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COLLINEAR COLLISION CHEMISTRY. I.

A Simple model for Inelastic
and Reactive Collision Dynamics

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In the last 15 years, enormous progress has been made in understanding the fundamental collisional processes by which molecules are transferred among their internal quantum states or converted by dissociation or metathetical reactions to new chemical species (1). A variety of experimental techniques have produced information that warrants rather detailed interpretation in terms of the structure and initial states of the reactants and the potential energy surfaces on which they interact. Consequently, a substantial and increasing number of theoreticians have given their attention to the time dependent problems of molecular dynamics. Unfortunately, much of the theoretical work has been at a level of sophistication which makes it largely inaccessible to those outside the field who may not be willing to devote a considerable amount of time to the study of molecular collision theory. However, it is now becoming clear that many of the most obvious collisional phenomena can be understood at least qualitatively in terms of the classical mechanics which is taught in introductory

college physics. It would be appropriate and valuable to introduce some of this material in the junior level physical chemistry course. It is the purpose of this article to make available a concise treatment of the simplest model for inelastic and reactive scattering--the collinear collision of an atom with a diatomic molecule on an exceedingly simple potential surface. The model has qualitative or semi-quantitative relation to the behavior of real systems, but its major advantage is that it provides a framework for thinking about molecular collisions and reveals many of the factors which affect the dynamics of reactive and inelastic collisions.

The Kinetic Energy of a Triatomic System

We consider an atom A and a diatomic molecule BC (2). What are the most convenient coordinates for the description of the system? It is tempting to use a Cartesian system whose origin is fixed in the laboratory. This would give us 9 coordinates and 9 velocities to be concerned with in any dynamic problem. However, an important simplification is possible if we realize that the motion of the center-of-mass of the three-particle system is unchanged by interactions between them. Consequently, this center-of-mass motion is of no interest in the discussion of the dynamics of the collision. Therefore, we want to use a coordinate system which moves with the center-of-mass and which describes only the relative motion of the three particles.

Perhaps the most obvious such system would be the "chemists coordinates": the internuclear separations r_1 and r_2, the bond angle θ, and the three angles needed to specify the orientation of the triatomic system in space. That is, $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ considered as vectors provide the 6 numbers necessary to locate the 3 particles relative to the center-of-mass. Such coordinates might be used, but are not the most convenient. It is much simpler to consider the behavior of the system as made up of the motion of B and C relative to each other, and the motion of A relative to the BC center-of-mass. The corresponding coordinate system in effect makes a "mobile" of the ABC system, as Fig. 1 shows.

It is now possible to write down the expression for the kinetic energy of the system in a very straightforward manner. Recalling that the relative kinetic energy of 2 particles is just the square of their relative velocity times one half their reduced mass, we see that the relative kinetic energy of B and C is just

$$T_{BC} = \frac{1}{2} \frac{BC}{B + C} \underset{\sim}{\dot{Y}^2} = \frac{1}{2} \frac{BC}{B + C} (\dot{Y}^2 + Y^2\dot{\theta}^2 + Y^2\sin^2\theta\dot{\varphi}^2) \qquad (1)$$

where B and C stand for the masses of the particles, and θ and φ are a pair of angles which locate the direction of the BC axis in space. Likewise, the system of A moving relative to the center-of-mass of BC is an effective 2-particle problem, and has associated with it a relative kinetic energy given by

$$T_{A(BC)} = \frac{1}{2} \frac{A(B + C)}{A + B + C} \underset{\sim}{\dot{X}^2} = \frac{1}{2} \frac{A(B + C)}{A + B + C} (\dot{X}^2 + X^2\dot{\theta}^2 + X^2\sin^2\theta\dot{\varphi})$$

$$(2)$$

where Θ and Φ are the angles which give the direction of line joining A to the center-of-mass of BC (the x axis) in space. The total relative kinetic energy is therefore

$$T = \frac{1}{2} \frac{A(B + C)}{M} \dot{X}^2 + \frac{1}{2} \frac{BC}{B + C} \dot{Y}^2 \tag{3}$$

where M is the sum of the masses of all three particles.

To study the exact classical mechanics of a triatomic system moving under the influence of an arbitrary potential $V(\underset{\sim}{X},\underset{\sim}{Y})$, the expressions for the kinetic energy and the potential energy would be conbined to give the Lagrangian function $L = T - V$, or the Hamiltonian function $H = T + V$. Then the 6 coupled second order differential Lagrange equations or the 12 coupled first order differential Hamilton equations would be solved numerically for the exact trajectories which result from chosen initial conditions. In this article, we shall make two drastic simplifications that will allow us to obtain the exact results of a collision by doing only trigonometry and algebra. First, we assume that all particles interact pairwise by angle independent potentials which are of the hard sphere or square well type indicated in Fig. (2). Second, the particles are arranged collinearly, and their initial motion is along this axis only. These two assumptions cause substanital loss of generality, but if used cautiously, the resulting model still demonstrates many of the essential physical characteristics of actual molecular collisions.

Since the three particles initially move collinearly and interact pairwise through spherical potentials, they will

remain collinear throughout the collision. Consequently, the time derivatives of the angles in Eqns. (1) and (2) are zero, and we can replace $\dot{\underset{\sim}{X}}$ and $\dot{\underset{\sim}{Y}}$ in Eqn. (3) by their scalar magnitudes, and get

$$T = \frac{1}{2} \frac{A(B + C)}{A + B + C} \dot{X}^2 + \frac{1}{2} \frac{BC}{B + C} \dot{Y}^2 \tag{4}$$

Equation (4) is a simple expression for the total relative energy, particularly since it does not involve any cross terms in $\dot{X}$ and $\dot{Y}$. This simplication is a result of using the "mobile" coordinate system whose formal relation to the "chemists coordinates" $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ is

$$\underset{\sim}{X} = \underset{\sim}{r}_1 + \gamma \underset{\sim}{r}_2 \tag{5}$$

$$\underset{\sim}{Y} = \underset{\sim}{r}_2$$

where

$$\gamma = C/(B + C)$$

However, there is a further transformation which allows a simple visualization of the behavior of the three particle collinear system. Let

$$x = X$$

$$y = \frac{Y}{a} \tag{6}$$

where a is a constant, and substitute into Eqn. (4). The result is

$$T = \frac{1}{2} \frac{A(B + C)}{M} \dot{x}^2 + \frac{1}{2} a^2 \frac{BC}{B + C} \dot{y}^2$$

Now chose $\underline{a}$ so that the coefficients of the two velocity terms are the same. This requires

$$a^2 = \frac{A(B + C)^2}{BCM}$$

and as a result

$$T = \frac{1}{2} \frac{A(B + C)}{M} (\dot{x}^2 + \dot{y}^2) \qquad (7)$$

The significance of Eqn. (7) is that if x and y are used as Cartesian coordinates and the potential energy $V(x,y)$ is represented in the third dimension, then a _single_ particle of mass $A(B + C)/M$ sliding frictionless on the potential surface will carry out an x-y motion which exactly represents the behavior of the real three particle system. In other words, the motion of three particles in two dimensions (collinear r_1, r_2) has been reduced to something which can be more easily visualized: the motion of one particle in two dimensions.

The relation between the x,y coordinates and the bond distances r_1, r_2 can be found in the following manner. From Eqns. (5) and (6)

$$y = \frac{r_2}{a} = \frac{1}{\gamma a} (x - r_1)$$

Thus a line of constant r_2 is parallel to the x axis, and a line of constant r_1 has a slope of $1/\gamma a$ when plotted in the Cartesian x - y coordinate system. This is shown in Fig. 3, where it is evident that lines of constant r_1 and r_2 appear skewed in the x - y coordinate system. If the angle between lines of constant r_1 and r_2 is β, then

$$\tan^2\beta = \left(\frac{1}{\gamma a}\right)^2 = \frac{BM}{AC} \tag{8}$$

and by straightforward trigonometic manipulation

$$\sin^2\beta = \frac{BM}{(A + B)(B + C)} \tag{9}$$

$$\cos^2\beta = \frac{AC}{(A + B)(B + C)} \tag{10}$$

Vibration Excitation of a Square-well Oscillator

The x - y coordinate system described above was introduced by Wigner in an early paper by Eyring and Polanyi (3). It has been discussed by several authors (4-7) since then, for the most part in connection with metathetical or recombination reactions. As our first example of its use, we shall discuss the simpler problem of the collision of a hard sphere particle A with an oscillator BC bound by a square well potential. Initial translational energy of A relative to BC is partly converted to vibrational energy of BC, and hence the process is a simple example of an inelastic collision. The appropriate potential energy surface is shown in Fig. 4. A flat bottomed trough is bounded by two infinitely high walls which correspond to the hard sphere repulsion between A and B, and between B and C. The outer or attractive wall of the BC potential constitutes the third wall of the trough, and is parallel to the x axis.

The simplest trajectory for this system results if B and C are initially at rest at a separation halfway between the parallel walls of the trough. The representative particle

then slides straight down the trough parallel to the x axis, as the real particle A approaches the real B. The A-B collision occurs as the representative particle encounters the left-hand wall of the trough where it is specularly reflected. The internal angle between the incoming and initial outgoing leg of the trajectory is easily seen to be $\pi - 2\beta$. If the internal energy acquired by BC is insufficient to dissociate the molecule, the trajectory is completed by the zig-zag path shown in Fig. 4, which represents the departure of A from the oscillating BC.

The final translational velocity of A relative to the BC center-of-mass is just the projection of the final velocity vector on the x axis, or

$$v_x = v \cos (\pi - 2\beta) = - v \cos (2\beta) \tag{11}$$

where v is the magnitude of the initial velocity of A relative to BC, and a positive value of v_x corresponds to separation of A from BC after the collision. The change in the relative translational energy due to the collision can be obtained in the following manner. If E is the initial, and E' is the final relative translational energy, then squaring Eqn. (11) and multiplying by $1/2 \, A(B + C)/M$ gives us

$$E' = E \cos (2\beta)$$

The quantity Q, the difference between the final and initial translational energy is therefore

$$Q = E' - E = E[\cos^2 (2\beta) - 1] = - E \sin^2 (2\beta) \tag{12}$$

Since the change in the vibrational energy ΔE_v is just the negative of Q, we get

$$\frac{\Delta E_v}{E} = \sin^2 (2\beta)$$

$$= 4 \sin^2 \beta \cos^2 \beta$$

$$= \frac{4ABCM}{(A + B)^2(B + C)^2}$$

(13)

Equation (11) is the exact expression for the change in vibrational energy ΔE_v which occurs as a result of a single hard-sphere A-B interaction. It applies not only to the case in which BC is bound by a square-well potential, but to any BC force law, as long as the A-B interaction is of the hard sphere type. The $\sin^2(2\beta)$ factor is the most compact expression of how the mass distribution effects the inelasticity of the collision, and appears (or should appear) explicity the expression for the inelasticity when the potential of interaction is more realistic. For example, if BC is a harmonic oscillator of circular frequency ω and the A-B interaction potential is an exponential repulsion with a range parameter L, that is,

$$V_{AB} = V_o \exp (-r_{AB}/L)$$

then the expression for the inelasticity can be shown (8) to be

$$\frac{\Delta E_\upsilon}{E} = \sin^2(2\beta) \left(\frac{\pi \omega L}{\upsilon}\right)^2 \operatorname{csch}^2 \left(\frac{\pi \omega L}{\upsilon}\right) \qquad (14)$$

Thus finite interaction between B and C (represented by ω in Eqn. (14)) and the finite range of the A-B potential act to diminish the inelasticity of the collision below the value $\sin^2(2\beta)$ given by the mass distribution alone.

Some comments concerning the qualitative relation between the mass distribution, the angle β, and the inelasticity of the collision are in order. If the mass of B is much greater than the masses of A and C, the angle β approaches 90°, and $\sin^2(2\beta)$ and the inelasticity approach zero. Consider, for example, a helium atom hitting the iodine end of the HI molecule. In this case $\beta = 89.1°$, and only 9.8×10^{-4} of the initial relative energy would appear as vibration after the collision, according to this model. If the masses of B and C are comparable, but that of A remains small, β decreases and the inelasticity increases. For a collinear collision of O_2^+ with He, $\beta = 71.5°$, and $\Delta E_\upsilon/E = 0.359$. In our (9) experimental studies of this system, we have found inelasticities which approach this amount, and in fact are given more accurately by the refined expression, Eqn. (14).

When the mass of B is comparable to or smaller than the masses of A and C, or if "steps" or wells are introduced into the potential surface, slightly more complicated trajectories result. Some of these situations are illustrated in Fig. 5. If β is less than 51°, the trajectory encounters the

reflecting wall at the end of the trough more than once, as Figure 5a shows. That is, A hits B, B hits C and then B returns to hit A a second time before the systems separate. As a result of the second A-B encounter, the internal energy of BC is modified considerably, and Eqn. (13) must be replaced with

$$\frac{\Delta E_v}{E} = \sin^2(2n\beta) \tag{15}$$

where n is the number of A-B encounters. Equation (15) can be derived by using the principle of the kaleidoscope outlined by Jepson and Hirschfelder (4), or by more tedious but straight-forward geometric considerations.

For more realistic potentials, the idea of multiple A-B encounters becomes rather imprecise, since it is essentially impossible to tell when the first A-B interaction ends and second begins. However, exact trajectory calculations with such potentials do show that when β is smaller than 50°, there is considerable compression of the BC oscillator during the collision, a rather extended A-B interaction time, and a diminished inelasticity, all of which would be expected from the multiple encounter phenomena observed on the hard sphere-square well surface.

Some new effects occur if the potential surface has a well, or a step down to a lower value as A approaches BC. The simplest such situation is shown in Figure 5b. We have chosen to have the boundary of the potential well perpendicular

to the x-axis, which corresponds to an attraction of A to
the center-of-mass of BC. That is, there is equal attraction
of A to B and to C. The consequences of this type of well
are easy to deduce. The representative particle proceeds
down the trough with initial energy E and crosses step into
the region of the well. At this point, the potential energy
decreases from zero to the (negative) value φ, so the kinetic
energy increases to E-φ. The representative particle then
strikes the wall at the end of the trough as the A-B collision
occurs, and is reflected through the angle 2β. After the
reflection, the vibrational energy of oscillator is the product
of the local total kinetic energy E-φ, and $\sin^2(2\beta)$, by exact
analogy to Eqn. (13). As A and BC separate, the representative
particle crosses the step again. Since the step is perpendicular
to the x-axis, only the relative translational energy is
changed (by φ) as it is crossed, and the excitation energy
that the oscillator acquired upon reflection is unchanged.
Thus the final vibrational energy of the oscillator is

$$\Delta E_v = (E - \varphi) \sin^2(2\beta) \tag{16}$$

In effect, this type of step makes it appear that the collision
took place on a flat potential surface, but with an increased
kinetic energy of E-φ. As far as the A-B interaction is
concerned, that is just what happened.

The attraction of A to the center-of-mass of BC is
only one simple form that the potential surface might take.
Another simple situation occurs when A is attracted to B alone.

Then, as Figure 5c shows, the potential step makes an angle β with the x-axis. In this case, when the representative particle crosses the step on the incoming leg of the trajectory, it is refracted according to Snell's law. That is, the component of velocity parallel to the step is unchanged, but the perpendicular component of the velocity is changed by an amount $(2|\varphi|/m)^{\frac{1}{2}}$, where $m = A(B + C)/M$ is the mass of the representative particle. Consequently, a change in the direction of the trajectory results. The magnitude of the deflection can be found in the following manner. Since the component of velocity parallel to the step is unchanged, we have

$$v_1 \sin \theta_1 = v_2 \sin \theta_2$$

where v_1 and v_2 are the magnitudes of the velocities before and after the step, and θ_1 and θ_2 are the usual angles of incidence and refraction, measured from the perpendicular to the potential step. Squaring and multiplying by one half the mass gives

$$E_1 \sin^2 \theta_1 = E_2 \sin^2 \theta_2 \tag{17}$$

which is the form of Snell's law which is appropriate for particle trajectories.

By using the laws of refraction and specular reflection, it is possible to deduce that if the representative particle follows the trajectory shown in Figure 5c, the result for the vibrational energy is just that given by Eqn. (13). That is, this type of potential step with this type of trajectory has

no influence on the inelasticity. This result is in fact rather obvious. In effect, the atom C is a spectator to the A-B collision for the trajectory shown in Figure 5c. The velocity changes that occur in an isolated head-on A-B collision are determined solely by energy and momentum conservation laws, and not by the form of their interaction potential. Thus it does not matter whether the step is up, down, or how large it is, as long as it makes an angle β to the x-axis, and B does not hit C while the system is in the vicinity of the step.

Figure 5d illustrates another important phenomenon that occurs when the potential surface contains a well. With the step again perpendicular to the x-axis, the initial parts of the trajectory are the same as in Figure 5b. However, when the representative particle attempts to cross the step on the outgoing leg of the trajectory, it finds that it has insufficient translational energy to do so. The condition which must be met to cross the step on the first try is

$$(E - \varphi) \cos^2 (2 \beta) \geqslant |\varphi|$$

so that if $|\varphi|$ is large enough, or β or E small enough, temporary trapping of the representative particle will occur. In the example shown, a second A-B collision converts all the energy to relative translation of A and BC. The representative particle then crosses the step on its second try, and a perfectly elastic collision is completed.

The most important aspect of this example is that it demonstrates how and why "sticky" collisions occur. A potential well and an internal degree of freedom (the B-C vibration) are

necessary. The collision is prolonged when some of the energy necessary to separate the partners resides temporarily in an internal degree of freedom. The model makes it clear why deepening the well, decreasing the initial collisional energy, and increasing the number of internal degrees of freedom increases the chance that a sticky collision will occur.

The potential energy surfaces used in this discussion are very primitive, and the restriction of the system to collinearity is highly unrealistic, so the quantitative application of the model to real phenomena must be done with caution. Nevertheless, the several examples discussed here qualitatively expose much of the basic physics of vibrational excitation by collision. The extension of this type of analysis to reactive collisions is straightforward, and will be discussed in a subsequent paper.

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Figure Captions

Figure 1. Coordinates for the atom-diatom system. The set X,Y which gives a simple expression for the kinetic energy also makes a "mobile" of the system, since X connects atom A to the center-of-mass of the BC pair.

Figure 2. Interaction potentials for the hard sphere square-well oscillator system. (a) The interaction potential of A with B. (b) The BC interaction potential.

Figure 3. In the Cartesian x-y coordinate system, lines of constant r_1 and r_2 intersect at an angle $\beta = \tan^{-1} (BM/AC)^{\frac{1}{2}}$.

Figure 4. Potential energy surface and trajectory for the collinear interaction of the hard sphere A with the square well oscillator BC.

Figure 5. Potential energy surface features which introduce complications into the trajectories. (a) For β less than approximately 51°, multiple A-B encounters occur. (b) When the surface has a step perpendicular to the x axis, the inelasticity is increased or decreased depending on the sign

of the potential step φ. (c). When A is attracted to B alone, the step makes an angle β with the x axis, and ΔE_{υ} is unaffected. (d) If the potential well is deep enough, temporary trapping of the representative particle may occur.

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Fig. 1

Fig. 2
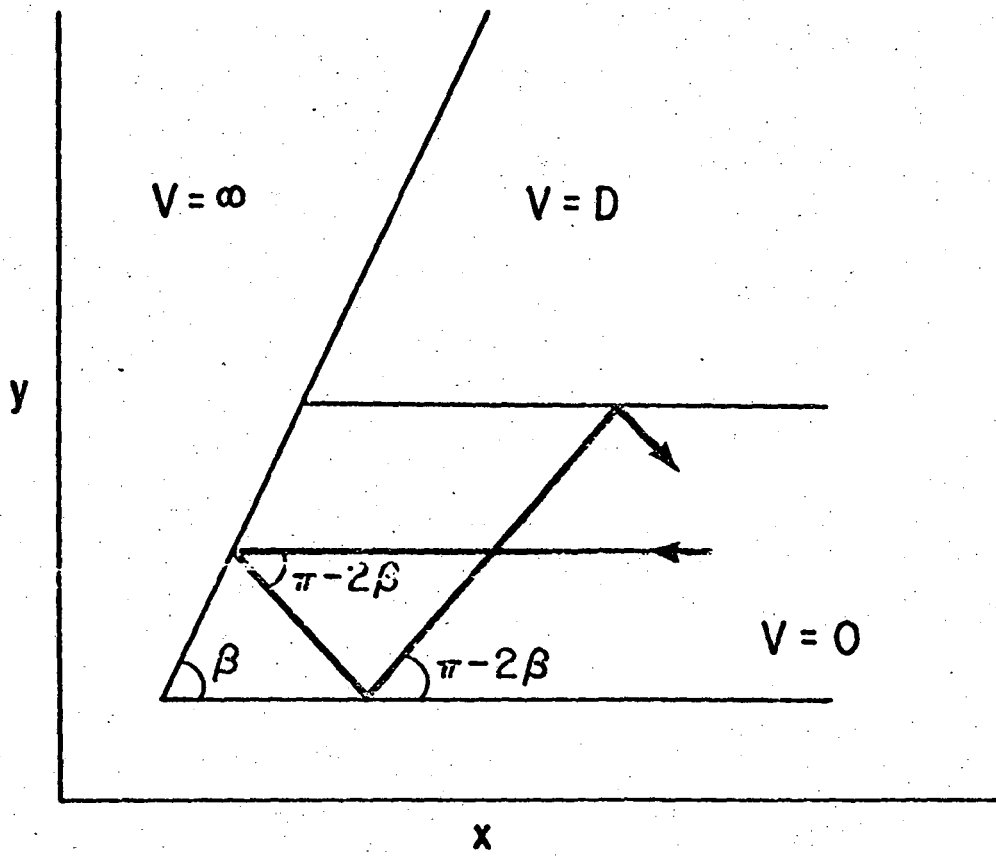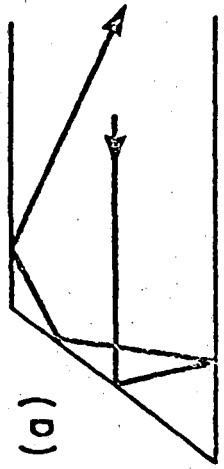
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-20-

r_1 = const.

β

r_2 = const.

y

x
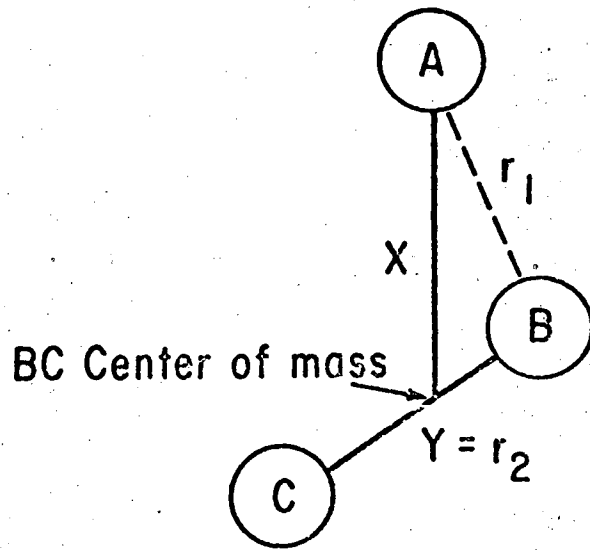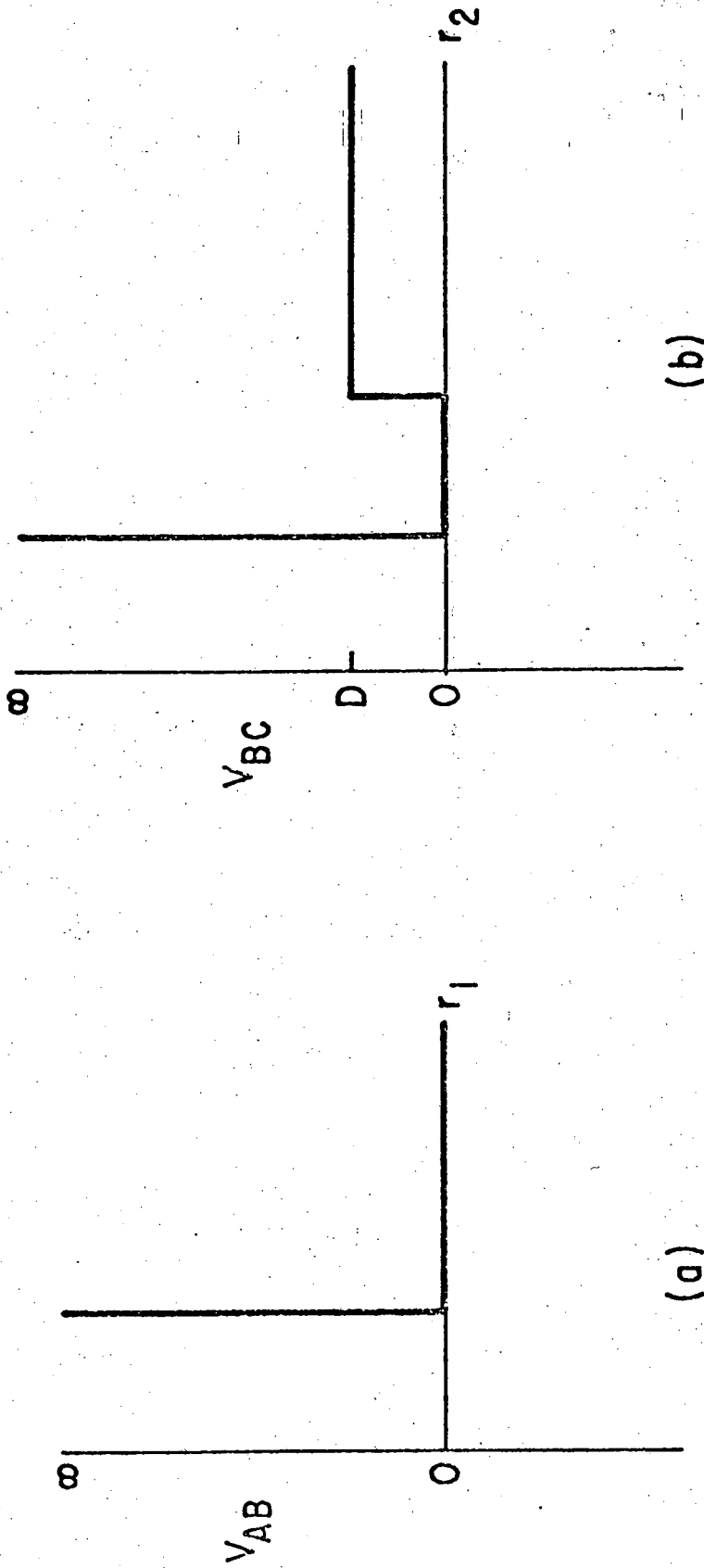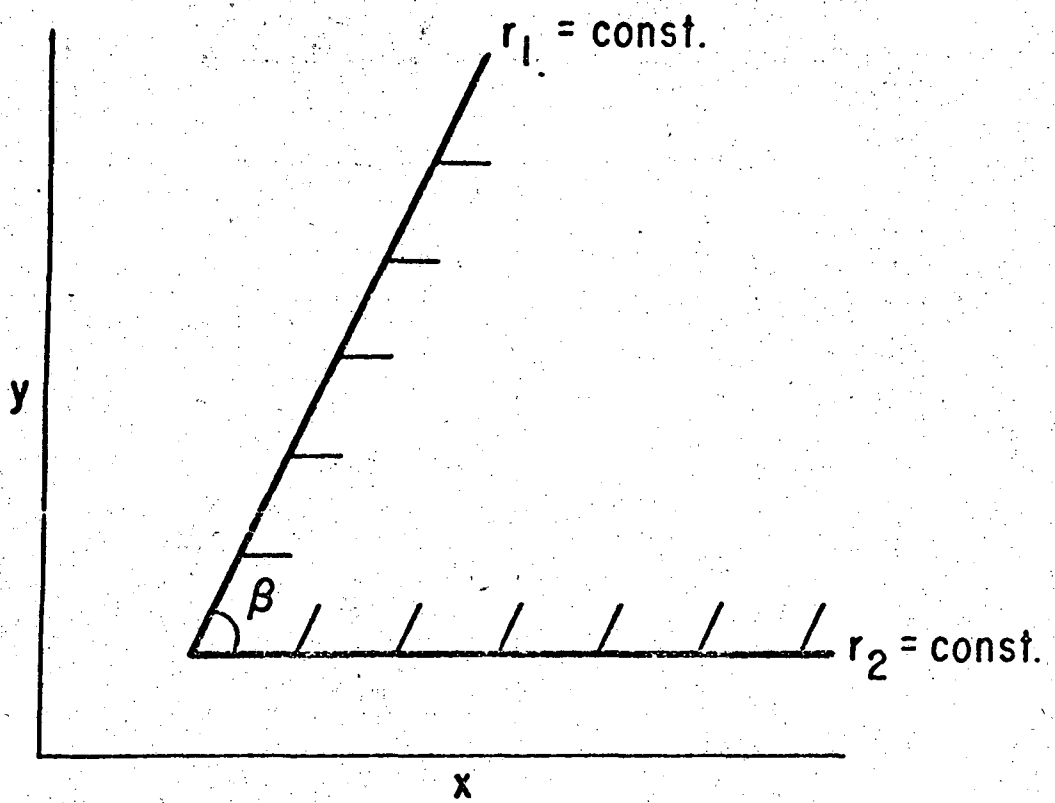
XBL738-1769

Fig. 3

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Fig. 4

(b)

$$\Delta E_v = (E - \varphi) \sin^2(2\beta)$$

(d)

$$\Delta E = 0$$

(a)

$$\Delta E_v = E \sin^2(2n\beta)$$

(c)

$$\Delta E = E \sin^2(2\beta)$$

XBL 737-6520

Fig. 5