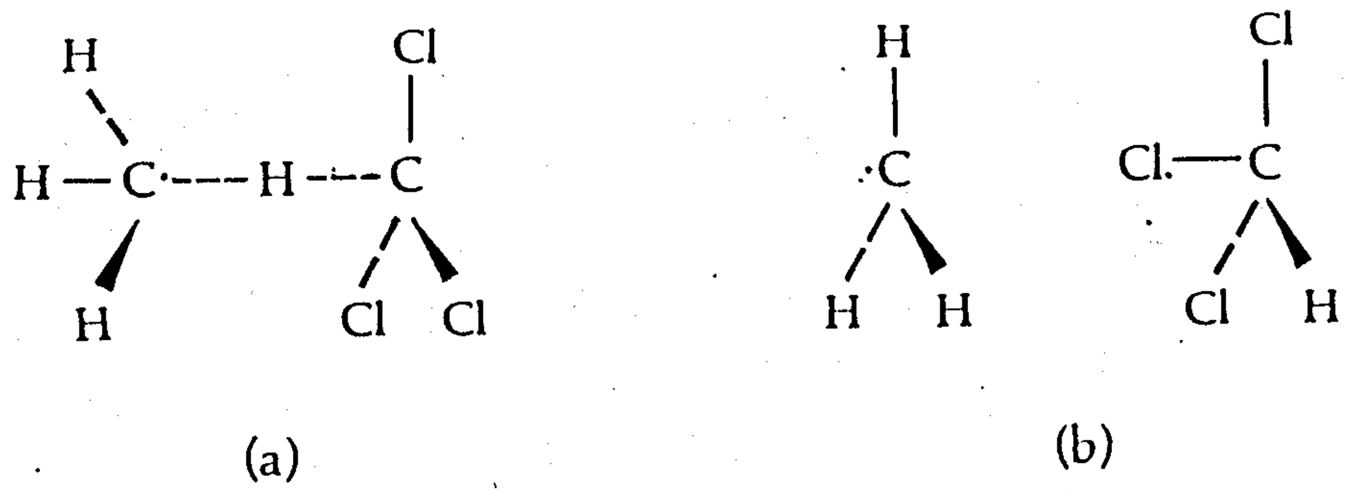


FIGURE 14.10 Two possible relative orientations of a CH_3 radical and a $CHCl_3$ molecule in the reaction to form CH_4 and CCl_3: (a) the geometry favors the reactio the dashed lines represent the new and the old C—H bonds in the act of being formed and broken, respectively; (b) the geometry disfavors the reaction—the carb and hydrogen atoms are on opposite sides of the approaching molecules.

ACTUALLY WE HAVE TO CONSIDER THAT A MINIMUM KINETIC ENERGY IS NECESSARY FOR THE REACTION TO OCCURR. THE ENERGY IS REQUIRED TO OVERCOME THE REPULSION FORCES SO THE ELECTRON CLOUDS OVERLAP. THE OVERLAPPING RESULTS IN BOND BREAKING AND BOND FORMING. THE MINIMUM ENERGY REQUIRED IS THE SO-CALLED ACTIVATION ENERGY.

FROM KINETIC THEORY WE KNOW THAT MOLECULAR COLLISIONS INDUCE A DISTRIBUTION OF VELOCITIES. THIS DISTRIBUTION IS GIVEN BY THE MAXWELL-BOLTZMAN DISTRIBUTION.

ONLY THE TAIL OF THE DISTRIBUTION HAS ENOUGH ENERGY TO REACT. THEREFORE THE FRACTION OF PARTICLES WITH ENERGY EQUAL OR GREATER THAN THE ACTIVATION ENERGY, E_a, HAS AN EXPONENTIAL FACTOR

$$e^{-E_a/RT}.$$

FINALLY, ORIENTATION HAS AN IMPORTANT ROLE. CONSEQUENTLY WE CAN DESCRIBE THE RATE CONSTANT AS:

$$R = \begin{pmatrix}\text{COLLISION}\\ \text{FREQ}\end{pmatrix} \otimes \begin{pmatrix}\text{FRAC OF COLLISION}\\ \text{WITH PROPER}\\ \text{ORIENTATION}\end{pmatrix} \otimes \begin{pmatrix}\text{FRACTION OF}\\ \text{COLLISIONS W/}\\ E_a \leq E\end{pmatrix}$$

OR

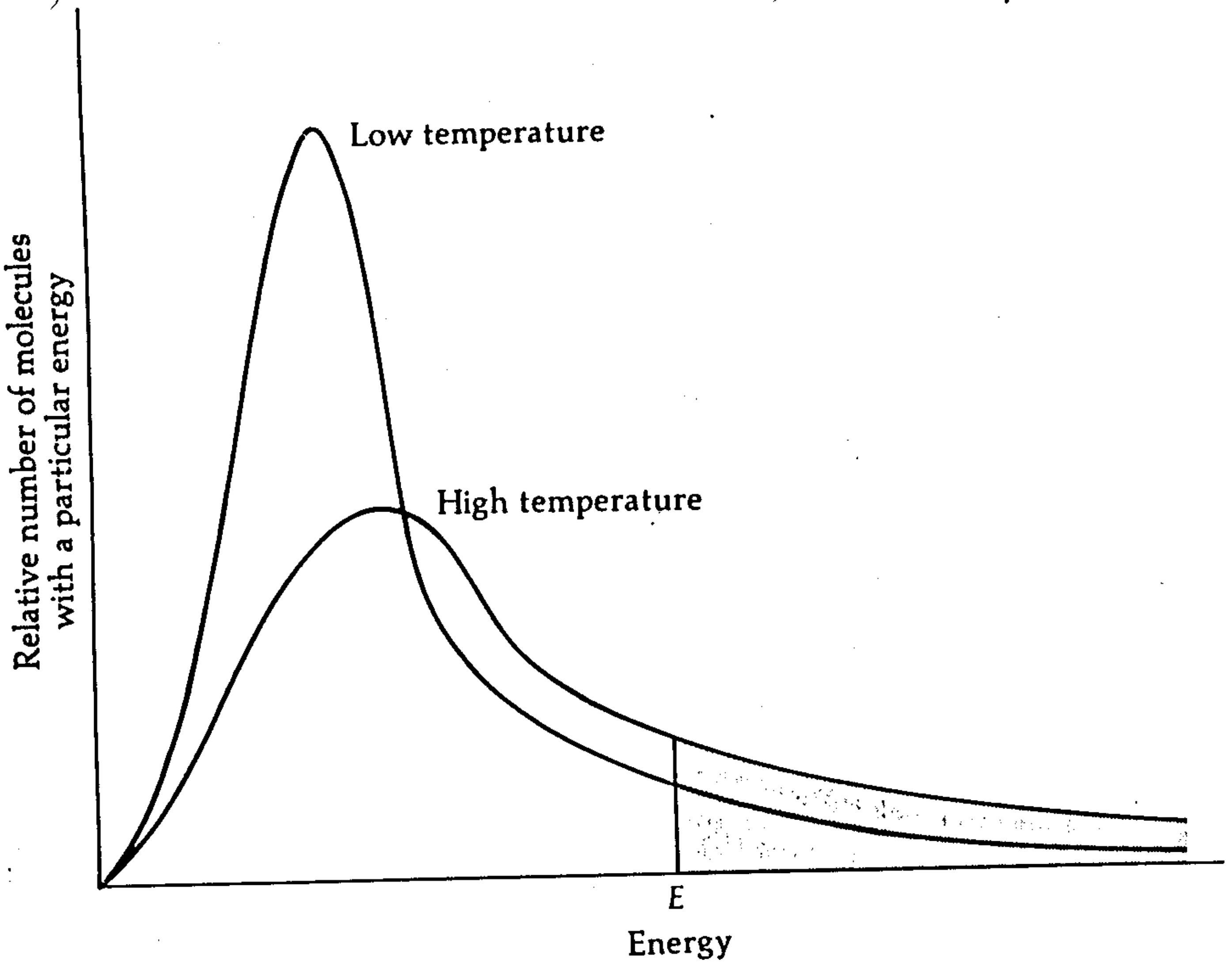


FIGURE 14.9. The distribution of molecular kinetic energies at low and high temperatures. The shaded area corresponds to the fraction of molecules whose energy is greater than or equal to E.

$$k = Z\, k_{coll}\, e^{-E_a/RT},$$

WHERE Z IS CALLED THE STERIC FACTOR.

THUS $$k = A\, e^{-E_a/RT}.$$

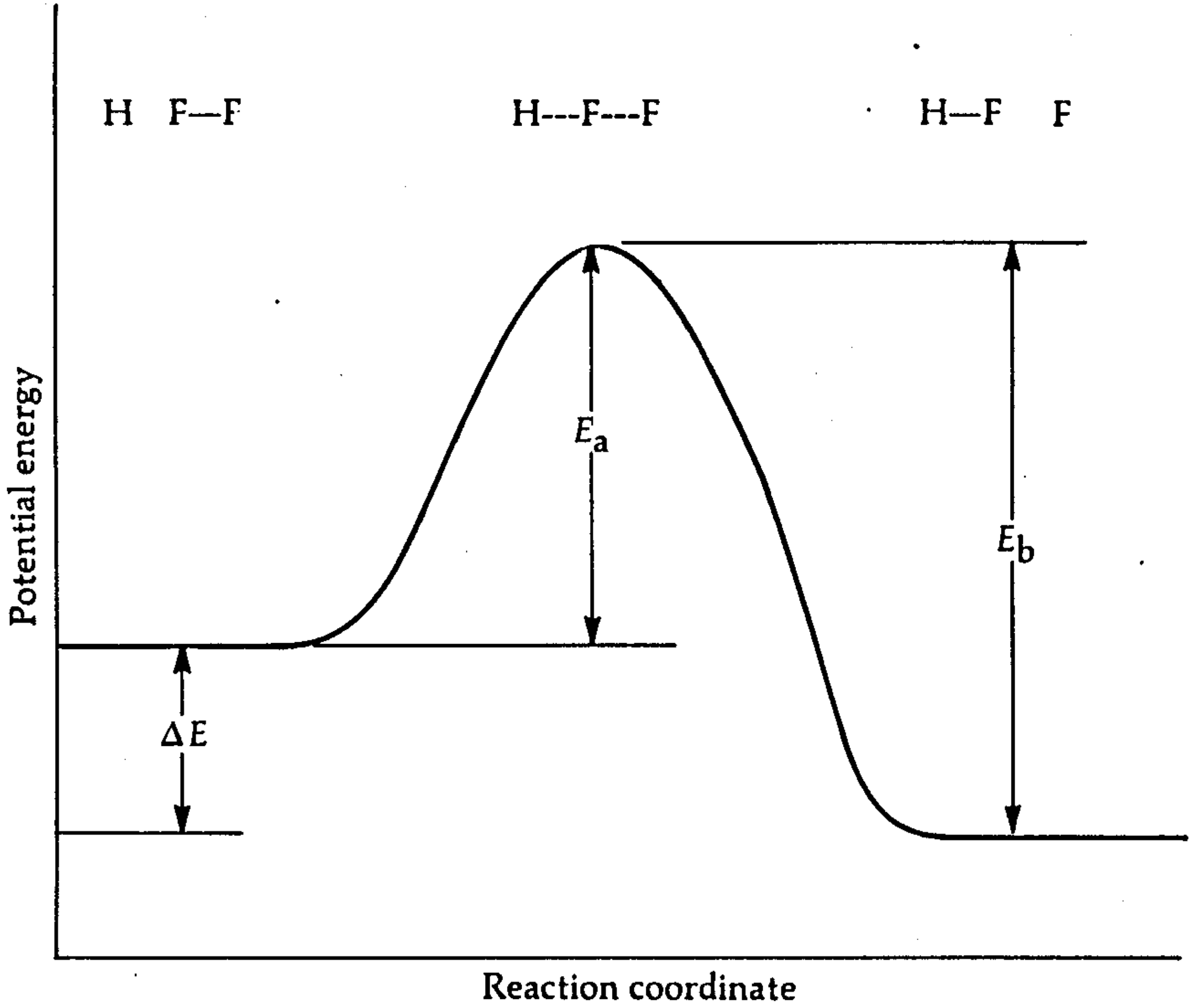


FIGURE 14.12 Potential energy versus reaction coordinate for the linear system of atoms in the reaction $H + F_2 \rightarrow HF + F$. The configuration of the atoms at various stages of the reaction is shown at the top. The activation energy E_a is equal to the energy difference between the activated complex and the reactants. The energy difference between products and reactants corresponds to the energy change ΔE in the overall reaction. The activation energy for the backward reaction, E_b, is shown.