THE EVAPORATIVE VECTOR: HOMOGENEOUS SYSTEMS*

Cornelius E. Klots

*Chemical Physics Section, Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831-6125, U.S.A.*

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Chemical Physics Section, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6125, U.S.A.

Introduction:

Molecular beams of van der Waals molecules are the subject of much current research. Among the methods used to form these beams, three -- sputtering, laser ablation, and the sonic nozzle expansion of neat gases -- will yield what are now recognized to be "warm clusters." They will contain enough internal energy to undergo a number of first-order processes, in particular that of evaporation.

Because of this evaporation and its attendant cooling, the properties of such clusters will be time-dependent. We shall review what has been learned about the states of matter which can be arrived at via an evaporative vector on a typical laboratory time-scale. Recent contributions by the author will be stressed. Topics will include the (1) temperatures, (2) metastability, (3) phase transitions, (4) kinetic energies of fragmentation, and (5) the expression of magical properties, all for evaporating homogeneous clusters.

Temperatures:

In 1982 Gspann[1] suggested that large isolated clusters could be characterized by the criterion that their rate constant for subsequent evaporation be the reciprocal of the time since their formation. Using an approximate (and somewhat ambiguous) model for evaporation, he suggested the relation:

$$\Delta E_{evap}/RT \approx constant \tag{1}$$

and showed that the available data were in close accord with his estimate of its constant. Equation (1) was rediscovered by Klots several years later.[2,3] this time empirically. Explicit calculations of evaporative rate constants. based on little more than microscopic reversibility, suggested its existence.

This relation can be most simply understood as a reflection of the Trouton-Hildebrand Rule. It should thus be most applicable to the liquid rather than a crystalline phase. although the initial investigations glossed over this difference. It is now understood[4] that such a relation can not be simultaneously applicable to both liquid and crystalline phases separately. It is nevertheless also understood that, on a time-scale of tens of microseconds. their respective "constants" will scarcely differ by ten percent. The relation

$$\Delta E_{evap}/RT = 25 \pm 2 \tag{1a}$$

should thus subtend most clusters for which Gspann's basic assumption is valid.

Previous work has also glossed over the question of how a relation such as Eq. (1) can generally pertain, independently of cluster size. Thus a larger aggregate, with its larger surface area, would seem to require a lower temperature to maintain a given rate of evaporation.

This expectation is mitigated however by two circumstances. The required energy of evaporation decreases with decreasing cluster size,[2] a trend which will tend to offset the surface area argument. Secondly, the empirical observation of Ref. (2) was actually that

$$\Delta E/R(TT_f)^{\frac{1}{2}} \simeq \text{constant} \tag{1b}$$

where T, T_f are the "temperatures" before and after evaporation. For small aggregates they can differ substantially. With this added understanding Eq. (1) can then be quite broadly applicable.

It is, incidentally, T_f which can be measured by the kinetic-energy release upon evaporation, as described below.

Kinetic Energies of Evaporation:

It is believed[2] that a population of an evaporating species will be better described by an evaporative than a canonical ensemble. The concept of temperature is then never strictly applicable. This becomes especially acute for small clusters. Nevertheless, a second kind of "thermometer" may still be used. The distribution of kinetic energies with which fragments leave an evaporating body with a well-defined temperature will be given by

$$p(\epsilon) \sim \epsilon \cdot \exp(-\epsilon/kT) \tag{2}$$

This can then be used to assign a temperature for the low-energy edge of an evaporative ensemble. The available data are consistent[3] with the temperatures of Eq. (1).

A rotationally-cold and otherwise quiescent cluster (such as obtained from seeded-nozzle expansions) may be photo-stimulated into evaporation if it contains a chromophore. The resulting kinetic energy distribution will, because of the absence of initial angular momentum, be different from Eq. (2) and instead of the form:

$$p(\epsilon) \sim \exp(-\beta\epsilon) - \exp(-6\beta\epsilon) \tag{3}$$

The difference between Eqs. (2) and (3) should be operationally discernible.

Metastable Abundances:

Metastable evaporation from a cluster beam is a direct consequence of Gspann's assumption. It is in fact just this evaporation which Eq. (2) purports to describe. A universal relation

$$-\delta \ln P_\alpha(t)/\delta \ln t \simeq 6 \times 10^{-3}(\alpha) \qquad (4)$$

describing the time-decay of an isolated population P_α of clusters containing α monomeric units, has been discovered.[2] The constant on the right-hand side of Eq. (4) is closely linked with that of Eq. (1) and thus is also a (weak) function of the pertinent time-scale. Supporting evidence for this relation has been cited.[2]

Phase Transitions:

Clearly one must not suppose that a liquid-like cluster, upon cooling to a nominal melting temperature, will automatically freeze. The heat of fusion would warm the "crystal" to some higher and quite arbitrary temperature.

A recent investigation[4] has suggested a different scenario. Super-cooling of a liquid-like cluster occurs down to a temperature typically twenty percent below the melting point. When an energy-conserving isomerization would also conserve entropy, freezing occurs. It is then rendered permanent as rapid evaporation lowers the momentarily elevated temperature.

Although all existing data are apparently consistent with this criterion, no strong test of it has yet been devised.

Magical Properties:

Local "aberrations" in either the abundances or the metastable fragility of clusters, as a function of their size, are often taken as evidence for magic numbers. It has been shown[2] how indeed small deviations from continuum theory can be magnified by the appropriate Carnot-Kelvin factors into consequences of macroscopic proportions. An interesting example is offered by the results presented by the Bielefeld group two years ago at Cannes.[5] They have been interpreted[2] as a consequence of an 0.1 eV even-odd alternation in the ionization potentials of copper clusters.

Prognosis:

We may anticipate the further quantification of magical properties of clusters. Of possibly greater interest, however, will be the insights that the study of perfectly ordinary clusters may bring to perfectly ordinary processes in physical chemistry. Phase transitions in isolated aggregates are clearly nontrivial; the propensity[6] for assuming cubic structures, for example, calls for explanation. The panoply of phenomena which can arise in mixed systems has hardly been touched upon.

References

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