ERRONEOUS CLOUD-PHYSICS APPLICATIONS OF RAOULT'S LAW

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Introduction.—The purpose of this note is to call attention to an error which has appeared repeatedly in statements of Raoult's law in the meteorological literature, and which has been incorporated into a recent paper by Howell [4]. The resultant inaccuracies in Howell's calculation of cloud-drop growth have not been evaluated, but rough estimates indicate that they may be significant.

Raoult's law.—When m' moles of a *non-electrolyte* are dissolved in m moles of water, the relationship between the vapor tension e' of the resulting solution and the vapor tension e of pure water is given by Raoult's law as

$$(e' - e)/e = - m'/(m' + m), \qquad (1)$$

which may also be rewritten as

$$e'/e = m/(m' + m). \qquad (2)$$

Equation (2) states that the ratio of the vapor tension of the solution to the vapor tension of the pure solvent equals the mole-fraction of the solvent present in the solution. In so-called ideal solutions, the law is (by definition) exact at all concentrations; and in real solutions of non-electrolytes, it holds to a good degree of approximation at low and moderate concentrations [2].

When lowering of the vapor tension of a solution is due, on the other hand, to an electrolyte, (1) and (2) no longer apply, because of dissociation of the solute. There is not, at present, unanimous agreement as to the exact nature of the solutes present in hygroscopic nuclei in the atmosphere; but the substances most frequently suggested as important (sea salts, nitrous acid, sulfuric acid) all have in common the property of dissociating into ions in solution and, hence, must give vapor-tension reductions different from those predicted by (1) or (2), which apply only to non-electrolytes. Despite this fact, Raoult's law is given only as one or the other of the above equations by Haurwitz [3], Lowell [7], and again quite recently by Neuberger [9]. [It might also be noted that, in the last reference, the symbols corresponding to m and m' in (1) and (2) are incorrectly identified with the masses rather than with the numbers of moles of solute and solvent.] The same form of Raoult's law appears in the recently revised *Smithsonian meteorological tables* [6], and forms the incorrect basis for all of the equilibrium supersaturations over solution droplets, tabulated on pp. 375–379 of those tables.

For *electrolytes*, Raoult's law must be modified to the form

$$(e' - e)/e = - im'/(im' + m), \qquad (3)$$

where i is a factor, often called the van't Hoff factor, which varies both with the chemical nature of the electrolyte and with the concentration of the solution. In the limit of infinitesimal concentration of the solute, i becomes simply the number of ions comprising one molecule of the solute (*e.g.*, two for NaCl, three for $MgCl_2$).

The van't Hoff i factor.—As the solute concentration increases from zero, the value of the van't Hoff factor first decreases, but then begins to rise again for moderate concentrations and, for most strong electrolytes, attains values in excess of the number of ions per molecule at concentrations near the saturation value. The latter effect is particularly marked in the cases of salts which characteristically form hydrates (*e.g.*, $MgCl_2.6H_2O$). The Debye-Hückel theory of inter-ionic attraction gives a fairly good explanation of the behavior of i near zero concentration, where i decreases with increasing concentration [2]. At high concentrations, it is believed that the clustering of the highly-polar water molecules about the ions (particularly about the cations) ties up a large fraction of the total population of water molecules, to decrease appreciably the number of water molecules escaping per second per unit area of surface of the solution, the latter thereby behaving as if there were an apparent ionic concentration greater than the actual value.

Since the variation of i with concentration is dependent upon the chemical nature of the solute in question, and since there is not yet complete agreement as to the nuclear substances operative under natural conditions, it would scarcely be in order here to undertake an exhaustive examination of the physical chemistry of any one nuclear substance or mixture. However, to show how Raoult's law should be treated for whatever solutes ultimately prove to be of chief importance in atmospheric condensation, the case of NaCl nuclei is considered here in somewhat more detail than has been done in the meteorological literature before. If sea-salt nuclei should prove to be the main atmospheric nuclei, then, since NaCl comprises some 77 per cent by weight of the mixture of salts present in sea water, the Raoult effect of that salt will be of primary interest, though $MgCl_2$, present to the extent of about 11 per cent, will have

to be considered carefully because its property of forming a hexahydrate will make it a quite significant factor in the physical chemistry of sea-salt nuclei under conditions of low relative humidity.

It is possible to compute the van't Hoff factor, as a function of molality for any given solute, from the variation of the activity coefficient of that solute with molality [2; 8]. The great wealth of data on activity coefficients would justify this approach, once there is clear evidence that some one substance is of dominant importance in atmospheric nucleation; but the method is quite tedious, involving as it does a numerical integration of the Gibbs-Duhem equation for each determination of i. As a more direct approach available in the case of NaCl, whose effect on vapor tension has been determined experimentally over a wide range of concentrations, i values have been computed here from the observed magnitudes of the reduced vapor tensions of solutions of NaCl. Tabulated values of this quantity are given in [12] for a range of molality of 0.1 to 6.0 (a saturated NaCl solution is about 6.05 molal at atmospheric temperatures). Three additional values needed for the very low concentrations attained in the later phases of drop growth were taken from the measurements of Dieterici and of Smits, reported in [10].

Table 1 shows the values of i computed from these observed data. It is to be noted that, even at the minimum point, $i = 1.82$, so the reduction of the vapor tension of a droplet containing a nucleus of NaCl is *at least* 82 per cent greater than the value implied by the erroneous form of Raoult's law given in [3], [7] and [9]. Note also that, near saturation, i has become so large (due to solvation of the ions) that an error of 191 per cent is made if these ionic effects are neglected in calculation of the Raoult effect. For the frequently accepted case of sea-salt nuclei, the corresponding error would be noticeably larger at this high concentration, because of the much more pronounced hydration of the magnesium ions.

TABLE 1. Values of the van't Hoff factor, i, for aqueous solutions of NaCl of molality M.

M	Mole-fraction of NaCl	i
0.0+*	0.0+	2.00 −
0.044	0.00080	1.96
0.070	0.00126	1.90
0.098	0.00177	1.86
0.1	0.0018	1.83
0.2	0.0036	1.82
0.4	0.0072	1.84
0.6	0.0108	1.85
0.8	0.0144	1.87
1.0	0.0180	1.89
2.0	0.0361	2.04
2.8	0.0505	2.19
5.0	0.0902	2.66
6.0	0.1083	2.91

* 0.0+ is used here to denote the limit of infinite dilution.

Köhler curves for NaCl nuclei.—That the forms of Raoult's law appearing in the literature cited are in need of correction is indicated by the fact that this error has been carried into the very valuable work of Howell [4] on cloud-drop growth. Curiously, the neglect of ionic effects seems to be an error appearing in the meteorological literature of just the United States. Köhler [5], in his work on the vapor tension of droplets, assumed a constant "dissociation factor" (as defined for the now-abandoned Arrhenius theory) of 0.75 for his assumed NaCl nuclei. Wright [13] considered several chemical possibilities for his nuclei and used constant factors to correct for the effects of ionization. His statement, that "the hygroscopic factor . . . may vary with the concentration of the solution, particularly when the solution becomes very dilute and the phenomenon of dissociation occurs," raises some doubt, however, as to whether he held a correct view of the underlying physical chemistry of Raoult's law. Best [1], in a recent paper on drop growth, merely employs Wright's constant correction for solute dissociation.

With use of the values of the van't Hoff factor given in table 1, (*i.e.*, effectively with use of the experimental values from which table 1 was derived), the equilibrium supersaturation values over droplets containing various specified numbers of moles of NaCl were computed, for comparison with Howell's values (presented in [4] as his fig. 1). Each Köhler curve corresponding to a given nuclear size was pushed down as a result of the correction of the Raoult's-law error made by Howell, and its peak value of critical supersaturation was moved towards a larger drop-size.[2] The corrected values of peak supersaturation are only about three-fourths as large as those found by Howell (not to be confused, however, with the supersaturations found by Howell in the course of his numerical integrations of the drop-growth equation, for comments on which see below).

The important question arises: What effects on Howell's computed growth rates would follow from a corrected treatment of Raoult's law? In an attempt to answer this, the writer calculated, from Howell's paper, the parameters needed to evaluate the growth rates for several different nuclear sizes, and then sought to compare these rates with those obtained with the incorrect form of Raoult's law.[3]

The degree of supersaturation, S in Howell's nomenclature, is a quantity which must be known before a calculation of growth rate can be made in

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[2] It has seemed to be a useful economy of expression, as well as a due recognition of Köhler's contributions to condensation theory, to refer to any such curves simply as "Köhler curves."

[3] It is worth noting here, for the benefit of readers concerned with the theory, that there appears to be an error of algebraic sign in Howell's formulation of the compensated diffusion coefficient, as well as a discrepant location of a factor of 2π in the asymptotic form of this coefficient for very small drops.

any given case. By reading off the S values from Howell's growth curves for various drop sizes and nuclear masses of interest, and by using these to calculate corrected growth rates, apparent errors of from 25 to 30 per cent in rates (at the points of maximum error) were found. However, this was a fallacious approach which overlooked the principal contribution of Howell's entire analysis, namely, the treatment of S as a dependent variable in the growth equation. The degree of supersaturation is itself strongly influenced by the vapor tension of the drops (in reality, and also in Howell's admirable analysis of the growth problem); so, to use Howell's supersaturations along with the *corrected* vapor tensions is not permissible, since this would appreciably overestimate the error in the growth rates.

There seems to be no other way to determine exactly how far off Howell's growth rates may be than to redo his integrations. This would entail an amount of labor which would carry this note considerably beyond its intended scope, so no final assessment of the Raoult's-law error in Howell's work is given here. However, from certain numerical-physical arguments, the writer is led to suspect that, in the regions of most rapid drop growth, Howell's rates may be too low by about 10–15 percent. If so, the later history of drop growth might be sensibly affected, since it is exactly at this stage of cloud formation that the peak supersaturation is determining the lower limiting size of nuclei (and hence the total number of nuclei) to be activated for rapid growth. For the region of growth beyond a few microns, dilution has proceeded so far that the Raoult effect virtually vanishes; hence, the latter phases of Howell's theoretical growth histories are not here in question, except inasmuch as they may be affected by the peak supersaturation.

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