

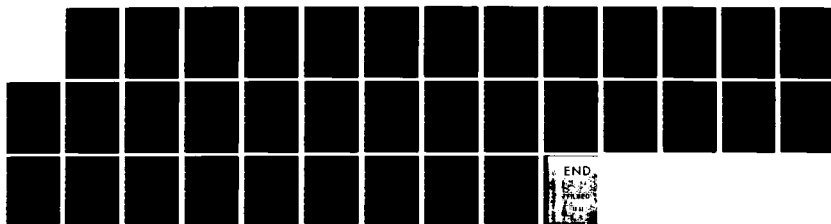
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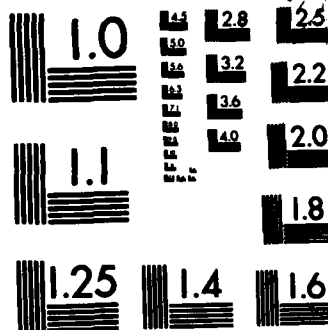
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Average Vibrational Energy Transfer During a Single Collision of
Excited Molecules with Heat Bath Molecules

I. Oref and B. S. Rabinovitch

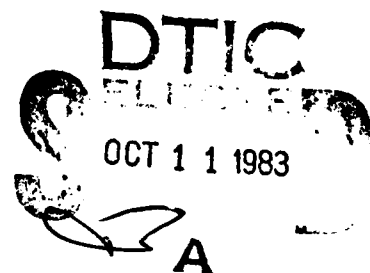
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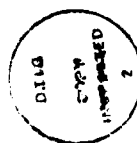
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ABSTRACT

A collisional energy transfer probability of the form $B(E+\Delta E) \int_{0, \Delta E}^{\infty} B'(E') B'(E'-\Delta E) dE'$ is assumed where $B(E)$ is the Boltzmann distribution and ΔE is the incremental energy transferred and which can display negative as well as positive values. Single collisions between vibrationally excited substrate molecules with heat bath molecules are considered. The dependence of the average energy per collision transferred up, down and overall on the initial energy content, on the temperature and on the size of the bath and substrate molecules is calculated and compared with experimental data in the literature.



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INTRODUCTION

Vibrational relaxation and energy transfer studies are of current interest in photophysics and molecular dynamics. At low levels of excitation energy transfer between polyatomic molecules by resonance vibrational-vibrational (V-V) energy transfer is frequently the most important mechanism. Studies have been done in the S_0 manifold using single mode excitation by CO_2 laser¹⁻⁷ and shock tube heating^{8,9}. In the S_1 manifold relaxation studies were made by tuned laser excitation followed by resolved $S_1 \rightarrow S_0$ fluorescence¹⁰⁻¹⁴. At high levels of excitation, recent photophysical¹⁵⁻¹⁷, multiphoton excitation^{18,19} and shock tube studies²⁰ support the finding from chemical activation studies²¹ that energy transfer by highly vibrationally excited polyatomic molecules takes place in the gas phase on virtually every collision, an important mechanism now being vibrational-translational, rotational (V-T, R) transfer. The pragmatic numerical value of the average energy which is transferred depends on the nature and energetics of the collision partners as well as on the collisional transition probability model which applies to the system.

In a thermal system at equilibrium, the average amount of energy gained by the substrate molecule equals the average lost²²⁻²⁵, and the equilibrium assumption forces the distribution to remain Boltzmann after any (statistical) sequence of collisional event. In a unimolecular reacting model system at high pressures, the Boltzmann distribution is essentially maintained over all energy space. At low pressures, and for the case $E_0 \gg RT$, an operational definition of a strong collision is that the Boltzmann distribution is maintained up to E_0 .

The above definitions are used in conjunction with weak collision models to obtain the degree of "weakness" of a collision, i.e. the collisional efficiency relative to strong collision. There are several empirical weak collider energy transfer models^{21,26,27} such as exponential or Poisson analytic forms. These models are used to evaluate the average energy transferred to the substrate $\langle \Delta E_U \rangle$ i.e. up transition, or from the substrate $\langle \Delta E_D \rangle$ i.e. down transition, or the overall average $\langle \Delta E \rangle$. The conservation relations are maintained by imposing detailed balance. The models are helpful in the correlation of experimental data.

In a non-equilibrium (frequently reacting) system the situation is more complicated. Such a system may correspond to chemical, photochemical^{28,29} and laser¹⁵⁻¹⁷ activation of reaction. Here, a molecule excited to a high vibrational level is allowed to collide with a thermal heat bath molecule. In the process, a quantity of energy is transferred. The $\langle \Delta E \rangle$ transferred depends not only on the energy content of the reactant molecule and the temperature of the bath but on the energy transfer probability model which is used. Detailed balance is not maintained in the non-equilibrium system and an alternative requirement to the conservation relation is that a non-reacting system reaches a Boltzmann distribution after a sufficient number of collisions.

The purpose of the present work was to evaluate $\langle \Delta E_U \rangle$, $\langle \Delta E_D \rangle$ and $\langle \Delta E \rangle$ in a non-equilibrium system with use of a model for strong collision energy transfer which allows for an equilibrium condition to obtain. For the purpose of gaining an understanding of how the size and temperature of the heat bath, and the size

and energy content of the excited molecule affect the magnitudes of the various $\langle \Delta E \rangle$'s, classical densities may be used. This does not detract from the general conclusions since for this purpose the behavior of a real molecule may be simulated by s classical oscillators. The results are compared with some existing experimental data.

PROBABILITY TRANSFER RELATIONS

Consider a dilute system of substrate molecules all excited to a single value of internal energy, E , in a bath gas of temperature T . The probability of transferring an amount of energy from the excited molecule to the bath $P(E, \Delta E)$ can be evaluated in the following manner²⁵:

When a collision takes place between a substrate molecule and a bath molecule an amount of energy ΔE is exchanged in the process. The probability that a molecule will start at E_i and reach the $E_i + \Delta E$ level while its partner will start at E_j and end at the $E_j - \Delta E$ level is:

$$P(E_i, E_j, \Delta E) = B(E_i)B(E_i + \Delta E) B'(E_j)B'(E_j - \Delta E); \quad (1)$$

$+\Delta E$ is for an up transition and $-\Delta E$ is for a down transition; $B(E)$ is the Boltzmann distribution and the primed quantities indicate the bath molecules. $B(E)$ has the form

$$B(E) = E^{s-1} e^{-E/RT} / (s-1)!(kT)^s \quad (2)$$

and for the bath molecule s' replaces s in eq. 2.

The probability that a substrate with initial state i will exchange a given ΔE regardless of the initial state j of the colliding bath molecule is:

$$P(E_i, \Delta E_U) = B(E_i + \Delta E) \int_{\Delta E}^{\infty} B'(E'_j) B'(E'_j - \Delta E) dE'_j \quad (3)$$

for the substrate up transition, and

$$P(E_i, \Delta E_D) = B(E_i - \Delta E) \int_0^{\infty} B'(E'_j) B'(E'_j + \Delta E) dE'_j \quad (4)$$

for the down transition. ΔE is the lower limit in the integral expression in eq. 3 since the bath molecule is losing energy and has to have at least energy E' equal to the amount transferred ΔE . In eq. 4 the lower limit is 0 since the bath is gaining energy and therefore can have any value. For the case where no energy is exchanged during a collision, $\Delta E = 0$ is placed in eq. 3 or 4.

Conservation of probability requires

$$\int_{-\infty}^{\infty} d\Delta E [P(E, \Delta E_U) + P(E, \Delta E_D) + P(E, 0)] = 1 \quad (5)$$

and detailed balance follow naturally from the form of eq. 3 and 4. For example, the equality in eq. 6,

$$B(E) P(E, \Delta E_U) = B(E+\Delta E) P(E, \Delta E_D) \quad (6)$$

is obtained by making the transformation $E''=E'-\Delta E$ and substituting it in eq. 3. It should be stressed again that detailed balance obtains only in an equilibrium (thermalized) system.

The average quantities which are sought in this work are

$$\begin{aligned} \langle \Delta E_U \rangle &= \int_0^{\infty} d(\Delta E) \Delta E P(E, \Delta E_U) \\ \langle \Delta E_D \rangle &= \int_{-\infty}^0 d(\Delta E) \Delta E P(E, \Delta E_D) \end{aligned} \quad (7)$$

where $P(E, \Delta E_U)$ and $P(E, \Delta E_D)$ obey the normalization condition of eq. 5.

RESULTS

The form of the collisional probability eq. 3, 4, for classical oscillators is given in Fig. 1 for four values of the internal energy of the reactant molecule with $s=s'=15$ and $T=1000K$. The normalized curves have a regular quasisymmetrical shape. The principal features are: a) The location of the maximum of the probability curve depends on the internal energy of the reactant molecule; the lower the value of E the higher the value of ΔE at which the probability curve peaks. b) The higher the value of E , the broader the peak; at $E=0$ kcal/mole the width at half height is ~ 11 kcal/mole while at $E=60$ kcal/mole

it is ~ 21 kcal/mole. c) The average energy transferred up is 21.6 kcal/mole for the $E=0$ kcal/mole case and down is -18.8 kcal/mole for the $E=60$ kcal/mole case, i.e., the value of $|\langle \Delta E \rangle|$ has to do with the location of the maximum and not with its width. d) The probability curve peaks at values of ΔE that are different from the original value of E . The same behavior is obtained in trajectory type calculations^{30,31} where a potential is assumed and a detailed study of the energy exchange is made. By contrast, weak collisions as evaluated by the simple exponential and stepladder models probe the regions close to E wherever it may be.

The dependence of the average energy up $\langle \Delta E_U \rangle$ and down $\langle \Delta E_D \rangle$ and total energy transferred in a collision $\langle \Delta E \rangle$ is given in Fig. 2 for 400K, 1000K, 2000K and $s=s'=15$. The major points which emerge are: a) At very low internal energy up collisions predominate and $\langle \Delta E \rangle \approx \langle \Delta E_U \rangle$. b) At high internal energies down collisions predominate and $\langle \Delta E \rangle \approx \langle \Delta E_D \rangle$. c) At internal energies around the average internal energy at equilibrium (sRT), up and down collisions are both significant and $\langle \Delta E \rangle$ is the average of the two. d) The higher the temperature the larger is $\langle \Delta E_U \rangle$ at lower values of E and the smaller is $|\langle \Delta E_D \rangle|$ at higher values of E . This is so because the model requires that a Boltzmann distribution be obtained in one collision for $s'=\infty$ (a few collisions when $s' \neq \infty$). As the temperature increases, larger up collisions are needed for a substrate with low E to obtain the value of $\langle E \rangle$ which increases with the temperature. By the same token, if the molecule is energy rich it takes smaller jumps for the high temperature system to get to $\langle E \rangle$ than for the lower temperature case, all other things being equal. It will be noted that the intercept at $E=0$ is not sRT . The

intercept will approach the limiting value more closely as $s' \rightarrow \infty$; the latter case is that of gas/wall strong collision interaction³².

The effect of the number of vibrational modes of the bath molecules on the average energy transferred is shown explicitly for $T=1000K$ in Fig. 3. a) The larger the heat bath the larger the absolute value of $\langle \Delta E \rangle$ (up and down). b) The incremental increase in ΔE is not directly proportional to the value of s' (see discussion below); an infinitely large bath molecule ($s'=\infty$) which collides with a substrate with $s=15$ transfers on the average only a little more than a molecule with $s'=30$. The size of the reactant limits the amount of energy which can be transferred up and down the energy scale. c) At lower values of internal energy up collisions predominate and at high internal energies down collisions are the most important. d) At values of internal energies close to the average thermal energy up and down collisions take place at the same time and the curves all cross at $E \sim 30$ kcal/mole (i.e. sRT). There are two effects to a change in the temperature of the system. At low values of T s' is small, therefore $\langle \Delta E \rangle$ should be small (Fig. 3). However, at low values of T , $\langle \Delta E \rangle$ should be larger since the bath is colder (Fig. 2). The two effects counteract each other.

The effect of the number of the vibrational modes of the bath on the average energy transferred can^{also} be seen in Fig. 4. a) The average energy of the substrate with $s=15$ at $1000K$ is 30 kcal/mole; if the internal energy is below that value up collisions will prevail; above this value down collisions are important as can indeed be seen from fig. 4. b) The effect of s and s' on $\langle \Delta E \rangle$ is introduced by using a reduced number of degrees of freedom parameter²⁵, s_r ,

which is defined as $s_r = 2(s-1)(s'-1)/((s-1)+(s'-1))$. c) A plot of $\langle \Delta E \rangle$ vs. $s_r^{1/2}$ yield a family of straight lines each belongs to a different value of the internal energy, E ; the linear correlation over such a large spread in the values of s' , and therefore of s_r , is a great simplification and enables easy correlation of various combinations of reactant and bath molecules. The limiting value of s_r , for $s' = \infty$, is $2(s-1)$, or $s_r = 5.3$ for the case $s = 15$ (see Fig. 4).

The dependence of the overall average energy transferred during a collision on the temperature and the internal energy is given in fig. 5 for $s=s'=15$. The slightly concave lines are almost parallel. The spacing between them decreases by a constant increment as the internal energy increases. The spacing between the lines of $E=10$ and $E=20$ kcal/mole is ~ 7.4 kcal/mole, while between the lines $E=40$ and $E=50$ kcal/mole is ~ 6 kcal/mole. Over a limited range, however, the curves can be approximated as straight lines.

One may examine collisional energy transfer in another systematic way. One may increase the size of the reactant while keeping the size of the bath molecule constant. Fig. 6 shows a graph of $\langle \Delta E \rangle$ vs. E for $s=10$ and 15 and $s'=15$. The results are very interesting; $\langle \Delta E_u \rangle$ increases as s increases, while $\langle \Delta E_D \rangle$ for $s=10$ is larger than that for $s=15$. In the up collision less energy is needed to bring the small molecule to its average energy while in the case of the down collisions $\langle \Delta E_D \rangle$ is larger for the small molecule since it is a smaller heat bath than the larger molecule and can retain less energy. This is precisely the prediction of the statistical theory³⁴ which says the larger the reactant

molecule the more energy it can retain and therefore the smaller $\langle \Delta E_D \rangle$ in a collision with a constant size heat bath.

Fig. 7 shows the dependence of $\langle \Delta E \rangle$ on the reduced number of degrees of freedom s_r . Here s_r increases because s increases while s' remains constant. The average energy transferred in a collision with a bath molecule ($s'=15$ and $T=1000K$) increases as the number of degrees of freedom of the reactant increases. The reasons for such behavior stem from the following facts. At low energy content (eg. $E=10$ kcal/mole), as s increases more energy is needed to bring the molecule to its average energy and hence $\langle \Delta E \rangle$ increases and is positive, that is to say, up collision predominate. At high level of excitation (eg. 70 kcal/mole), as s increases the absolute value of ΔE decreases and is negative. In this case down collisions take place to bring the molecule to its equilibrium average energy; but as s increases, its equilibrium average energy increases and a smaller down step is needed. The model which is presented here anticipates the limiting energy transfer behavior of various experimental systems and does it in a simple and a consistent fashion.

SOME COMPARISONS WITH EXPERIMENT AND OTHER THEORIES

How do the results which were obtained here compare with the experiment? One system available for comparison is chemical activation. There, a substrate molecule is excited by an insertion of an atom or a radical into a double bond. For example, it is possible to obtain a butyl radical with average excess energy

of 43 kcal/mole by the reaction $C_4H_8 + \cdot H \rightarrow C_4H_9$. The energy spectrum of the molecule is not a delta function since the butene possesses initial thermal energy. Nevertheless, the energy spectrum is narrow and energy transfer studies on such systems are instructive.

It was found that when excited butyl radical collides with a series of bath molecules, the larger the collider the larger $\langle \Delta E \rangle$ ²¹. The inert gases transfer ~2 kcal/mole, the diatomics a little more and the polyatomic cis-butene and SF_6 ~9 kcal/mole.

Also, cyclopropane excited by chemical activation by 1CH_2 addition to C_2H_4 has been reported to transfer ~4 kcal/mole in a He bath, ~6 kcal/mole in N_2 and ~10 kcal/mole in a C_2H_4 bath²¹. Many more examples of such systems can be found in ref. 21 but the trend is clear: the larger the bath (s'), the larger is $\langle \Delta E \rangle$. This result agrees with statistical model results³³⁻³⁹ and with our findings. Of course two effects influence collisional efficiency: one is the size of the heat bath and the other is the potential for the collisional interaction. Insofar as the former effects operate, the results in this series follow qualitative statistical expectation. However, it is possible to make a more quantitative comparison between theory and experiment for the case of the polyatomics butyl radical and SF_6 that function operationally in that study²¹ as strong colliders. Thus, at $E = 43 \text{ kcal/mole}^{-1}$ and $s \approx 15$ for the butyl radical and $s' = 3$ for the SF_6 (found by calculating the average energy of SF_6 and then calculating s' from $\langle E \rangle = s'kT$ when $T=300K$), the value of $\langle \Delta E \rangle$ calculated from eq. 7 is 6.2 kcal/mole. This prediction is in reasonable agreement with the experimental value of ~9 kcal/mole.

Not much data exist for the temperature effect on the magnitude of $\langle \Delta E \rangle$ in chemically activated systems. The little there is, covers the low temperature range 200-700°K and seems somewhat contradictory.

Cyclopropane colliding with C_2H_4 shows²¹ an increase and then a decrease in $\langle \Delta E \rangle$ on going from 300 K to 700 K. For excited $C_2H_4F_2$ ⁴⁰ colliding with CH_2ClF , $\langle \Delta E \rangle$ remains constant at 300 K and 475 K. For excited C_2H_5F colliding with N_2 there is a five fold increase in $\langle \Delta E \rangle$ on going from 315 K to 560 K - a somewhat unexpectedly large temperature effect²¹. The present model predicts a moderate increase in $\langle \Delta E \rangle$ with temperature rise (Fig. 5) and reliable experimental data are clearly needed to verify this point.

In recent experiments⁴⁵ azulene was photoexcited by laser and its energy transfer behavior was investigated by allowing it to collide with 17 bath gases. It was found that molecules with energy content of 17500 cm^{-1} transferred to the bath molecules less energy than molecules excited to 30600 cm^{-1} level. The trend is similar to the one shown in Figs. 2 and 3. It was found as well that the larger s' the larger the value of $\langle \Delta E \rangle$, in agreement with Figs. 3 and 4. In other experiments⁴⁶ the energy transfer behavior of laser excited cycloheptatriene was studied for a variety of bath gases where it was found that there is practically no energy dependence of $\langle \Delta E \rangle$, in contradiction with the results reported in ref. 45.

Another type of experiment involves changing size of the substrate (increase in the value of s) at constant s' . This type of experiment is harder

to interpret since different substrate molecules have different threshold energy for decomposition, E_0 , and different working temperatures, usually. Statistical theory predicts that the larger the substrate the smaller is $\langle \Delta E \rangle$, since more energy remains in the substrate molecule³⁹. The best way to obtain reliable results is to change s in an homologous series where E_0 and the activated complex remain unchanged. One such system is the alkyl radical system where excited butyl, pentyl, hexyl, and octyl were allowed to collide with various di- and polyatomic gases⁴¹. A slight increase in the magnitude of $\langle \Delta E \rangle$ was found going from butyl to octyl. This is opposed to the prediction of the present and statistical model given in ref. 39. Cyclopropane transfers²¹ ~ 10 kcal/mole with C_2H_4 as a bath and 9 ± 3 kcal/mole with $n-C_5H_{10}$.¹⁷ Dimethyl cyclopropane transfers²¹ 11.4 kcal/mole with cis-butene as bath⁴³. Methylcyclopropane is reported to transfer³⁹ 7 ± 1 kcal/mole in a collision with $n-C_5H_{10}$ while ethylcyclopropane is reported to transfer³⁹ 7 ± 4 kcal/mole with 2 methylpentane as bath. Clearly, a clear correlation is difficult to make. Pentyl-2 and dimethyl pentyl-2 are reported^{21,44} to transfer 4.6 kcal/mole in collisions with CF_4 . Again a change in the number of modes of the substrate does not appear to cause a change in $\langle \Delta E \rangle$. More systematic and reliable experiments must be performed in order to understand the effect that increasing s has on the magnitude of $\langle \Delta E \rangle$.

It is useful here to compare other statistical models. The transition modes model³⁹ calculations give good agreement with the experimental results. However, a cut-off energy in the transitional stretching mode correlating with relative translational motion along the line of centers is introduced and empirically adjusted. The empirical adjustments were done in such a way as to force the

calculations for the value of $\langle \Delta E \rangle$ for methylcyclopropane to reproduce the experimental one. The empirical values were then used in other collision pairs calculations.

The ergodic collision theory⁴⁷ predicts values which are generally larger than the reported experimental values. For dimethyl cyclopropane colliding with cis-butene-2, instead of the reported value of 11.4 kcal/mole it predicts values in the range of 27-51 kcal/mole. For 2 pentyl radical colliding with CF_4 it predicts 9.6 kcal/mole instead of 4.5 kcal/mole. Generally, about a factor of two or better is obtained between theoretical and experimentally reported values.

An improvement of the results calculated by the previous theory is obtained by the impulsive collision theory⁴⁸. In this theory the collisional period is very short and therefore only kinetic energy is available for redistribution. The value of $\langle \Delta E \rangle$ for the collision between dimethylcyclopropane and C_4H_8 is now reduced to the range 14-27 kcal/mole compared with the experimental 11.4 kcal/mole. If one makes the common assumption that the classical s is half the number of modes, good agreement of the present treatment is obtained with the ergodic collision theory⁴⁷ as one would expect. The advantage of simplicity and lack of empiricism makes it as a useful tool in understanding the dependence of $\langle \Delta E \rangle$ on the size and temperature of the collision partners.

CONCLUSIONS

a) The collisional energy transfer probability $P(E, \Delta E)$ as given by eq. 3 and 4 is a smooth function which obeys the conservation of probability, eq. 5, and detailed balance eq. 6.

b) The width at half height of $P(E, \Delta E)$ is smaller at lower values of E , fig. 1.

c) At lower values of E most of the collisions are up transition and $\langle \Delta E \rangle = \langle \Delta E_U \rangle$. At higher values of E most of the collisions are down transitions and $\langle \Delta E \rangle = \langle \Delta E_D \rangle$ fig. 1, 2, 5. At intermediate regions up and down collisions are operative.

d) Increasing the temperature of the bath effects larger $\langle \Delta E_U \rangle$ and smaller $\langle \Delta E_D \rangle$ fig. 2.

e) Increasing the size of the bath molecule increases the size of the average energy jump up and down, fig. 3.

f) The reduced number of degrees of freedom is a good parameter to use in order to show the effective molecular size dependence of the energy jumps, Fig. 4.

g) At low level of excitation $\langle \Delta E \rangle$ is larger, the greater the size of the substrate, s . The collisions are up transitions, fig. 6.

h) At high level of excitation $\langle \Delta E \rangle$ is smaller, the larger s . The collisions are down transitions, fig. 6.

i) As s increases for a given level of excitation the value of $\langle \Delta E \rangle$ increases. It is still negative at high level of excitation and positive at lower ones.

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FIGURE CAPTIONS

Figure 1. Collisional energy transfer probability $P(E, \Delta E)$ vs. ΔE at 1000K for reactant and bath molecules with 15 degrees of freedom. The curves shown are for internal energies of 0, 10, 28 and 60 kcal/mole.

Figure 2. Average energy transferred per collision $\langle \Delta E \rangle$ vs. internal energy E at 400K, 1000K and 2000K for $s = s' = 15$. The solid line above $\langle \Delta E \rangle = 0$ is for $\langle \Delta E_U \rangle$ and below the line is for $\langle \Delta E_D \rangle$. The barred line indicates the overall energy transferred $\langle \Delta E \rangle$.

Figure 3. The average energy transferred, $\langle \Delta E \rangle$ vs. the internal energy E at 1000K and $s=15$ for four values of the number of degrees of freedom of the bath molecule $s'=5, 15, 30, \infty$. Full lines indicate $\langle \Delta E_U \rangle$ and $\langle \Delta E_D \rangle$. The barred lines indicate $\langle \Delta E \rangle$.

Figure 4. The average energy $\langle \Delta E \rangle$ vs. the square root of the reduced number of modes, s_r for various values of E (kcal/mol) at 1000K and $s=15$.

Figure 5. The average energy $\langle \Delta E \rangle$ vs. the temperature of the bath for $s = s' = 15$ for the various values of E (kcal/mole) indicated on the curves.

Figure 6. $\langle \Delta E \rangle$ vs. the internal energy E for $s=10, 15$ and $s'=15$, $T=1000K$. The dashed line indicates the average value of the energy transferred while the full lines indicate $\langle \Delta E_U \rangle$ and $\langle \Delta E_D \rangle$.

Figure 7. $\langle \Delta E \rangle$ vs. the square root of the reduced number of degrees of freedom s_r values of initial energy E as indicated in the figure (in Kcal/mole) for $s' = 15$ and $T = 1000K$.

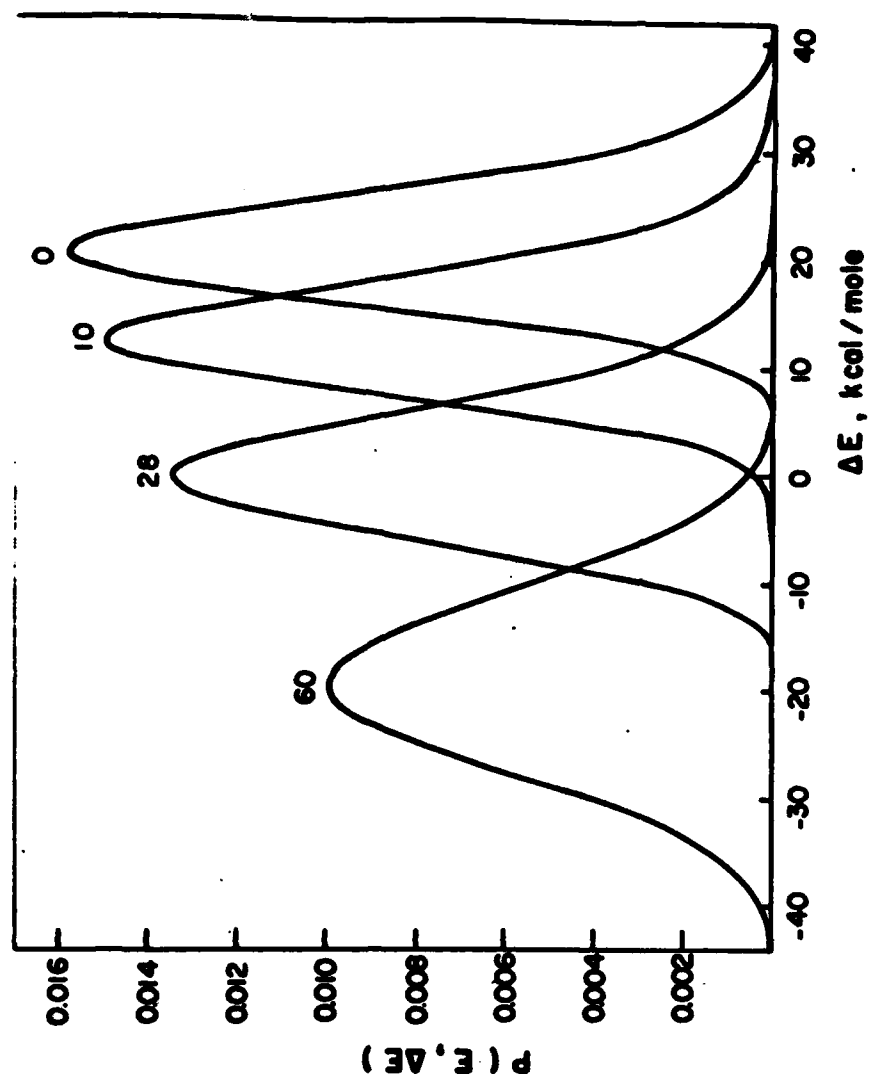


Fig 1

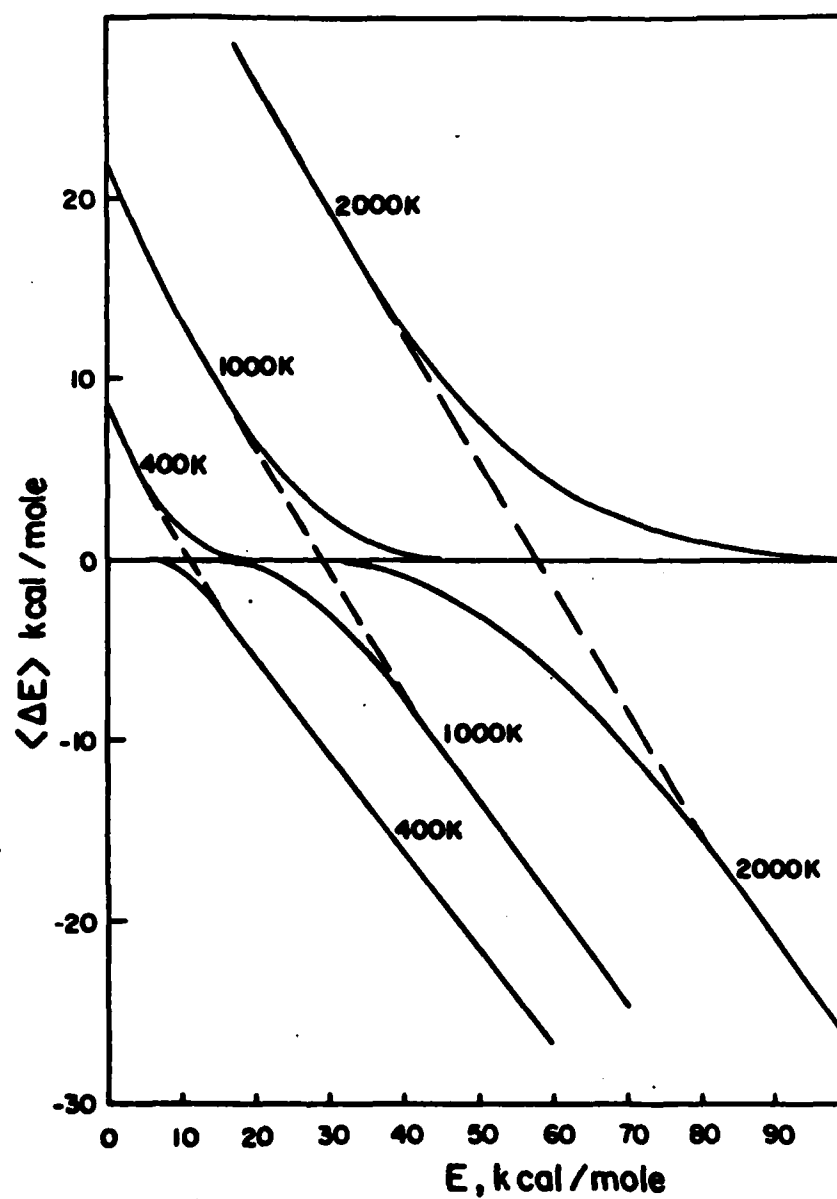


Fig 2

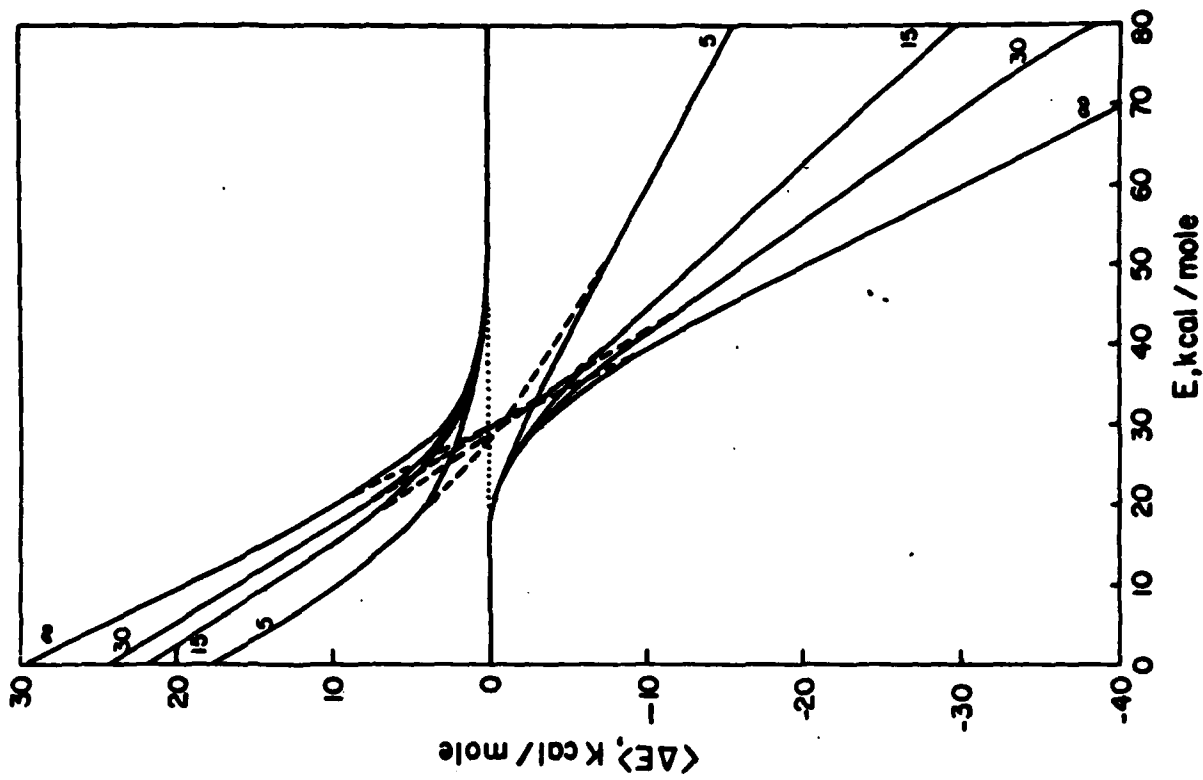


Fig. 3

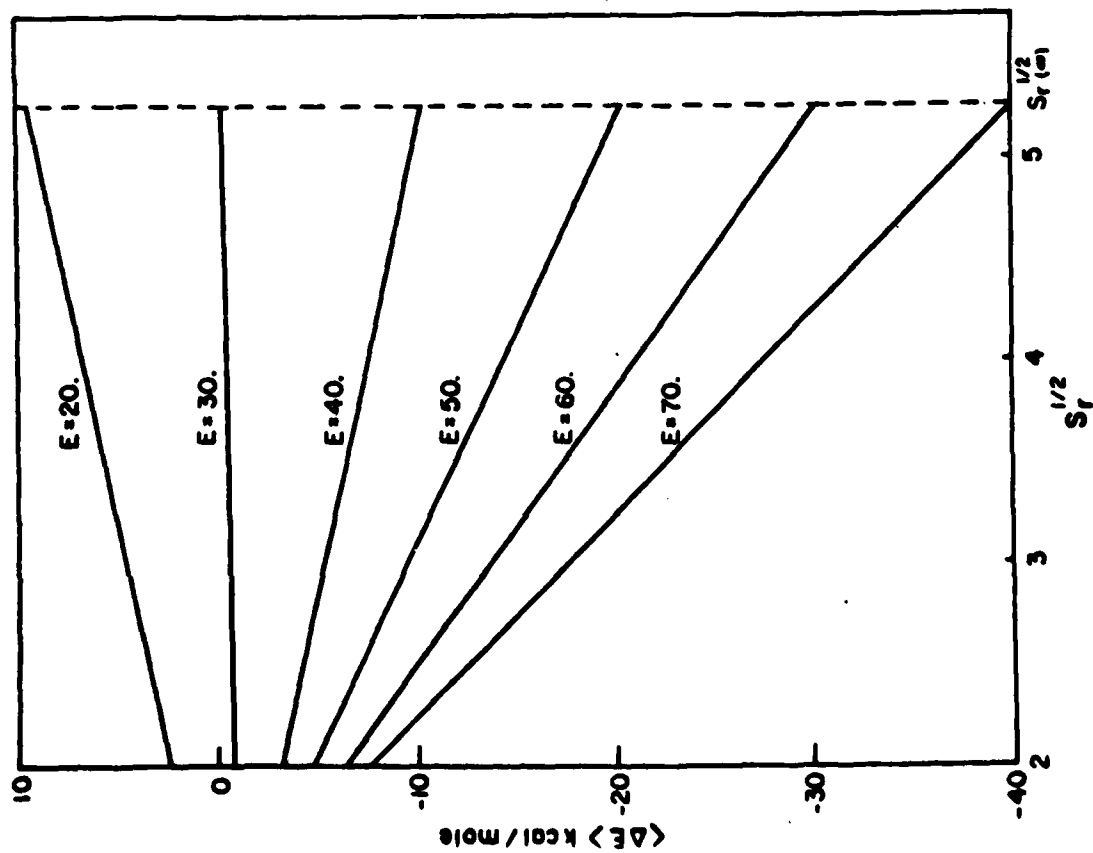


Fig 4

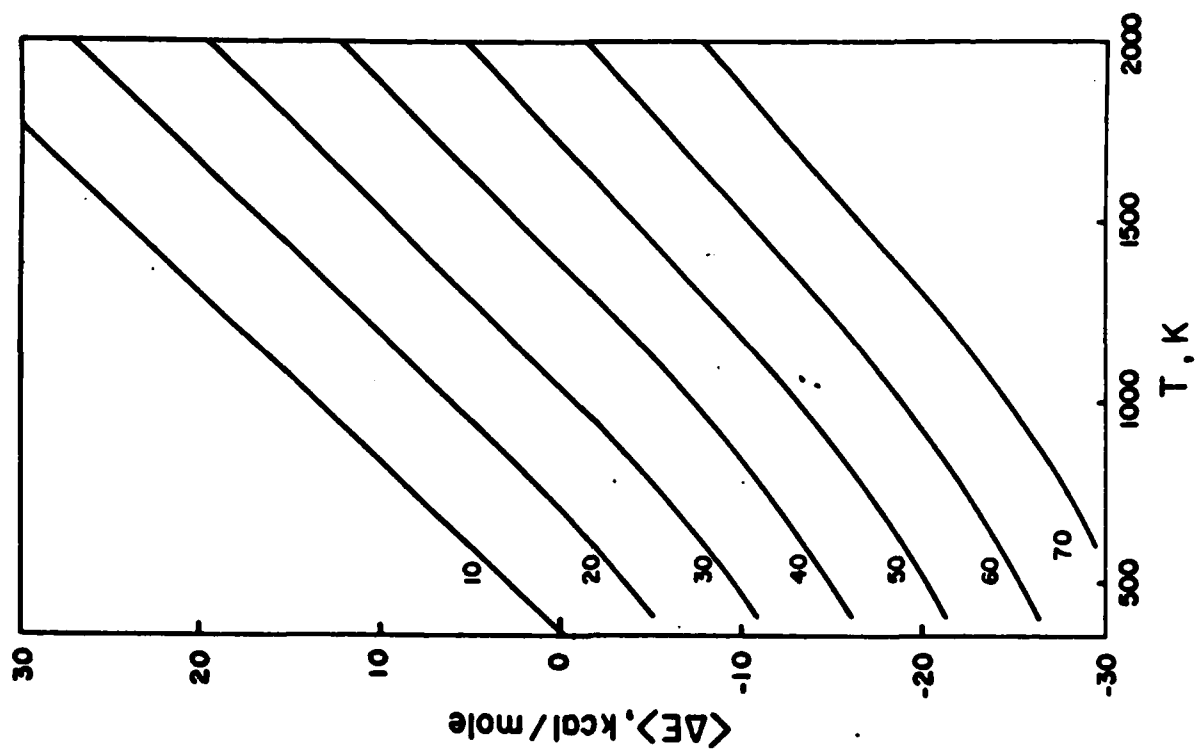


Fig 5

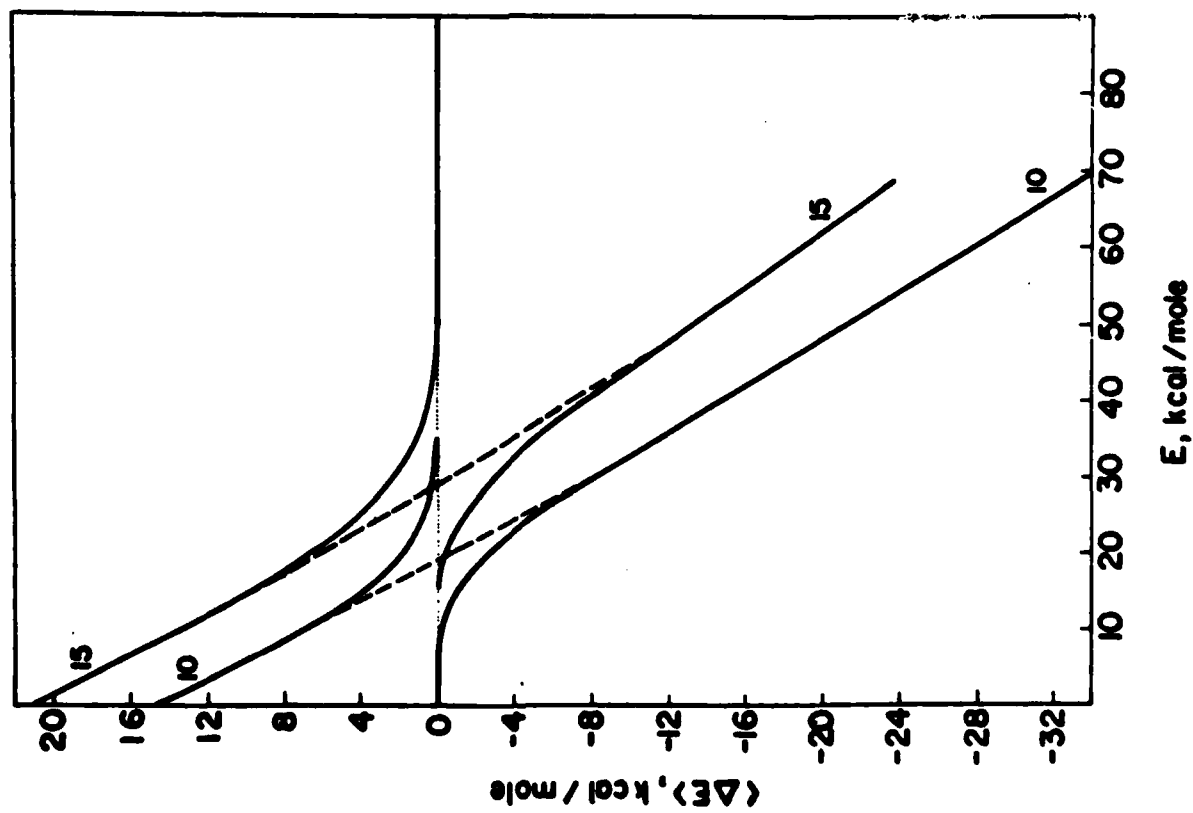


Fig. 6

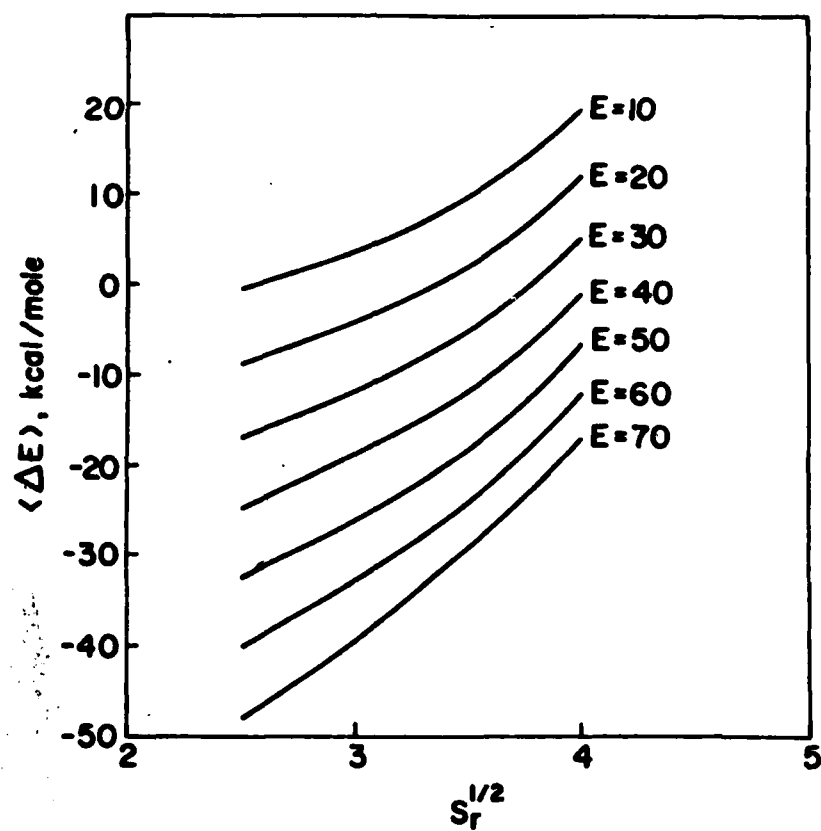


Fig 7

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