does not subsequently radiate. All possibilities probably exist, from complete emission of the transferred energy (subject to internal quenching of the solute molecules) to complete nonradiative dissipation of this energy. The behavior[9] of solid solutions in anthracene of naphthacene, which emits, and acridine, which quenches, illustrates the two extreme types of behavior. The results shown in Table I indicate that in several systems, where $f_{max} < 1$, the solute acts partially as an energy acceptor, partially as a quencher. This may account for the fact that the scintillation efficiencies of the best organic liquid and plastic solution scintillators are only 50–70% of that of the best pure organic crystal scintillator.[10]

The complexities of quenching processes are nicely illustrated by the concentration quenching of fluorescent acene solutions in n-hexane.[11] The concentration quenching of solutions of benzene is consistent with simple collisional quenching. In solutions of naphthalene and anthracene the concentration quenching proceeds via an unstable excited complex, resulting from the interaction of an excited and a nonexcited molecule. The fluorescence efficiencies of the benzene and anthracene solutions fall to 0 at high concentrations, but that of the naphthalene solutions tends to a value 75% of that at infinite dilution. This remarkable effect is attributable to a contribution of the excited naphthalene complex to the total fluorescence intensity. Thus three simple related molecules display three distinct types of quenching behaviour. Apart from illustrating the pitfalls of attempting to generalize from the particular, the unusual behavior of naphthalene at high concentrations appears directly relevant to the

studies of Kallmann, Furst, and Brown[7],[12] on the effect of the addition of high concentrations of naphthalene on the behavior of organic solutions, from which some of their ideas are derived.

Other aspects of energy transfer—the radiative process and the nonradiative migration and single-step processes—have been recently discussed elsewhere.[5]

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Erratum: Vibrational Spectra of Primary and Secondary Aliphatic Amines

[J. Chem. Phys. 30, 1259 (1959)]

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EQUATIONS (1) and (2) should read

$$2V = k_N(\Delta R)^2 + k_H[(\Delta h_1)^2 + (\Delta h_2)^2] + k_\delta(\Delta\delta)^2$$
$$+ k_R[(\Delta\alpha_1)^2 + (\Delta\alpha_2)^2] \quad (1)$$

$$2V = k_N[(\Delta R_1)^2 + (\Delta R_2)^2] + k_H(\Delta h^2) + k_\delta(\Delta\delta)^2$$
$$+ k_R[(\Delta\alpha_1)^2 + (\Delta\alpha_2)^2]. \quad (2)$$

Erratum: Size Effect in Heterogeneous Nucleation

[J. Chem. Phys. 29, 572 (1958)]

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A NUMERICAL error occurred in the calculation of Fig. 5 of this paper, giving the effects of size and surface parameter m (the cosine of the angle of contact of ice upon the particle in water) upon nucleation efficiency in freezing. The recalculated figure is shown here, assuming a value of 20 erg cm^{-2} for the free energy of the ice-water interface. On the basis of the

TABLE I. Energy transfer coefficient f_{max} for organic solution.

Solution	Excitation wavelengths $(m\mu)$	f_{max}	Reference
p-terphenyl-toluene	250–265	0.48	Birks and Cameron[a]
p-terphenyl-toluene	220–235	0.7	Birks and Cameron[a]
p-terphenyl-toluene	254	~1.0	Cohen and Weinreb[b]
anthracene-anisole	265	~0.76	Cohen and Weinreb[b]
TPB-polystyrene	240–270	0.5	Birks and Kuchela,[c] and Birks[d]
DPO-polystyrene	254–265	~0.7	Avivi and Weinreb[e]
DPO-styrene	254–265	~0.4 (at 40 g/l)	Avivi and Weinreb[e]
PBD-anisole (relative to PBD-dioxane)	230–285	~0.94 (at 10 g/l)	Brown, Furst, and Kallmann[f]
fluoranthene-anisole (relative to fluoran-thene-cyclohexane)	230–280	~0.95 (at 10 g/l)	Brown, Furst, and Kallmann[f]
fluoranthene-anisole (relative to fluoran-thene-cyclohexane)	240–310	~0.66 (at 20 g/l)	Brown, Furst, and Kallmann[f]

[a] See reference 1.
[b] See reference 3.
[c] See reference 4.
[d] See reference 5.
[e] See reference 6.
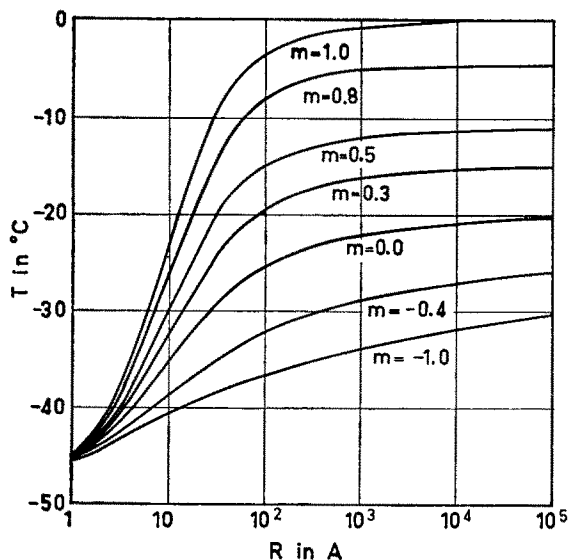[f] See reference 7.

LETTERS TO THE EDITOR

FIG. 5. Temperature T at which freezing occurs in 1 second on a spherical particle of radius R suspended in water. Parameter is $m = \cos\theta$.

assumptions made in the calculation, the threshold for homogeneous nucleation is about $-30°C$ for micron-size drops, so that particles active only below this temperature will not be unimportant in freezing processes.

Notes

Simplified Analytical Representation of Klein-Dunham Potential Energy Functions*

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(Received June 5, 1959)

THE literature on potential energy functions contains a rather confusing multiplicity of empirical or semiempirical forms and many criteria for judging their worth.[1] Since fairly exact quantum-mechanical calculation of potential curves has been practical only for the simplest molecules, whenever accurate potentials are needed the next best approaches are perhaps those of Klein[2] and Rydberg[3] and of Dunham.[4]

Objections to the Klein-Rydberg method have been based first on the supposition that its semiclassical foundations rendered it invalid at low vibrational quantum numbers, and secondly, on recognition of approximate results due to its graphical nature.[5] The latter shortcoming was eliminated by the analytical treatment of Rees.[6] In the present work, Rees' formulation has been generalized and, except for cases where only two vibrational constants are known or higher

order constants are insignificant, considerably simplified for computation. Also, the first objection has been removed by showing that the Klein-Rydberg potential is identical to Dunham's first approximation which is accepted as accurate near the potential minimum.

A known progression of vibrational energy levels is assumed to be adequately represented by a polynomial in $V \equiv v + \frac{1}{2}$, with the degree unrestricted except by availability of experimental measurements. Notation throughout for both vibrational and rotational data is conventional.[7] The Klein-Rydberg-Rees method with modifications then yields the following simple formula for the classical turning points $r_{1,2}$ in terms of V:

$$r_{1,2}(V)/r_e = 1 + (2B_e/\omega_e + \alpha_e/3B_e)V$$
$$+ (10kB_e/3\omega_e - 2B_e{}^2/\omega_e{}^2 - 2\alpha_e/3\omega_e$$
$$+ k\alpha_e/45B_e + \alpha_e{}^2/6B_e{}^2 - 4\gamma_e/15B_e)V^2$$
$$+ \{B_e/\omega_e[256k^2/45 - 22m/5 + 2\alpha_e/\omega_e] - 20kB_e{}^2/3\omega_e{}^2$$
$$+ 4B_e{}^3/\omega_e{}^3 - \alpha_e/\omega_e[52k/45 + \alpha_e/9B_e] + \alpha_e/B_e$$
$$\cdot[32k^2/945 - m/21 - 4\gamma_e/15B_e] + k\alpha_e{}^2/45B_e{}^2$$
$$+ 5\alpha_e{}^3/54B_e{}^3 + 8\gamma_e/15\omega_e - 8k\gamma_e/315B_e\}V^3 + \cdots$$
$$\pm 2B_e{}^{\frac{1}{2}}\omega_e{}^{-\frac{1}{2}}V^{\frac{1}{2}}[1 + (5k/6)V + (43k^2/40 - 11m/10)V^2$$
$$+ (177k^3/112 - 81km/28 + 93n/70)V^3 + \cdots], \quad (1)$$

where r_e = equilibrium internuclear separation, $k = \omega_e x_e/\omega_e$, $m = \omega_e y_e/\omega_e$, and $n = \omega_e z_e/\omega_e$. Coefficients are available to $V^{9/2}$ by making use of four vibrational and three rotational 'constants.' Equation (1) is very easily applied because certain ratios of spectroscopic constants occur repetitively and convergence is rapid, more so for heavy than for light molecules. Terms in V and V^4, for example, have coefficients $\sim 5 \times 10^{-3}$ and 4×10^{-10}, respectively, for N_2, $X\ {}^1\Sigma_g{}^+$, and $\sim 2 \times 10^{-2}$ and 6×10^{-7} for OH, $X\ {}^2\Pi_i$. Equation (1) can also be employed formally for nonintegral v, and thus the potential curve can be interpolated in a consistent manner between observed energy levels. This representation is not generally valid near the dissociation limit however, in fact cannot safely be used outside the range of energy levels from which the spectroscopic constants were derived.

The widely used Morse function can easily be expanded in the form of Eq. (1). In short, this procedure shows that if the vibrational energy is adequately described by a two-constant formula, and if experimental values of the rotational constants happen to agree with those implied by the Morse potential,[4,8] then that function is identical with (1). In practice the latter proviso is seldom satisfied exactly but sometimes to a good approximation. Thus the Morse curve may occasionally be very close to the 'true'[7] potential. Left-hand turning points for N_2, $X\ {}^1\Sigma_g{}^+$, derived from (1) and from the Morse function (dissociation energy $\omega_e{}^2/4\omega_e x_e$) are, respectively, 1.051(4) and 1.051(2) A at $v=0$, and 0.906 and 0.902 A at $v=16$. Similarly,

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