to Nelson,[12] the photo emf represents the energy separating the levels between which transfer of charge carriers occurs (i.e., between the conduction band of the dye and the conduction band of the zinc oxide or between valance bands). Since the photo emf at the erythrosin-zinc oxide junction was found to be 0.1 eV we may conclude that the charge transfer does not take place between the valence bands, which are separated by about 0.8 eV. Using the experimental data reported here, charge transfer must be to some intermediate level in the zinc oxide. This yet uncharacterized level would be 0.1 eV below the conduction band of the dye (i.e., at -3.5 eV) from whence the charge carriers could be thermally excited to the conduction band of the zinc oxide where they are evident from increased photoconductivity.

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Joule–Thomson Effect on Gaseous Helium

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THE Joule–Thomson coefficients for helium were reported by Roebuck and Osterberg.[1,2] Unfortunately they interpreted these data incorrectly. Since

TABLE I. Zero-pressure Joule–Thomson coefficient (in Centigrade degrees per atmosphere).

Temperature (°C)	Joule–Thomson
-190	-0.0344
-175	-0.0411
-150	-0.0492
-100	-0.0572
-50	-0.0595
0.0	-0.0614
$+50$	-0.0628
$+100$	-0.0637
$+150$	-0.0644
$+200$	-0.0643
$+250$	-0.0633
$+300$	-0.0609

the isenthalps are straight lines, the Joule–Thomson coefficient is independent of pressure on any "isenthalp." The data are reported as being independent of pressure on any "isotherm." This led to errors of from 1% to 10% in the tabulated results[3] and hindered the theoretical interpretation of the data.[4,5]

The data of Table I are recalculated from Roebuck's original experimental records,[6] corrected for a pressure-gauge error.[7]

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Transfer of Vibrational Energy from Internally Converted States

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IN the photochemistry of some simple, conjugated 1,3-dienes[1] and 1,3,5-trienes[2,3] it is known that most of the decomposition processes that are observed in the gas phase occur from vibrationally excited ground-state molecules that are formed by internal conversion from the initially produced electronically excited singlet states. The vibrational energy in these species (which at room temperature must be nearly uniform) is of the order of 5 eV. It has also been shown[1-3] that before thermal reactions can occur, the vibrational energy can be lost by collision with molecules of its own kind or other molecules that may be added to the system.

It appeared possible to gain some understanding of the rate of loss of vibrational energy from the internally converted molecules by the use of quencher molecules which are themselves capable of undergoing thermal decomposition. Thus, if the photon is absorbed by a species M to give an excited state M*, then the following reactions are possible:

$$M^* \rightarrow M_n, \tag{1}$$

$$M_n \rightarrow \text{products}, \tag{2}$$

$$M_n + Q \rightarrow M_m + Q_p, \tag{3}$$
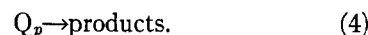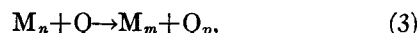
$$Q_p \rightarrow \text{products}. \tag{4}$$

The diminution in the rate of formation of products from the internally converted molecule (M_n) is indicative of the rate of transfer of energy to the quencher

TABLE I. Experimental conditions and composition of mixtures used.

Absorber	P_{mm}	Quencher	P_{mm}	Wavelength	Exposure (min)
1,3-Butadiene-d_6	6.5	Cyclobutane	39.7	2000–2200	10
1,3-Butadiene	6.0	Cyclobutene-d_6	30.0	2000–2200	10
1,3,5-Cycloheptatriene	5.8	Cyclobutane	49.1	2300–2600	70
1,3,5-Cycloheptatriene	4.0	Cyclobutene	40.0	2300–2600	20

(Q), while the rate of decomposition of the quencher (4) is a measure of (i) the amount of vibrational energy transferred per collision, and (ii) the number of such vibrationally excited quencher molecules that survive deactivation by secondary collisions. For reasons which are discussed briefly later, it was believed that almost all of the quencher molecules that acquired energy in excess of the activation energy for decomposition in (3) would undergo decomposition. This meant that the rate of decomposition of the quencher is solely determined by the amount of vibrational energy transferred to it in a collision. By the use of two quencher species whose activation energies for decomposition differed widely although their quenching cross sections would be approximately the same, it should be possible to calculate (within broad limits) the magnitude of the quantum of energy that is transferred in a collision with such highly vibrationally excited molecules.

The absorber molecules used were 1,3-butadiene and 1,3,5-cycloheptatriene. The quenchers used were cyclobutane ($E_A = 62.5$ kcal/mole[4]) and cyclobutene-d_6 ($E_A \sim 34$ kcal/mole[5]). Mixtures of absorber and quencher species were prepared by standard high-vacuum techniques, irradiated with a high-pressure mercury arc filtered by chlorine gas at 1 atm and analyzed by gas chromatography and mass spectrometry. A summary of the reaction conditions is presented in Table I.

In every one of the four systems that were studied, it was observed that addition of the quenchers decreased the decomposition of the absorber molecules, but at the same time the decomposition products from the quenchers were not observed at all. It was estimated that if Reaction (2) in the absence of the quencher is taken as the measure of the formation of the internally converted species M_n (which must certainly be the *minimum* rate of formation of M_n), then in the presence of the quencher (3) is followed by (4) in less than 1 collision in 10 000. Or, in other words, the energy transferred to the quencher is almost always less than even the 34 kcal/mole required to bring about the decomposition of cyclobutene-d_6 even when the internally converted molecule has 115 kcal/mole of vibrational energy. An alternative explanation may also be considered. This is the possibility that although sufficient energy is transferred to the quencher in a collision (3), the activated quencher molecule that is produced is, in turn, deactivated in another collision. This explan-

ation has been discarded in view of the fact that the experiments in this study have, in part, been carried out in a pressure range in which the thermal decomposition-rate constant shows pressure dependence.[6] If thermal activation is dependant on the rate of collision, then in the present system, in which the activated molecule is produced photochemically, the deactivation would not be favored by the collision rate.

There is only one other series of studies[7] in which the transfer of vibrational energy from very "hot" molecules to quenchers has been investigated. The conclusions reached therein placed an upper limit of about 30 kcal/mole for the quantum of vibrational energy that was transferred per collision. This result is in entire agreement with the conclusion reached here.

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A more important objection may be that activated molecules with a narrow energy distribution just above the critical value may have unusually long lifetimes. While this could be a serious factor with any given quencher, it certainly could not be a factor in all three of the quenchers that were used.
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Influence of the Radii of Neighboring Ions on the Optical Absorption of Thallium in Alkali Halides*

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IN thallium-doped alkali halides, there are three bands known as the A, B, and C bands. The A band is toward the visible, C lies on the uv side, and the B band lies between the two. The A band is attributed to a 6^1S_0–6^3P_1 transition, and the C band to a 6^1S_0–6^1P_1 transition in the thallium (i) ion, situated in a cubic crystal field.[1–4]