QUARTERLY REVIEWS

ENERGY TRANSFER IN GASEOUS COLLISIONS

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Theories of energy transfer have been given by Oldenberg and Frost [1] and by Massey.[2] Certain special topics in this field have more recently been considered in a number of books.[3-6] The purpose of this Review is to present the unifying aspects and some of the recent work in this expanding field, in particular such work as has been related to molecular structures. The scope has been limited to transfers involving vibration or rotation since these are of primary importance for chemical reactivity. Considerable attention has been paid to energy transfer involving low-lying energy levels.

1. General Introduction

Low Energy Levels.—Many physicochemical processes are concerned with systems perturbed from the equilibrium position by uptake of energy which then revert to equilibrium. A sudden input of energy may be transmitted to the system in some quite definite form, *e.g.*, by an increase in translational energy ; this input energy will ultimately become redistributed by collisions through all the available levels of the system at a rate dependent upon the nature and number of these levels.

A rapid change of an external parameter affecting the energy of the system, followed by the subsequent shift of equilibrium which proceeds with a finite time lag, forms the basis of a so-called relaxation process.[3, 6] Experimentally this finite relaxation of equilibrium or energy-transfer effect is studied in terms of the bulk properties of the gas.

Examples of relaxation effects may be found in experiments on the change of velocity of sound with frequency at high frequencies [7] or in the rapid expansion of gases out of jets or nozzles.[8] In these experiments

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[1] O. Oldenberg and A. A. Frost, *Chem. Reviews*, 1937, **20**, 99.

[2] H. S. W. Massey, *Reports Prog. Phys.*, 1949, **12**, 248.

[3] H. S. W. Massey and E. H. S. Burhop, " Electronic and Ionic Impact Phenomena ", Clarendon Press, Oxford, 1952.

[4] K. J. Laidler, " The Chemical Kinetics of Excited Species ", Clarendon Press, Oxford, 1955.

[5] A. F. Trotman-Dickenson, " Gas Kinetics ", Butterworths, London, 1955.

[6] K. F. Herzfeld, " Thermodynamics and Physics of Matter ", Ed. Rossini, Princeton, 1955.

[7] L. Bergman, " Der Ultraschall ", 5th edn., Herzel, Zürich, 1949.

[8] P. W. Huber and A. Kantrowitz, *J. Chem. Phys.*, 1947, **15**, 275 ; W. Griffiths, *J. Appl. Physics*, 1950, **21**, 1319.

the steady-state condition set up depends to some extent upon the rate of redistribution of translational energy into internal molecular modes.

In sound propagation or ærodynamic phenomena comparatively small changes in translational temperature are involved in the compressions or rarefactions so that the internal modes into which energy must be equilibrated are *not far from the ground state*, *e.g.*, only one or two vibrational quanta above the zero-point half quantum.

Higher Energy Levels.—The action of light upon molecules may in general bring about changes of both electronic and vibrational quantum numbers. Subsequent chemical reactivity of these molecules or their re-emission of light is conditioned by the way in which all or part of their excess energy may be transferred to other molecules.[9, 4] Under these conditions we may be concerned with vibrational energy levels *ten to twenty above the zero-point energy.*

A number of thermal reactions, such as occur in flames or oxidations, involve the formation of transient species which contain sufficient energy to make them decompose again without taking further part in the main reaction. Removal of this excess energy serves to stabilise these intermediate species.[4, 5] The energy transferred in this case is vibrational *in the region of the self-dissociation level.*

Magnitude of Energy Levels.—If the molecular potential-energy curve were a perfect parabola, *i.e.*, a perfectly harmonic oscillator, all the vibrational energy levels of a molecule would be equally spaced. Real potential-energy curves refer to anharmonic oscillations; the vibrational energy levels of such an anharmonic oscillator may be approximately expressed by two terms in a simple power series.

The separation between levels is given (in units of cm.$^{-1}$)[10] by

$$\Delta G = \nu/c - x_e(\nu/c)(2Q + 2)$$

where ν is the vibration frequency, Q the quantum number, x_e an anharmonicity factor, and c the velocity of light.

It follows that the separation between vibrational levels ΔG decreases with increasing value of the quantum number. The magnitude of energy quanta will therefore vary considerably for the same molecule in relation to experiments on aerodynamic, photochemical, and reactivity phenomena. In consequence the detailed mechanisms of energy transfer may vary considerably in these different cases.

2. Transfer of Energy between Translation and Vibration or Rotation Quanta involving Low-lying Energy States of Molecules

(*a*) A Study of the Dispersion and Absorption of High-frequency Sound.—The most frequently used technique for studying transfer involving low-lying energy states has involved high-frequency sound in gases.[11, 12] When

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[9] G. Herzberg, " Spectra of Diatomic Molecules ", Van Nostrand, New York, 1950.

[10] A. G. Gaydon, " Dissociation Energies ", Dover, New York, 1950.

[11] J. J. Markham, R. T. Beyer, and R. B. Lindsay, *Rev. Mod. Physics*, 1951, **23**, 353.

[12] W. T. Richards, *ibid.*, 1939, **11**, 36.

a sound wave is propagated through a fluid, the fluid is subjected to periodic cycles of compressions and rarefactions with accompanying periodic temperature changes. For a perfect gas the speed with which the adiabatic sound wave is propagated is given by Laplace's classical equation

$$V^2 = (RT/M)(1 + R/C_v) \quad . \quad . \quad . \quad . \quad (1)$$

where C_v is the total heat capacity at constant volume and M is the molecular weight. In this classical treatment, some absorption of sound occurs, owing to energy losses from viscosity and heat conduction.[11]

When the frequency of the sound wave is low, the time between successive compressions or rarefactions is long and all the energy states of the gas are excited by the sound wave at rates sufficient to maintain practically equilibrium distribution with reference to the fluctuating temperature produced by the sound wave. At sufficiently high frequencies, the time interval between the fluctuating temperature changes becomes markedly shorter than the time required for the redistribution of energy into the various internal modes. At this stage the effective specific heat of the fluid subjected to the sound wave becomes less than the maximum specific heat. In the limit, at very high frequencies sound propagation may involve none of the terms due to internal energy changes of the molecule. Physically this means that the velocity of sound in a gas will change with frequency between the low and high frequency limits, if the energy-transfer process translational $\rightleftharpoons$ internal modes is sufficiently slow. Such changes of velocity with frequency are usually called dispersions. In the high-frequency sound wave, since the molecules are not able to redistribute their translational energy to internal modes before passing it on by collision, there is a phase displacement of pressure relative to density and part of the sound energy is irreversibly absorbed by conversion into thermal energy.[11] This leads to an absorption over and above that due to viscosity and heat conduction.

At moderate frequencies (50—2000 kc./sec.) many experimentally observed changes of velocity with frequency or high non-classical absorptions are due to phase lags between translation and vibration ; dispersions have also been observed for phase lags between translation and rotation at still higher frequencies.

Under given static conditions at low frequencies the effective heat capacity may be written C_0 and the velocity V_0. At very high frequencies when none of the vibrational states is operative the corresponding parameters are C_∞ and V_∞. We consider first the case of a gas with only one vibrational mode of frequency ν which becomes inoperative as the frequency is raised.[11, 12] The energy $E = h\nu$ is assumed to be such that only the first excited state is appreciably populated. At any instant there will be a number of molecules N_0 in the ground state and a number N_1 in the excited state ; $N_0 + N_1 = N$, the total number of states occupied per mole.

At equilibrium $\bar{N}_1 = \bar{N}_0 \exp(-h\nu/kT)$

Without assuming any mechanism for the interconversion of state we can write

$$\mathrm{d}N_1/\mathrm{d}t = k_{01}N_0 - k_{10}N_1 \quad . \quad . \quad (2)$$

where k_{01} and k_{10} are the probabilities of exciting and de-exciting state 1, *i.e.*, numbers of transitions per molecule per second.

At equilibrium

$$\mathrm{d}N_1/\mathrm{d}t = 0 \quad \text{and} \quad k_{01}/k_{10} = \bar{N}_1/\bar{N}_0 = \exp\,(-\,\boldsymbol{h\nu/kT})$$

For displacement of the system from equilibrium by a small amount ΔN_1, within the limits of irreversible thermodynamics we may write[13]

$$\mathrm{d}(\Delta N_1)/\mathrm{d}t = -\,\Delta N_1/\tau \quad . \quad . \quad . \quad . \quad (3)$$

Here τ measures the relaxation time necessary for the departure from equilibrium to be reduced to 1/e of its initial value, in the two-state case it can readily be shown[14] that $1/\tau = k_{01} + k_{10}$; since in our case $\boldsymbol{h\nu/kT} \gg 1$, $k_{01} \ll k_{10}$ and $1/\tau \simeq k_{10}$.*

At ideally low frequencies the sound wave increases the temperature by ΔT at each peak compression, and hence the population of the excited state by $\Delta\bar{N}_1$, since $C_i\,\Delta T = E\,\Delta\bar{N}_1$ where $C_i = C_0 - C_\infty$ is the total internal heat capacity. At ideally high frequencies the sound wave passes through the gas without substantial alteration in N_1.

At intermediate frequencies the population of N_1 increases at peak compression by $\Delta N_1{}^{\omega}$, an amount less than $\Delta\bar{N}_1$ and dependent upon $\omega = 2\pi f$, where f is the cyclic frequency of the sound:

$$\Delta N_1{}^{\omega} = \Delta\bar{N}_1/(1 + i\omega\tau)\,; \quad C_i{}^{\omega} = (C_0 - C_\infty)/(1 + i\omega\tau) \quad . \quad (4)$$

The measured velocity V and absorption coefficient μ vary with frequency according to the equations[11, 12, 15]

$$V^2 = \frac{\boldsymbol{R}T}{M}\left(1 + \frac{\boldsymbol{R}(C_0 + C_\infty\omega^2\tau^2)}{C_0{}^2 + C_\infty{}^2\omega^2\tau^2}\right) \quad . \quad . \quad . \quad . \quad (5)$$

$$\mu = \frac{2\pi\omega C_\infty\tau}{C_0}\left[\frac{V_\infty{}^2/V_0{}^2 - 1}{(V_\infty{}^2/V_0{}^2)(C_\infty\omega\tau/C_0)^2 + 1}\right] \quad . \quad . \quad (6)$$

Equations (5) and (6) are used to deduce τ from experimental observations.

(*b*) **Analysis of Ultrasonic Measurements to obtain Energy-transfer Data.**—In computing τ from experiment by use of (5) and (6), the measured values must be corrected to zero pressure by means of a suitable equation of state.[16]

Equation (2) implies no specific mechanism for the energy-transfer process. It is generally assumed that energy transfer is effected by two-body

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[13] S. R. de Groot, " Thermodynamics of Irreversible Processes ", North Holland, Amsterdam, 1952.

[14] M. Eigen, *Discuss. Faraday Soc.*, 1954, **17**, 194.

[15] S. Petralia, *Nuovo cim.*, 1952, Suppl. to Vol. 9, 1.

[16] A. Van Itterbeek and W. Van Donninck, *Proc. Phys. Soc.*, 1946, **58**, 615.

* The general theory of relaxation for the two-state process $\mathrm{A} \underset{k_{01}}{\overset{k_{10}}{\rightleftharpoons}} \mathrm{B}$ gives $\tau = 1/(k_{10} + k_{01})$.[14] For the case of a harmonic oscillator the system will only approximate to the two-state case in the condition that $\boldsymbol{h\nu} \gg \boldsymbol{k}T$; when this obtains $\tau \simeq 1/k_{10}$. This condition is fulfilled in a number of experimental cases. For a multi-state relaxation process in a harmonic oscillator it has been shown that $\tau = 1/(k_{10} - k_{01})$.[12] This relation will probably apply for vibrations where $\boldsymbol{h\nu} \leqslant \boldsymbol{k}T$. All of these expressions for τ involve a certain amount of approximation.

collisions. If this hypothesis is correct then the probability factors k_{10} and k_{01} will be proportional to the collision rate in the gas. The two-body collision rate is proportional to the pressure p, which means that the relaxation time τ will be proportional to $1/p$. For bimolecular mechanisms the effect of reducing the pressure is exactly the same as increasing the frequency, *i.e.*, it prevents equilibrium of excited species from being established under the action of the sound wave. The usual experimental variable is the effective frequency ω/p, and the standard relaxation time is referred to one atmosphere pressure.[12, 15] Early experimental work in this field was mainly on inorganic molecules.[17] More recent work has covered a wide range of organic molecules.[18]

When observations of relaxation time are made upon polyatomic molecules, the supposition that the internal energy is contained in a single mode is no longer adequate, since the number of normal vibrations of a molecule increases with the number of bonds. If each molecular vibration were excited separately from the translational energy, a separate relaxation process would be expected for each mode. Such complexity is not generally observed. Usually the whole vibrational specific heat is governed by a single relaxation time; for a few polyatomic molecules, however, two relaxation times are observed from ultrasonic measurements.[19]

The experimental phenomenon of a single relaxation process for polyatomic molecules may be interpreted in terms of two possible mechanisms.[20]

(1) Individual transfer processes for different modes of vibration, 1, 2, 3 . . ., are treated as independent; if the separate relaxation times are all approximately equal the observed relaxation time τ [from (5) and (6)] is equal to $\tau_1 = \tau_2 = \tau_3$ . . . Theoretical considerations suggest that this is rather unlikely (cf. 3.1).

(2) Excitation is consecutive; transfer is generally assumed to take place from translation to the *lowest vibrational mode* 1 with characteristic relaxation time τ_1, from this mode to 2, and so on. The internal relaxation times τ_{12}, τ_{13} . . . are assumed to be much smaller than τ_1. In this case

$$\tau_1 = \tau C_1/(C_1 + C_2 + C_3 + \ldots) \qquad (7)$$

and the rate of transfer to all the internal modes on collision is controlled by a single value. In equation (7), C_1 is the heat capacity associated with mode 1 and $(C_1 + C_2 + C_3 + \ldots)$ is the total internal vibrational heat capacity associated with the molecule, due allowance being made for the degeneracy of the levels.

This series excitation of vibrational energy must involve a considerable coupling of the anharmonic oscillators (simple harmonic oscillators vibrate independently). Such coupling enables the potential energy initially supplied to the molecule by collision to be apportioned to the various vibrators by rapid internal re-adjustments. It seems likely that not all molecular

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[17] R. A. Walker, National Advisory Committee for Aeronautics, Technical Note No. 2537, Washington, 1951.

[18] P. G. T. Fogg and J. D. Lambert, *Proc. Roy. Soc.*, 1955, *A*, **232**, 537.

[19] D. Sette, A. Busala, and J. C. Hubbard, *J. Chem. Phys.*, 1955, **23**, 787.

[20] K. Schäfer, *Z. phys. Chem.*, 1940, *B*, **46**, 212.

vibrations will couple together readily. If coupling does not occur then internal redistribution of energy may be a much slower process than the direct excitation of separate vibrations by collision. This corresponds to the case of more than one relaxation time sometimes observed (cf. Table 2).

Writing the single relaxation time $1/\tau_1 \simeq k'_{10}$, we define a transition probability per collision averaged over the whole system

$$P'_{10} = k'_{10}/Z = 1/Z'_{10} \quad . \quad . \quad . \quad . \quad (8)$$

where Z is $4n\sigma^2(\pi RT/M)^{1/2}$, the number of collisions made by one molecule in one second,[21] n is the molecule density at one atmosphere pressure, σ the

TABLE 1. *Observed relaxation times τ, relaxation times for lowest mode τ_1, and numbers of collisions Z'_{10} required to de-excite lowest quantum $h\nu_1$ for a selection of molecules, obtained from ultrasonic data*

Molecule	Temp. (° C)	$\tau \times 10^7$ (sec.)	$\tau_1 \times 10^7$ (sec.)	Z'_{10}	ν_1/C (cm.$^{-1}$)	Ref.
O_2	20	—	—	500,000	1580	22, 3
Cl_2	18	42	42	32,000	560	24
CO_2	20	116	108	108,000	667	23
N_2O	20	9·3	8·7	7000	589	25
COS	20	16·7	13·5	14,000	527	26
SF_6	36	5·89	1·76	1400	363	27
CH_4	109	8·4	6·0	6000	1306	26
CF_4	100	6·6	2·4	1300	435	28
CCl_4	100	0·83	0·23	130	218	28
CH_3F	100	32	8·9	6000	1048	28
CH_3Cl	100	1·8	0·62	400	732	28
CH_3Br	100	1·0	0·36	190	611	28
CH_3I	100	0·45	0·16	76	533	28
CCl_2F_2	27	0·78	0·16	165	260	29
CBr_2F_2	27	0·29	0·05	47	165	29
C_2H_4	15	2·5	0·71	700	810	30
cis-$C_2H_2Cl_2$	100	0·25	0·049	31	173	18
trans-$C_2H_2Cl_2$	100	0·082	0·016	10	227	18
C_2F_4	100	0·14	0·020	11	190	18
cyclo-C_3H_6	100	2·7	0·62	600	740	31
C_6H_6	96	1·5	0·28	200	405	31
n-C_6H_{14}	100	—	—	20	<100	31

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[21] J. R. Partington, " Advanced Treatise on Physical Chemistry ", Vol. 1, Longmans, Green and Co., London.

[22] H. O. Kneser, *Ann. Phys.*, 1935, **21,** 682.

[23] A. Van Itterbeek, P. De Bruyn, and P. Mariens, *Physica*, 1939, **6,** 511.

[24] A. Eucken and R. Becker, *Z. phys. Chem.*, 1934, *B*, **27,** 235.

[25] A. Eucken and H. Jaacks, *ibid.*, 1935, *B*, **30,** 85 ; A. Eucken and E. Nümann, *ibid.*, 1937, *B*, **36,** 163.

[26] A. Eucken and S. Aybar, *ibid.*, 1940, *B*, **46,** 195.

[27] C. L. O'Connor, *J. Acoust. Soc. Amer.*, 1954, **26,** 361.

[28] P. G. T. Fogg, P. A. Hanks, and J. D. Lambert, *Proc. Roy. Soc.*, 1953, *A*, **219,** 490.

[29] T. D. Rossing and S. Legvold, *J. Chem. Phys.*, 1955, **23,** 1118.

[30] J. C. McCoubrey, J. B. Parke, and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1954, *A*, **223,** 155.

[31] J. D. Lambert and J. S. Rowlinson, *ibid.*, 1950, *A*, **204,** 424.

collision diameter, and M the molecular weight. The quantity Z'_{10} is the number of collisions required to de-excite one quantum of the lowest vibration $h\nu_1$.

Alternative collision efficiencies sometimes defined are written

$$Z_{\text{eff}} = 1/P_{10} = Z/k_{10} \quad . \quad . \quad . \quad . \qquad (9)$$

Here P_{10} and k_{10} refer to average values for the whole molecule obtained from the relation $\tau \simeq 1/k_{10}$.

For diatomic molecules Z_{eff} is equal to Z'_{10}; in general,

$$Z'_{10} = Z_{\text{eff}} C_1/(C_1 + C_2 + C_3 + \ . \ . \ .)$$

Tables 1 and 2 give a selection of relaxation times and collision efficiencies for translation–vibration transfers. Also included are values of the lowest spectroscopic vibration " frequencies " ν_1/c. A value of ν_1/c of 100 cm.$^{-1}$ corresponds to an energy change $0 \longrightarrow 1$ of 286 cal./mole.

TABLE 2. *Observed relaxation times for molecules in which double dispersion is indicated by experiment at* 30° C

Molecule	$^1\tau \times 10^8$ (sec.)	$^2\tau \times 10^8$ (sec.)	Ref.
CH_2Cl_2	9·46	0·195	19
1 : 1-$C_2H_4Cl_2$ . . .	36	0·535	32
1 : 2-$C_2H_4Cl_2$ . . .	6·6	0·425	32

From Table 1 it appears that there is a wide spectrum of values of Z'_{10} ranging from about 10^6 for oxygen to about 10 collisions for some organic molecules.

For polyatomic molecules exhibiting a single relaxation the energy-transfer probability depends broadly upon the magnitude of the lowest vibration frequency. Molecules with low vibration frequencies are more readily de-excited. There is, however, no strict parallel between Z'_{10} and ν_1.

When molecules are divided into classes of common spectroscopic type then the correlation in any class between Z'_{10} and ν_1 becomes more nearly quantitative. Thus the molecules CH_3F, CH_3Cl, CH_3Br, and CH_3I, in which the lowest frequency is a carbon–halogen stretching, show an excellent linear relationship between $\log Z'_{10}$ and ν_1.[18]

Another property of the lowest vibration frequency which affects the value of Z'_{10} is whether or not the oscillation is infrared-active.[18] Molecules for which the lowest vibration is infrared-active have been differentiated from those in which the lowest vibration is active only in the Raman spectrum. This may be due to differences in the electrical behaviour of the vibrations which are perturbed by the dipole moment of the approaching molecule in a collision (see Fig. 1).

[32] T. S. Rao and J. C. Hubbard, *J. Acoust. Soc. Amer.*, 1955 **27**, 321.

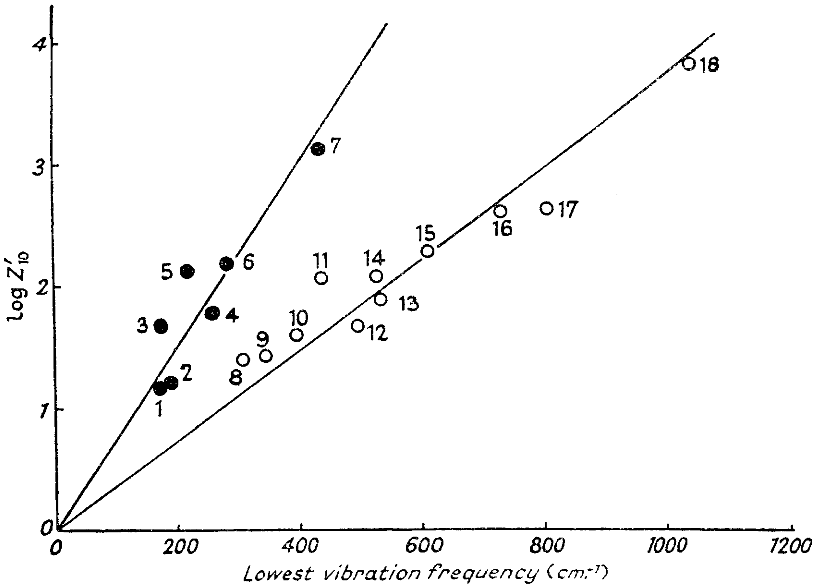

FIG. 1

(Substantially copied from P. G. T. Fogg and J. D. Lambert, *Proc. Roy. Soc.*, 1955, *A*, **232**, 537.)

Collision lifetime for lowest vibrational state in polyatomic molecules (Fogg and Lambert's data).

Infrared inactive vibrators: (1) $CHCl{:}CCl_2$; (2) $CF_2{:}CF_2$; (3) *cis*-$CHCl{:}CHCl$; (4) $CHCl_3$; (5) CCl_4; (6) CH_2Cl_2 (cf. Table 2); (7) CF_4.

Infrared active: (8) $CH_2{:}CHI$; (9) $CH_2{:}CHBr$; (10) $CH_2{:}CHCl$; (11) $CH_2{:}CF_2$; (12) $CH_2{:}CHF$; (13) CH_3I; (14) CH_2F_2; (15) CH_3Br; (16) CH_3Cl; (17) $CH_2{:}CH_2$; (18) CH_3F.

(*c*) **Translation–Vibration Transfer in Two-component Systems.**—Values of the overall relaxation time τ may be obtained for mixtures from the equations (12) and (13). This value of τ corresponds to effects due to collisions between all possible species AA, AB, and BB. If a molecule A itself exhibits a dispersion, addition of a molecule B may cause some shift of the dispersion region in terms of frequency. If collisions AB are more efficient in transferring internal energy to A than collisions AA, the dispersion shifts to higher frequencies. If the mixture is sufficiently dilute, effects due to BB interactions are negligible. It is possible to segregate effects due to interactions AA and AB. If only binary collisions are effective then their effect is given [15, 17] by an equation of the form

$$1/\tau = x_A/\tau_{AA} + x_B/\tau_{AB}$$

where x_A and x_B correspond to mole-fractions.

The value of τ_{AB} obtained from this equation refers to a hypothetical mixture of A and B in which only AB collisions are effective and in which the partial pressure of B is one atmosphere.

By analogy with the treatment given above for pure gases, τ_{AB} should be multiplied by a factor $[C_1/(C_1 + C_2 + C_3 + \ldots)]_A$ to give ${}^{AB}\tau_1$, where

${}^{AB}\tau_1$ represents the relaxation time associated with a deactivation of the lowest vibrational mode of A by a molecule of B.

From this quantity ${}^{AB}\tau_1$ we may define a collision efficiency ${}^{AB}P'_{10}$ for de-excitation of a vibrational quantum of A by B

$${}^{AB}P'_{10} = {}^{AB}k'_{10}/Z_{AB} = 1/{}^{AB}Z'_{10}\,; \quad {}^{AB}k'_{10} \simeq 1/{}^{AB}\tau_1 \qquad . \quad (10)$$

where Z_{AB} is the collision number for AB encounters in the above hypothetical gas.

Numbers of collisions required to de-excite vibrational quanta are given for a range of molecules in Table 3.

TABLE 3.* *Energy-transfer data expressed in number of collisions to de-excite lowest vibrational quantum of parent gas by additive* ${}^{AB}Z'_{10}$, *obtained from ultrasonic data*

Temp. (° K)	293	293	293	293	293	288
Parent	Cl_2	O_2	COS	CO_2	N_2O	C_2H_4
Additive						
Self	32,000	500,000	14,000	108,000	7000	700
H_2	700	20,000	160	500	600	70
He	850	150,000	1000	1500	1500	—
D_2	—	—	—	1500	450	550
N_2	41,000	100,000	3000	—	—	1400
CH_4	180	—	—	2100	800	—
H_2O	—	400	6	130	70	24
D_2O	—	—	—	270	—	—
$C_6H_5{\cdot}CH_3$ . .	—	—	—	23	190	—
$CH_3{\cdot}OH$ . . .	—	—	30	35	90	—
n-C_5H_{12} . . .	—	—	—	—	—	11
n-C_6H_{14} . . .	—	—	—	—	—	8
NH_3	—	390	—	—	450	—
Ref.	24	22	26, 33	23, 24 33, 34	25 33	30, 35

* Where the data for one compound are drawn from different sources the figures may not be self-consistent to better than a factor of two.

Table 3 shows the wide range of effects found with additives in ultrasonics. Light molecules such as H_2 or He have a high efficiency in transferring to their translational modes the vibrational energy of other molecules.

Molecules which possess permanent dipoles such as NH_3, $CH_3{\cdot}OH$, or H_2O are in general found to be efficient. Molecules of quite high molecular weight such as toluene, n-pentane, or n-hexane may also show a very high efficiency in energy transfer.

In several cases such as CO_2–H_2O and Cl_2–CO incipient chemical reactivity produces a high transfer efficiency.

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[33] V. O. Knudsen and E. F. Fricke, *J. Acoust. Soc. Amer.*, 1938, **10,** 89 ; 1940, **12,** 244.

[34] D. Sette and J. C. Hubbard, *ibid.*, 1953, **25,** 994.

[35] W. T. Richards and J. A. Reid, *J. Chem. Phys.*, 1934, **2,** 206.

In general, binary collisions are responsible for energy transfer though evidence for the importance of three-body collisions in mixtures at high concentration of additives has been obtained in a few cases.[36]

(*d*) **Ultrasonic Study of the Transfer of Energy between Translation and Rotation.**—A treatment similar to that given above for translation–vibration may be applied to transfers occurring between translation and rotation.

Since the magnitude of rotational energy quanta is small (often $\leqslant 50$ cal./mole), redistribution of energy to and from rotational states is a much more efficient process than for vibration. Experimentally it is necessary to go to much higher frequencies to observe dispersion or absorption due to this cause.[37, 38] A relaxation time for the translation–rotation process may be evaluated from equations similar to (5) and (6) and the product of this time with the number of collisions per molecule per second Z gives an approximate number of collisions Z_{eff} required to effect transfer between translation and rotation.

Experimental values are given for a few diatomic molecules in Table 4.

TABLE 4.—*Relaxation times* τ *and numbers of collisions* Z_{eff} *required to effect translational–rotational energy transfer in diatomic molecules, calculated from ultrasonic data*

Molecule	Temp. (° K)	Relaxation time, $\tau \times 10^8$ (sec.)	No. of collisions, Z_{eff}	Ref.
N_2	302	0·12	6	37
O_2	303	0·524	30	38
Air	305	0·304	21	
		0·229	16	39
H_2	298	1·9	320	
		1·7	285	40
H_2	273	2·2	390	41
D_2	273	2·0	250	41

(*e*) **Other Experimental Methods of Study for Transfer at Low Quantum Levels.**—*Heat capacity lag in gas dynamics.* In the flow of gases about obstacles such as aerofoils, compressions and rarefactions occur with enthalpy changes due to loss or gain of mass motion. If gas initially contained in a chamber is expanded through a faired nozzle isentropically it undergoes an enthalpy decrease. If the gas is now brought to rest rapidly at the nose of an impact tube, its enthalpy is increased rapidly and part of the heat capacity (the internal modes) may fail to reach equilibrium immediately on the compression.

In the impact tube the final state of the gas then involves an irreversible return to equilibrium and the gas suffers an increase in entropy S and a

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[36] R. A. Walker, *J. Chem. Phys.*, 1951, **19**, 494.
[37] A. J. Zmuda, *J. Acoust. Soc. Amer.*, 1951, **23**, 472.
[38] W. J. Thaler, *ibid.*, 1952, **24**, 15.
[39] C. Ener, A. F. Gabrysh, and J. C. Hubbard, *ibid.*, p. 474.
[40] E. S. Stewart, *Phys. Review*, 1946, **69**, 632 ; J. E. Rhodes, *ibid.*, 1946, **70**, 932.
[41] E. S. Stewart and J. L. Stewart, *J. Acoust. Soc. Amer.*, 1952, **24**, 194.

decrease in pressure $p_0 - p_2$ from the initial values S and p_0. The observed pressure defect between chamber and impact tube, and hence the entropy increase $\Delta S = \mathbf{R} \log p_0/p_2$, will vary with the ratio of the compression time to the relaxation time. The maximum entropy increase occurs for an instantaneous compression. Hydrodynamic equations relating ΔS to τ have been obtained for different types of impact tubes.

This technique has been used experimentally to determine translation–vibration relaxation times for gases such as N_2, CO_2, CF_2Cl_2, H_2O, and C_3H_8,[8] covering values ranging from 10^{-2} sec. in nitrogen to $<6 \times 10^{-9}$ sec. in propane. Data obtained in this way refer to the same process as ultrasonic measurements and are in reasonable agreement with them.

Study of moving shock waves. A shock wave is a positive pressure wave which moves through the gas with a velocity greater than the normal velocity of sound in the unshocked gas. Shock velocities are therefore equal to or greater than the mean molecular velocity.

The region of abrupt temperature, pressure, and density rise in the front of a gaseous shock wave is known as the shock front. The thickness of this shock front region is of the order of a few mean free paths. As the shock passes through the gas, the molecules in the shock front have their translational, rotational, and vibrational energy increased in a period of the order of a few collision times. If there is a lag in equilibrium the heat capacity effective in the shock front is initially that of a monatomic gas (translation only) and behind the shock front it rises to the equilibrium value. The effect of such a lag is to distort the shock front; the initial increase in the translational temperature is greater and the increase in density less than for the same gas in equilibrium. If the rotational or vibrational energy is not appreciably excited instantaneously with the shock, the shock front will be thicker than for the equilibrium value.

An optical method has been reported for measuring the thickness of the shock front and distortions in it, from a study of the total density change across the front.[42] Results have been used to determine the number of collisions Z_{eff} required to obtain rotational equilibrium in shock fronts in diatomic gases. Values of $Z_{\text{eff}} \sim 10$ for O_2 and N_2 are closely similar, but differ slightly from those found in ultrasonics;[37, 38] there is also an indication of two or more distinct relaxation times for these gases.

Pressure broadening of microwave lines. Lines in the microwave spectrum correspond to transitions between closely spaced internal energy levels, *e.g.*, rotation–rotation or inversion transitions (*e.g.*, $\Delta E = 1$—2 cal./mole). The breadth of a microwave line $\Delta\nu_{\text{P.B.}}$ due to pressure broadening depends upon the time interval over which the radiating processes are unaffected by collisions. $\Delta\nu_{\text{P.B.}} = 1/2\pi t$ where the collision time $t = 1/\sqrt{2}\, n\pi\sigma^2_{\text{P.B.}}v$. Here v is the velocity of the molecule, $\sigma_{\text{P.B.}}$ the collision diameter, and n the number of molecules per c.c.

Collisions of importance for microwave pressure broadening involve energy exchange between the colliding molecules leading to a change in

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[42] E. F. Greene and D. F. Hornig, *J. Chem. Phys.*, 1953, **21**, 617.

the internal state of the radiating molecule. Such collisions can have attributed to them a characteristic diameter $\sigma_{P.B.}$ which determines t.[43]

Measurement of $\Delta\nu_{P.B.}$ as a function of pressure gives $\sigma_{P.B.}$ which is a relative measure of the efficiency of molecules in transferring energy between their translational modes and the appropriate internal states of the radiating molecule.

Pressure broadening of the NH_3 inversion (3, 3) line shows that the effective collision diameters of molecules such as N_2, H_2, or He for this process are close to those deduced from gas kinetic properties such as viscosity, indicating a ready transfer of energy. Polar molecules such as NH_3, HCN, and CClN, give $\sigma_{P.B.} > \sigma$ gas kinetic. This is probably due to long-range electrostatic interaction with energies comparable to the transition energy. High values of $\sigma_{P.B.}$ for self-broadening in pure rotation spectra are also observed for a number of polar gases such as OCS, CH_3F, and H_2O.[43]

3. Theoretical Treatments of Energy Transfer in Low-lying States

(*a*) **Translation–Vibration Transfers.**—Early quantitative notions of energy transfer arise from the concept of an adiabatic collision. If the collision process is sufficiently slow, readjustments of translational energy in a single collision do not occur quickly enough to affect the fast internal movements of the molecule, but act only upon the centres of gravity of the molecules.[3, 6] In order for the translational energy changes to influence the internal modes during a collision, collisions must be non-adiabatic. The time taken for the translation energy change to occur must be of the order of the time taken for the internal vibration. For vibrations of frequency ν this time is $1/2\pi\nu$. The time taken for the molecule to change its kinetic energy is x/v, where x is the distance travelled in the repulsion potential field which converts the kinetic energy into potential energy and v is the average velocity of the molecule. Thus when $2\pi\nu x/v$ is of the order of unity or less, appreciable energy transfer may occur.

This simple relation shows that the probability of energy transfer depends upon the frequency of vibration, upon the repulsion potential which determines how quickly the kinetic energy is dissipated, and upon the molecular velocity of approach, *i.e.*, molecular mass and temperature ; faster molecules should be more efficient.

Landau and Teller[44] have extended this concept to obtain the probability for $1 \longrightarrow 0$ transitions by collision, in a diatomic molecule.

The transition probability for the collision of two molecules of reduced mass μ along a line of centres distance r apart in a repulsion field

$$U(r) = U_0 \exp(-\alpha r)$$

is found to be proportional to $\exp(-4\pi^2\nu/\alpha v)$. Values of the velocity v giving appreciable transition probabilities are much greater than gas kinetic

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[43] W. Gordy, W. V. Smith, and R. Trambarulo, " Microwave Spectroscopy ", Wiley, New York, 1953.

[44] L. Landau and E. Teller, *Physikal. Z. Sowjetunion*, 1936, **10**, 34 ; C. Zener, *Proc. Camb. Phil. Soc.*, 1933, **29**, 136.

average velocities. The probability of such velocities' occurring is given by the usual Boltzmann term $\exp(-\mu v^2/2\boldsymbol{k}T)$.

The majority of transitions will occur for molecular collisions having a velocity which mutually satisfies both of these conditions. This velocity is obtained by minimising the total exponent term $4\pi^2\nu/\alpha v + \mu v^2/2\boldsymbol{k}T$. The value of v which satisfies this is $v = (4\pi^2\boldsymbol{k}T\nu/\alpha\mu)^{1/3}$. Substitution of this value of the velocity in the total exponential gives P_{10} proportional to $\exp - 3(2\pi^4\mu\nu^2/\alpha^2\boldsymbol{k}T)^{1/3}$. A formal quantum-mechanical treatment of the collision problem of translation–vibration transfer was first given by Jackson and Mott,[45] using the method of distorted waves. Recent developments of this have been made without substantial change in the physical picture.[46, 47, 48] For the two-molecule interaction the transition probability calculated for approach of free rotationless particles in a potential field based on $U(r) = U_0 \exp - \alpha r$ to produce a change in internal quantum number from $1 \longrightarrow 0$ is given by an equation similar in essentials to that of Landau and Teller. The effective repulsion potential $U(r)$ is strictly the potential interaction between the nearest atoms of the two molecules. This may be approximated by the potential between molecular centres in the region of repulsion if the molecules behave as spherically symmetrical and if the internally effective force is proportional to the intermolecular force.

By using a suitable molecular velocity distribution function, the transition probability per collision statistically averaged over all molecules is found to be

$$P_{10} = \frac{\pi}{\sqrt{3}} \frac{\left(\mu/\mu_{\text{int}} \times \dfrac{32\pi^4\mu\nu}{\boldsymbol{h}\alpha^2}\right)\left(\dfrac{4\pi^2\boldsymbol{k}T\nu}{\alpha\mu}\right)^{1/3}}{\sqrt{\pi\boldsymbol{R}T/M}} \exp - 3\left(\frac{2\pi^4\mu\nu^2}{\alpha^2\boldsymbol{k}T}\right)^{1/3} \qquad (11)$$

Here the quantity μ_{int} is the effective reduced mass of the oscillator being de-excited.

On the assumption that the main dependence of P_{10} upon mass, frequency, and temperature comes from the exponential term, the form of (11) may be used to interpret some of the main features of experimental results.

(1) P_{10} and hence Z_{10} depend exponentially upon the magnitude of the frequency. The form of (11) applies strictly only to diatomic molecules with a single vibrational state. For polyatomic molecules we may use the transition probabilities P'_{10} referring to the lowest mode of vibration and apply (11) in the same way to show the qualitative dependence of Z'_{10} upon the frequency. Equation (11) requires a quantitative dependence of $\log Z'_{10}$ upon $\mu^{1/3}\nu^{2/3}$. Experimental work provides little confirmation of this relation, and the extensive work of Lambert [18] and of Rossing and Legvold [29] suggests a closer dependence upon ν (cf. Fig. 1).

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[45] J. M. Jackson and N. F. Mott, *Proc. Roy. Soc.*, 1932, *A*, **137**, 703.

[46] K. F. Herzfeld, R. N. Schwartz, and Z. I. Slawsky, *J. Chem. Phys.*, 1952, **20**, 1591 ; K. F. Herzfeld and R. N. Schwartz, *ibid.*, 1954, **22**, 767.

[47] T. L. Cottrell and N. Ream, *Trans. Faraday Soc.*, 1955, **51**, 159, 1453.

[48] K. Takayanagi and T. Kishimoto, *Prog. Theor. Physics, Japan*, 1952, **8**, 497.

(2) P_{10} in (11) increases markedly with a decrease in the reduced mass of the colliding pair of molecules. This gives a qualitative explanation of the efficiency of light molecules such as H_2 or He (cf. Table 3).

(3) Making certain assumptions about inter- and intra-molecular forces, we can calculate transition probabilities from (11) to give reasonable agreement with experiment at one reference temperature.[47]

(*b*) **Quantitative Comparison of Theory with Experiment.**—*Temperature coefficients.* Equation (11) may be used to obtain values of α directly from experimental data for P_{10} at different temperatures, by plotting log P_{10} or log P'_{10} as a function of $1/T^{1/3}$ and deriving α from the slope ; α so obtained measures the exponent of the repulsion potential effective in energy-transfer collisions.

It is also possible to calculate α from the average repulsion potential constants obtained from equilibrium and transport properties of gases by comparing, for example, the Lennard-Jones 6, 12 potential which has been fitted to these properties with the exponential repulsion potential. The values of α obtained in the two different ways do not agree ; [47] *e.g.*, α (energy transfer) for methane and benzene is at least three times greater than α (viscosity).[44] Thus, although it may be possible by adjustment of parameters to obtain agreement between P_{10} as calculated by equation (11) and as found experimentally at one particular temperature, it will not in general be possible, using these parameters, to obtain agreement at other temperatures. *A priori* calculations of P_{10} using the average repulsion potentials usually assumed between molecular centres are not adequate. There is evidence for an additional highly specific temperature-independent factor ρ required as a multiplier in (11) to bring about agreement between theoretical and experimental values of P_{10}.[49] Introduction of such a " steric " factor suggests a reason for the high degree of specificity found in energy-transfer phenomena. Transition probabilities may not depend in any simple way upon vibration frequencies and may be complicated by specific steric factors.

More complex interactions. The theoretical treatment given above makes no attempt to explain several significant phenomena found in energy transfer.

(1) The effects of dipole moment. More elaborate calculations indicate that these depend mainly upon the additional attractive forces between dipoles which give rise to increased velocities of approach.[50] Faster relative velocities give more instantaneous collisions which are more efficient.

(2) The effect of additives with incipient chemical reactivity. It is well known that water has a remarkable efficiency for transferring translational energy to vibrations of carbon dioxide. Widom and Bauer [51] have recently shown that when two substances have incipient chemical reactivity the shape of the intermolecular potential curve is altered in such a way that much more efficient energy transfer results.

(3) The effects of additives of high molecular weight containing a number

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[49] J. W. Arnold, J. C. McCoubrey, and A. R. Ubbelohde, in course of publication.
[50] Z. I. Slawsky and F. W. De Wette, *Physica*, 1954, **20**, 1169.
[51] B. Widom and S. H. Bauer, *J. Chem. Phys.*, 1953, **21**, 1670.

of low-lying internal vibrations. Herzfeld, Schwartz, and Slawsky [46] have shown that in such cases transfers of energy may occur which involve the internal states of the heavy molecule in such a way as to produce an easier alternative route for the energy transfer, *e.g.*, a vibrational resonance mechanism. Such an explanation may well account for the high efficiency of molecules such as toluene or *n*-pentane in de-exciting carbon dioxide or ethylene (cf. Table 3).

(*c*) **Transfer of Energy between Translation and Rotation.**—For molecules other than the hydrogen isotopes and diatomic hydrides rotational quanta are small ; this means that appreciable numbers of energy levels will be populated even at low temperatures. The rate of populating and depopulating all the rotational levels by exchange with translational energy has been treated by a single relaxation process.

A quantum collision method similar to that used in deriving (11), but with an angle-dependent repulsion potential, has been employed to calculate probabilities for rotation–translation transfers. For diatomic molecules of molecular weight $\gg 20$ a considerable simplification is obtained.[52] Effects of mass and also of temperature cancel in these rotational transfers (since both translational and rotational energies depend upon these quantities). Since the collision time is short relative to times of rotation, and since therefore these transfers are insensitive to repulsion potential, we may write an approximate equation

$$1/Z_{\text{eff}} = \tfrac{1}{2}(d_0/\sigma)^2$$

where d_0 is the internuclear distance and σ the collision diameter. Probabilities calculated from this equation give reasonable agreement with experiment for N_2 and O_2. This equation will not, however, hold for H_2 and D_2 where the rotational quanta are large and where ortho- and para-states may be differentiated. More detailed quantum collision calculations made for H_2 and D_2 [53, 54] give calculated transition probabilities in good agreement with experiment. Separate relaxations are attributed to ortho- and para-states and to different rotational transitions within the para-state. This corresponds with the experimental observation that for H_2 the relaxation region is broader than that for a single process.[44, 41]

4. Energy Transfer in Higher Energy States

(*a*) **Photochemical Phenomena.**—*Flash photolysis.* Norrish and his co workers [55, 56] have shown that when ClO_2 or NO_2 is flash-photolysed, molecular oxygen in its electronic ground state is formed with a considerable population in the fifth, sixth, and seventh vibrational levels. The efficiencies of additives in deactivating these vibrationally excited species from the sixth to the fifth quantum have been examined. Free radicals, and

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[52] R. Brout, *J. Chem. Phys.*, 1954, **22**, 1189.

[53] J. C. Beckerle, *ibid.*, 1953, **21**, 2034.

[54] K. Takayanagi and T. Kishimoto, *Progr. Theor. Physics, Japan*, 1953, **9**, 578.

[55] R. G. W. Norrish and B. A. Thrush, *Quart. Rev.*, 1956, **10**, 149.

[56] F. J. Lipscomb, R. G. W. Norrish, and B. A. Thrush, *Proc. Roy. Soc.*, 1956 *A*, **233**, 429.

molecules with vibrational levels close to those of the excited oxygen, are most efficient. Collision numbers range from 10^7 for N_2 to <500 for NO_2.

Fluorescence in small molecules. Molecules excited by light may pass into states of higher electronic energy. Owing to the accompanying change in shape of the electronic potential-energy curves such transitions normally involve changes in the vibrational quantum number, as follows from the Franck–Condon principle.[9, 10] For example, when molecular iodine is irradiated with mercury light of wavelength 5431 Å the excited electronic state is produced in the twenty-sixth vibrational level.[57] Examination of the fluorescence spectrum of iodine suggests that de-excitation of these high vibrational levels by collision with inert gases occurs much more readily than de-excitation of lower levels in similar collisions. Similar observations have been made on sulphur.[58]

Fluorescence in complex molecules. If a complex molecule is excited to a higher electronic state with an increase in vibrational quantum number it may, in the absence of collisions, leave this state by alternative processes: (1) It may revert to the ground state with emission of energy as fluorescence. (2) It may pass over into a third state by accumulating vibrational energy from the rest of the molecule in a critical degree of freedom. From this state it returns to the ground state by a radiationless transition. Collisions with the excited molecule may remove electronic energy directly by quenching, thereby decreasing the fluorescence yield. This direct quenching is not of immediate interest for the present Review. Alternatively, collisions may remove vibrational energy thereby stabilising the excited molecule and increasing the fluorescence yield. This process can be discussed on the same lines as other vibrational transfers.[59]

If a molecule with translational temperature T_1 possesses vibrational energy ΔE in excess of the equilibrium value for T_1, its effective vibrational temperature $T_{1(\text{vib.})}$ is defined as $T_1 + \Delta E/C_{\text{vib.}}$. On collision with another molecule X it may lose vibrational energy, attaining a vibrational temperature $T_{2(\text{vib.})} = T_1 + \Delta E'/C_{\text{vib.}}$ and increasing the temperature of X from T_1 to $T_2 = T_1 + \Delta E - \Delta E'/C_X$. The efficiency of this process which increases the fluorescence yield may be written as

$$\gamma = (T_2 - T_1)/(T_{2(\text{vib.})} - T_1).$$

When $\Delta E - \Delta E' = 0, \gamma = 0$. When $T_2 = T_{2(\text{vib.})}$ equilibrium is established and $\gamma = 1$. Even when $\gamma = 1$, the amount of energy transferred, $\Delta E - \Delta E'$, cannot equal ΔE; the magnitude of $\Delta E - \Delta E'$ depends upon the heat capacity of X, and for $T_2 = T_{2(\text{vib.})}$ the ratio $\beta = (\Delta E - \Delta E')/(\Delta E)$ could only be unity if the heat capacity of X were infinite.

Values of the quantities ΔE and $T_{1(\text{vib.})}$ must first be obtained experimentally from the decrease in fluorescence yield in the presence of a quencher, at different temperatures and wavelengths of exciting light. Values of $T_{2(\text{vib.})}$ and hence $\Delta E - \Delta E'$ and γ can then be obtained from experiments

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[57] F. Rossler, *Z. Physik*, 1935, **96**, 251.

[58] E. Durand, *J. Chem. Phys.*, 1940, **8**, 46.

[59] H. G. Curme and G. K. Rollefson, *J. Amer. Chem. Soc.*, 1952, **74**, 28; B. S. Neporent, *Zhur. Fis. Khim.*, 1950, **24**, 1219.

on foreign gases which increase the fluorescence yield of β-naphthylamine excited by 2652 Å light. Typical values of γ are H_2 (0·1), C_5H_{12} (0·2), $CHCl_3$ (0·5), SF_6 (0·5), NH_3 (0·9).[60] Out of an excess energy ΔE of 8400 cm.$^{-1}$ in β-naphthylamine, only 70 cm.$^{-1}$ is taken up by helium in an efficient collision whereas N_2 removes 190, SF_6 570, $CHCl_3$ 1000, and C_5H_{12} 1280 cm.$^{-1}$. Clearly, energy transfer involving vibrations in this region of the potential-energy curve (probably $Q > 5$ for some modes) is not a completely efficient process.

(*b*) **Atom Recombination Reactions.**—When atoms or radicals recombine, the molecule resulting from the primary step of recombination will contain sufficient energy to cause redissociation. Only when some of this excess energy is removed in collisions will the molecule become stable. In the case of atom recombinations the excited " molecule " having only one bond will have a very short lifetime ; the excess energy cannot be shared into other bonds but stays in the single vibrational mode so that in the absence of collisions the " molecule " will redissociate before completion of a single vibration, *i.e.*, in a time of about 10^{-13} sec.[61] Only if a collision with a third body which can remove energy occurs within this period will a quantised stable molecule result.[62] In discussing the energy transfers involved here we are considering the removal of energy from a molecular species in which the vibrational energy is not quantised ; this is different from most of the other cases considered in this Review and the results may not be directly comparable with those of Sections 4(*a*) or 4(*d*).

Two recent determinations of the rate of recombination of iodine atoms in the presence of a number of different molecules acting as third bodies have been made by using a flash of light of high intensity ; [63] recombination following the dissociation of iodine in a shock wave has also been studied.[64]

Recombination reactions have been analysed in terms of third-order rate constants for the reaction $X + X + M \rightarrow X_2 + M$. The rate constants show that, although simple atoms and molecules can facilitate the reaction, complex molecules are considerably more efficient and remove energy easily. It is suggested that this increase of ability to transfer energy is due to the high van der Waals attraction of the polyatomic molecules, and this is substantiated by a plot of the velocity constant for recombination of iodine atoms against the boiling point of the added molecular gases (taken as a measure of the van der Waals forces).[63] Fig. 2 shows this plot for the case of iodine-atom recombinations.

The value of the temperature coefficient of the reaction $I + I + M \rightarrow I_2 + M$ in terms of an Arrhenius plot yields an activation energy of the order of -2 kcal./mole, *i.e.*, the three-body complex is more stable than

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[60] M. Boudart and J. T. Dubois, *J. Chem. Phys.*, 1955, **23**, 223.

[61] G. E. Kimball, *J. Chem. Phys.*, 1937, **5**, 310 ; E. P. Wigner, *ibid.*, 1939, **7**, 646.

[62] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, 1936, **32**, 907.

[63] K. E. Russell and J. Simons, *Proc. Roy. Soc.*, 1953, *A*, **217**, 271 ; M. I. Christie, R. G. W. Norrish, and G. Porter, *ibid.*, 1953, *A*, **216**, 152.

[64] D. Britton, N. Davidson, and G. Schott, *Discuss. Faraday Soc.*, 1954, **17**, 58.

the reactants. The value of this activation energy is fairly constant for a number of different molecules acting as third bodies.[63, 64] Such constancy for large and small molecules may indicate that some of the marked stabilising effects of complex molecules are to be found not in energetic but in specific steric factors or alternatively in the removal of the excess energy of I_2 into the numerous vibrational modes of the complex molecule.

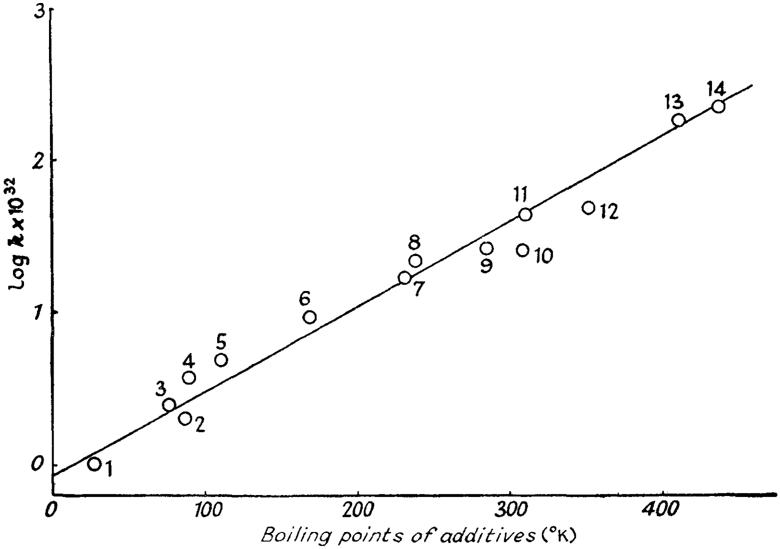

FIG. 2

(Substantially copied from K. E. Russell and J. Simons, *Proc. Roy. Soc.*, 1953, *A*, **217**, 271.)

Horizontal axis : Boiling points (° K) of additives. Vertical axis : Log $k \times 10^{32}$.

Third-order rate constant k (mole^{-2} cm.^{6} sec.$^{-1}$) for recombination of iodine atoms in presence of third body M, *as a function of the van der Waals forces of* M *(boiling points).*

(1) Neon ; (2) argon ; (3) nitrogen ; (4) oxygen ; (5) methane ; (6) ethylene ; (7) propane ; (8) *cyclo*propane ; (9) ethyl chloride ; (10) *n*-pentane ; (11) ethyl bromide ; (12) benzene ; (13) *p*-xylene ; (14) mesitylene.

(*c*) **Vibrationally Excited Reaction Intermediates.**—Another problem similar to that of the stability of newly formed diatomic molecules is concerned with the lifetime of small radicals containing a total vibrational energy in the molecule in excess of the dissociation energy of a bond. These species are formed in the course of certain reactions and may act as chain carriers. In the absence of contact with other molecules such species have only a transitory existence and will dissociate into atoms or radicals with excess translational energy.

For example, in the hydrogen–oxygen reaction the encounter $H + O_2$ gives rise to the radical $HO_2{}^*$ containing energy in excess of the dissociation limit ;[65] this energy may be shared between the two bonds but will rapidly revert into a single bond, causing dissociation ; *i.e.*, the radical will have

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[65] C. J. Danby and C. N. Hinshelwood, *J.*, 1940, 464.

a very short lifetime. If another collision involving HO_2^* can occur sufficiently rapidly after the first encounter the excess energy may be removed and a stable HO_2 radical may be formed. Patrick and Robb [66] have shown experimentally that about 1 in 10^3 collisions between H and O_2 results in the formation of stable HO_2.

Hinshelwood and his co-workers have shown experimentally that CO_2 and H_2O are considerably more efficient than N_2 or H_2 in removing energy from HO_2^*. Walsh [67] has suggested an explanation for the differences in efficiency of various molecules in terms of their vibrational structure. It seems likely that a form of resonance transfer involving removal of energy from HO_2^* direct to vibrational energy of the additive is involved. This would be possible if a quantised energy jump $-\Delta E$ in HO_2^* is close to the available energy uptake of a bond in the additive molecule, a factor which would tend to favour H_2O and CO_2 rather than N_2 or H_2.

In the oxidation of *n*-hexane it has been shown experimentally that the use of hydrogen as a diluent gives rise to an inhibitory effect which can be explained on the basis of energy transfer from the energy-rich hydroperoxide radical $R{\cdot}O_2{\cdot}^*$ to hydrogen.[68] Such energy transfer phenomena may well underlie the remarkable effects of structure on hydrocarbon oxidation.[69]

In a number of addition or radical recombination reactions vibrationally hot complexes may be formed which will, if their lifetime is sufficiently long, undergo de-energising collisions to yield stable products. Experimental and theoretical work [70, 71] has shown that the lifetime of vibrationally excited species increases markedly with the number of degrees of freedom; *i.e.*, the energy wanders away from the dissociating bond into other bonds and will require a time long with respect to the time between collisions to return in the form available for dissociation. During this lifetime a number of collisions may occur sufficient to remove the excess energy. The recombination of large radicals to give stable products seems to occur on practically every collision.[72]

(*d*) **Effects of Energy Transfer on the Rate of Unimolecular Reactions.**—Certain gaseous reactions which are unimolecular at sufficiently high pressures become bimolecular at low pressures.

Unimolecular reaction is possible when collisions maintain a stationary Boltzmann state with a fraction of molecules independent of pressure possessing the critical energy for reaction. A small proportion only of this fraction of activated molecules is chemically transformed, the majority

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[66] C. R. Patrick and J. C. Robb, *Discuss. Faraday Soc.*, 1954, **17**, 98.

[67] A. D. Walsh, *Fuel*, 1954, **33**, 247.

[68] N. J. H. Small and A. R. Ubbelohde, *J.*, 1952, 4619.

[69] A. R. Ubbelohde, *Rev. Inst. franç. du Pétrole*, 1949, **4**, 315; A. D. Walsh, *Discuss. Faraday Soc.*, 1951, **10**, 320.

[70] G. B. Kistiakowsky, *ibid.*, 1954, **17**, 94; D. Garvin and G. B. Kistiakowsky, *J. Chem. Phys.*, 1952, **20**, 105.

[71] R. A. Marcus, *ibid.*, p. 355.

[72] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, 1951, **19**, 55; K. J. Ivin and E. W. R. Steacie, *Proc. Roy. Soc.*, 1951, *A*, **208**, 25.

being deactivated by collision before undergoing chemical decomposition. As the pressure falls the number of collisions decreases, and can become insufficient to maintain the Boltzmann concentration of activated molecules, owing to their concurrent removal by reaction. At sufficiently low collision rates this results in a bimolecular-type reaction.[73, 74] Addition of a chemically inert gas at this stage may be used to restore unimolecular kinetics. The ratio of the pressure of the reacting molecule itself required to restore the rate constant to the high-pressure limit relative to the pressure of additive which brings about this same change in rate constant measures the relative efficiencies of the two molecules in producing the steady-state concentration of activated molecules by collisions. If collision diameters are known we may express the efficiencies of the additives relative to the reacting molecules themselves on a collision for collision basis.

TABLE 5. *Selected values of relative efficiencies of gases in energy transfers with reacting molecules in unimolecular reactions*

Reactant additive	*cyclo*Propane	*cyclo*Butane	N_2O_5	Azomethane	N_2O
Temp.	492°	448°	50·5°	310°	653°
Self	1	1	1	1	1
He	0·05	0·07	0·07	0·07	0·66
H_2	0·12	0·10	—	—	—
Ne	—	0·12	0·09	—	0·47
Ar	0·07	0·21	0·15	—	0·20
N_2	0·07	0·21	0·23	0·21	0·24
CH_4	0·24	0·38	—	0·20	—
H_2O	0·74	0·44	—	0·46	1·5
CO_2	—	—	0·39	0·25	1·3
SF_6	—	—	0·44	—	—
C_6H_5Me	1·10	1·12	—	—	—
$C_6H_3Me_3$	0·89	1·23	—	—	—
Ref.	75	76	77	78	79

Table 5 shows the high relative efficiencies of polyatomic molecules and the comparatively small effect of small molecules, even including H_2 and He, which by contrast are found to be efficient in low-energy transfers. The numerical spread of efficiencies is however much smaller than in the case of low-energy transfers. Different theoretical treatments of unimole-

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[73] L. S. Kassel, " The Kinetics of Homogeneous Gas Reactions ", Chemical Catalog Co., New York, 1932.

[74] N. B. Slater, *Phil. Trans.*, 1953, *A*, **246**, 57 ; *Proc. Roy. Soc.*, 1953, *A*, **218**, 224.

[75] H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *ibid.*, 1953, *A*, **217**, 563.

[76] *Idem, ibid.*, 1953, *A*, **218**, 416.

[77] H. S. Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 1567, 5763.

[78] D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, 1936, **4**, 608.

[79] M. Volmer and H. Froehlich, *Z. phys. Chem.*, 1932, *B*, **19**, 89 ; M. Volmer and M. Bogdan, *ibid.*, 1933, *B*, **21**, 257.

cular reaction rates have been given by Kassel [73] and by Slater [74] resulting in the same overall expressions for the rate constants. The treatments differ in the detailed mechanism assumed for the activation process. It does not appear possible at present to discriminate between these two theoretical models from experiment ; more extensive measurements are required. Both of these treatments make the assumption that all gas-kinetic collisions are effective. Neither is immediately suited to a discussion of the relative effects of foreign molecules in bringing about energy transfer.

(*e*) **Comparison of the Results obtained from Low-energy and High-energy Transfers.**—Whereas experimental results on low-energy transfer can be used to give direct numerical values of the transition probability of a single fairly well-defined molecular process, the complexity of the phenomena involved in higher-energy transfers makes it difficult at present to adduce a numerical value for the transition probability of a particular molecular step ; most of the results are of a comparative nature and are referred to a convenient norm.

Transfers of energy involving large vibrational quanta low in the potential-energy curve may require between, say, 10 and 10^6 collisions in different pure gases depending upon the size of the quantum and upon highly specific molecular interactions. Large variations in the effect of additives have been observed ; both light and heavy molecules can be efficient in transfers with the same molecule. For transfers involving higher-energy quanta which are still well below the dissociation level, efficiencies may again range from 10^6 collisions required to de-excite the large sixth quantum in oxygen to one or two collisions required to de-excite the small 26th quantum in iodine.

In the neighbourhood of the dissociation energy level the quanta are small and energy transfer between translation and vibration should occur readily in all cases since the non-adiabatic condition is automatically fulfilled [cf. Section 3(*a*)]. There is, however, quite a considerable variation in the efficiencies of additives in transfer with the same excited molecule, large complex molecules being more efficient than small ones. It seems clear [cf. Sections 4(*a*), (*b*), (*c*)] that large molecules can effect transfer with the excited species in larger amounts of energy and by more numerous routes than can small molecules (*e.g.*, *via* their internal modes as well as with translation) and this will affect the relative rates of the observed processes. From the observed relative efficiencies we can say that, if small molecules transferred the appropriate energy on every collision as calculated from kinetic theory, then large molecules would have collision diameters for the same transfer greatly in excess of the simple kinetic theory diameters. Alternatively, the complex molecules may be considered to transfer energy on every collision as calculated from kinetic theory and the light molecules then appear to require several collisions for each effective transfer. At present no decision between these alternatives is possible from experiment, though the results of Section 4(*d*) suggest a limiting unit efficiency for polyatomic molecules in transfers with reacting polyatomic species.

Rapid redistribution of energy within a molecule by vibration coupling is usually observed in low-energy transfers. In the case of higher-energy states preliminary evidence suggests a rapid exchange of energy between vibrations[80] but this important point requires much further study.[81]

Finally, we ought to say something about the present links between theory and experiment. In general, some measure of prediction is possible from theoretical treatments of low-energy transfers from equations such as (11). In the case of higher-energy states although theoretical work gives information about the relation between the stability of excited species and their internal structure[71, 74, 81] little has been done to examine the effects of intermolecular forces on energy transfer or to study the detailed potential-energy surfaces involved in collisional transfers. The importance of these effects in a wide variety of molecular and radical reactions, together with a growing body of experimental results of more theoretical interest, makes it probable that the quantitative aspects of this important branch of reaction kinetics will develop considerably in the near future.

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