Comments

Second-Order Interactions between Polar Molecules

A. D. Buckingham

School of Chemistry, The University of Bristol, Bristol 8, England

(Received 23 January 1967)

In a recent paper with this title,1 van der Avoird and Hofelich reached a strange conclusion. They asserted that the dipole-induced-dipole interaction energy, calculated in accordance with the principles of quantum mechanics, differs considerably from the well-known classical result. They went on to state that another recent treatment2 of the theory of long-range intermolecular forces included an approximation which is not a good one (they erroneously asserted that this approximation always overestimates the second-order energy), and that had it not been made, the result would have been in qualitative agreement with their strange conclusion.

The purpose of this Comment is to promote calm—all of us should not now be searching for the flaw, or the flaws, in classical electrostatics, or in the principles of quantum mechanics.

Consider a very simple model system that can be handled precisely—it consists of restricting the significant excitations in each of the free molecules to a single degenerate set. If the molecules are similar, the polarizabilities of each are (in the notation of Ref. 1)

$$\alpha_{ii}(1) = \alpha_{ii}(2)$$

where $\alpha_{ii}(1)$ is the dipole operator for Molecule 1 and $\alpha_{ii}(2)$ is the dipole operator for Molecule 2, and $I_1$ is the excitation energy.

The second-order dipolar energy of the pair is

$$\varepsilon_2 = - T_{ij} T_{kl} \sum_{m, n} \frac{\langle m, n | \rho_1(1) \rho_2(2) | m, n \rangle (\langle m, n | p_k(1) p_l(2) | 0 \rangle)}{E_m(1) - E_0(1) + E_n(2) - E_0(2)},$$

where $T_{ij}$ is the dipole–dipole interaction tensor and the summation is over all excited states of the unperturbed molecular pair, whose excitation energies are the denominators in (2). There are three contributions to this sum, corresponding to $n = 0$, $m = 0$; $n = 0$, $m \neq 0$; and $m = 0$, $n \neq 0$, with excitation energies $I_1(1)$; $I_1(2)$; and $I_1(1) + I_1(2)$ (the conclusion1 was based on the assumption that these excitation energies are equal). Hence (2) becomes

$$\varepsilon_2 = -\frac{1}{2} T_{ij} T_{kl} [\mu_j(2) \mu_l(2) \alpha_{ik}(1) + \mu_i(1) \mu_k(1) \alpha_{jl}(2)]$$

+ $\frac{1}{4} I_1 \alpha_{ik}(1) \alpha_{ji}(2).$

The first two terms in (3) are equal to the classical dipole-induced-dipole energy and the final term is the dispersion energy; the result is identical to that obtained elsewhere,2 and has long been established. The dipole-induced-dipole energy (which is the interaction energy of the permanent dipoles with the dipoles they induce, together with the energy required for this induction) is always given by the first two terms of (3); the uncertainty1 arose because this particular energy was not defined.


Second-Order Interactions between Polar Molecules

A. Van der Avoird and F. Hofelich

Battelle Institute, Advanced Studies Center, Geneva, Switzerland

(Received 6 February 1967)

In reply to the remarks formulated by Buckingham in the preceding Comment1 we underline that our treatment of the second-order interaction between polar molecules2 is mathematically correct, as well as physically valid. This is not disproven by Buckingham's highly hypothetical example, in which, omitting essential features of a real quantum-mechanical system, the averaging over excited states is avoided. Our method can be applied to this example and yields the correct total second-order energy, although the division between the dipole-induced-dipole energy and the dispersion energy is not so trivial as the division obtained by Buckingham for this case.

In Buckingham's analysis the second-order interaction between two polar molecules is immediately divided into three terms. The first two terms contain explicitly the expectation values of the dipole operators; after substitution of the polarizabilities they reduce to the usual expressions for the dipole-induced-dipole energies. The third term has the form of a dispersion energy and may, in the general case, be transformed into the London formula by averaging over the excited states.

In our method, on the other hand, the averaging over the excited states of the total unperturbed system is made first. Then the second-order energy splits into three terms, two of which have the form of a dipole-induced-dipole energy, provided with a factor, the third expression being a dispersion energy.

Comparing the results obtained in these two different ways, the total second-order energy for the interaction between polar molecules is the same, as long as the exact average excitation energies are used. The difference is that in our treatment a smaller quantity is ascribed to the dipole-induced-dipole interaction, $I_{total}$ being larger than $I_1$ and $I_2$; the dispersion energy is larger, since $1/I_{total}$ resulting from an averaging over all excited states of the two polar systems, is larger than
the corresponding expression in Buckingham's dispersion energy, where the averaging is made after subtraction of the terms explicitly containing the expectation values of the dipole moment.

_In the case of two real polar systems_ a variation in the dipole moments of the systems will, via the wavefunctions, also cause a change in the matrix elements and the energy eigenvalues; therefore not only the dipole–induced-dipole energy is affected by such a variation but also the dispersion energy. For this reason an averaging over the total system, without first subtracting terms due to the intrinsic dipole moments, is, besides being mathematically an exact procedure, also physically justified.

We have shown in our previous paper that the second-order interaction between polar molecules can be divided into a dipole–induced-dipole energy and a dispersion energy in a way that differs from the usual one. The difference between the two formulations would be of theoretical value only, if the _exact_ expression for the second-order energy could be evaluated. In general, however, such a determination is practically impossible. The semiempirical value for the dispersion energy which is adopted may correspond to either one of the two possible expressions.

The dipole–induced-dipole energy is physically defined as the _interaction energy of the permanent dipoles with the dipoles they induce_, together with the energy required for this _induction_. Adopting the "classical" formula for this energy would imply, however, a more restrictive and formal definition of the dipole–induced-dipole energy, namely the _interaction energy of two polar systems_, where one of the systems is always kept in its _ground state_ (as we remarked also in our paper2). The latter definition is certainly not identical to the former one. However, the resultant uncertainty has no meaning for the experimentalist, since one cannot separate experimentally the second-order interaction energy of polar systems into dipole–induced-dipole energy and dispersion energy.


**Thermal Properties of Solid Lithium Tetrammine**

N. Mammano* and L. V. Coulter

Department of Chemistry, Boston University, Boston, Massachusetts

(Received 20 February 1967)

A recent study1 of the electrical conductivity in concentrated lithium–ammonia solutions appears to have established the existence of a compound, probably "Li(NH₃)₄," in the solid below the "eutectic" temperature of the solution, 89.6°C. The bronze color, high electrical conductivity, and appearance of transitions at 82° and 69°K, in this solid, are evidence for the presence of this "tetrammine."

However, the phase equilibria of the system remain ambiguous. If 89.6°C is a simple binary eutectic temperature as suggested in the recently proposed phase diagram,1 then it represents the low-temperature intersection of the solubility curves for pure solid lithium and pure solid ammonia in equilibrium with the saturated solution. Consequently, the solid freezing isothermally at the 89.6°C eutectic should be a two-phase eutectic mixture of solid lithium and solid ammonia crystals, and not "Li(NH₃)₄."

We wish to report here some preliminary thermal data for the lithium–ammonia system, as well as some considerations which bear on the eutectic-vs-compound question. Adiabatic heat capacities have been measured for several compositions in the 12% to 22% range from about 60°C to 110–200°C. The following observations are relevant at this time.

(a) Two first-order transitions have been observed, one at 88.79°C and one at 82.18°C, which we associate with a "eutectic" and a solid-state transition, respectively. There is no experimental basis for differentiating between these two temperatures of the transitions indicated by the conductivity measurements.2 Our measurements were made with a platinum resistance thermometer3 under equilibrium conditions and are believed to be more reliable than the temperatures found in the conductivity studies. A third transition at 69°C, detected in the conductivity work,1 was not observed in these thermal studies. No transitions were observed at temperatures above 89°C.

(b) The results on the 88.79°C transition are somewhat incomplete, but the present data indicate just a single experimentally detectable transition in the 89°C temperature range at 88.79°C. The 82.18°C transition is quite sluggish, several hours being required for thermal equilibration under adiabatic conditions. The 88.79°C transition is clearly more "rapid," thermal equilibrium being achieved in approximately 10 to 15 min.

(c) The enthalpy change associated with each transition was determined for each composition studied by diluting the solution in the calorimeter with known increments of ammonia and measuring the transition heats following each increment. We have found at each transition temperature that, for compositions with lithium in excess of NH₃/Li = 4.15, the enthalpy change was directly proportional to the amount of NH₃ present; for compositions with NH₃ in excess of NH₃/Li = 4.15, the enthalpy change was directly proportional to the amount of Li present. This composition dependence (with enthalpy maximization at NH₃/Li = 4.15) rules out solid solution formation4 and also indicates that the