Third-Order Ion–Molecule Clustering Reactions

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Contents

I. Introduction

The technical advances of the past few years have led to a vast widening of the scope of the mass spectrometer in the investigation of ion–molecule reactions. It is now possible to study such reactions at higher pressures and over a wider range of temperatures than before. This has meant that many slow reactions, hitherto undetectable in the conventional low-pressure ion source, could be investigated. Such studies have led, in turn, to the recognition that many ion–molecule reactions display third-order kinetics.

This review will be concerned primarily with thermal "clustering" reactions of the general type:

$$I + A + M \rightarrow I{\cdot}A + M \qquad (1)$$

where I denotes a positively or negatively charged ion and A and M are neutral species. As indicated, most clustering reactions are reversible, though not necessarily appreciably so for all experimental conditions. The bonding between ion and "solvent" is generally found to be weak relative to normal chemical bond strengths; D°(I–A) is typically 200 kJ mol^{-1} or less, often much less. It seems likely that the I–A bond derives primarily from electrostatic forces such as ion–dipole attraction.

Apart from their intrinsic interest as a new type of chemical process, such clustering reactions can provide a great deal of information on the nature of solvation.[1,2] Equation 1 may be regarded as representing merely the first step in a series of reactions leading to the fully solvated ion.

It has also been found that ion–molecule clustering is a particularly important process in the ionosphere.[3] These two apparently divergent areas of interest can in practice be investigated using identical techniques, and the present article is intended to cover both fields. The literature has been surveyed up to the end of 1973, although some more recent work has also been included.

A. Units

Third-order rate constants will be quoted in units of $molecule^{-2}$ cm^3 sec^{-1} throughout, while second-order rate constants will be expressed in units of $molecule^{-1}$ cm^3 sec^{-1}. For convenience, the exponent involved will be given in brackets after the numerical value; thus 1(−27) indicates a rate constant value of 1×10^{-27}. Free energies, enthalpies, and activation energies are quoted in units of kJ mol^{-1}, entropies in J K^{-1} mol^{-1}, all referred to a standard state of one atmosphere unless otherwise indicated (N.B. 4.184 J $\equiv$ 1 calorie).

II. Apparatus

No attempt will be made in this article to give a detailed account of the numerous experimental systems which have

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been employed in the investigation of clustering reactions. It is, however, useful to mention certain of the basic types of instrument which have been developed. These may conveniently be divided into two categories.

A. Drift and Flow Methods

The conventional type of drift-tube experiment,[4] in which a cloud of ions moves, under the influence of a weak electric field, through a static gas, has been widely used in the measurement of ionic mobilities, equilibrium constants, and kinetic data.[5] Improved drift tubes are still in use for these purposes.[6,7]

The main drawback of the method is the necessity of subjecting the ions to the accelerating electric field, which, however weak it may be, nevertheless excites the ions above their thermal energies. Data applicable to true thermodynamic equilibrium can only be obtained by the extrapolation of results obtained over a range of field strength (E/N) values.

More recently, techniques have been developed in which the entire gas sample passes through a flow system. The ions are produced at some point in this flow, either by photoionization[8] or by electrical discharge,[9] and, after a certain reaction time, regulated by the rate of flow, the ions are mass-analyzed. The "flowing-afterglow" technique of Ferguson et al.[10] is the most powerful flow method yet developed. Further gases may be added downstream from the ionization, and so the reactions of chosen ions with a whole range of neutral reactants may be studied. Reactions have normally been carried out in a stream of helium which, being in excess, acts as the third body, M, in clustering reactions. The reaction region of the flow system is free of electric fields and the collisional deactivation of excited species is rapid at the pressures employed, which may be as high as several Torr. The satisfaction of these two criteria should ensure that the data obtained are those for conditions of thermal equilibrium.

Time-of-flight mass spectrometers can also provide relevant kinetic data,[11] although here again electric fields can be troublesome. The flow in this case occurs, of course, outside the reaction region, and decomposition of large ions during the lengthy period of flight down the mass analysis system is a distinct possibility. In principle, this decomposition could be taken advantage of in a study of the kinetics of fragmentation of clusters.

B. Static Methods

Very slow reactions, or long sequences of consecutive reactions, are difficult to study in flow systems, where the gas flow may be varied only within certain limits. For this reason, various static methods have been developed.

Many of the early observations of clustered products were made in static systems in which high-pressure ion sources were attached to conventional mass analyzers. Ionization was brought about by techniques such as field-emission[12,13] and high-energy electron impact.[14] The latter method has been developed by Field and coworkers[15] into the technique of "chemical ionization", whereby traces of the neutral precursor of the desired reactant are added to several Torr of a substrate, usually CH_4. Equilibrium data obtained in this way will be discussed below.

A number of high-pressure ion sources have been constructed by Kebarle and coworkers[2] for the investigation of thermodynamic equilibria and reaction kinetics in cluster systems. Ionization by means of α-particles[16,17] and by proton impact[18] have both been employed in sources having ion-residence times of several milliseconds, in which it is possible for thermodynamic equilibrium to be attained. The subsequent mass analysis yields values of the equilibrium constants, K_p, for the product clusters, and repetition over a range of temperatures leads to the evaluation of $\Delta H°$, $\Delta S°$, and $\Delta G°$ at some chosen temperature, usually 298 K, by means of a van't Hoff plot of log K_p against $1/T$.

No kinetic information can be obtained by any of the methods so far discussed in this section, nor is it explicitly shown that the clustering reactions are, in fact, third order.

In order to measure rate constants for sequences of clustering reactions, an ion-source pulsing technique was developed by Durden and Kebarle,[19,20] and this has subsequently been employed in equipment capable of operating over a very wide temperature range.[21] In this method, the ionizing beam of high-voltage electrons was switched on only in brief pulses, so that the subsequent production and decay of ions could be studied in the absence of further ionization. Pulses of product ions were admitted for mass analysis a known "delay time" after the ionization pulse[19,20] or were identified and counted using a multichannel analyzer.[21]

These techniques permitted the calculation of rate constants for the production and removal of species involved even in highly complex reaction sequences. The use of a "field-free" ion source allowed the system to reach thermodynamic equilibrium, at least in principle.

The whole question of the attainment of equilibrium in ion sources has been the subject of some controversy,[22,23] and K_p values differing by as much as ten orders of magnitude have been reported from different instruments.[24,25] Such discrepancies, while not invalidating the bulk of the published data, underline the need for extreme care in the design and use of the ion source and sampling system and indicate that equilibria far removed from the "thermal" are easier to generate than they are to identify.

The "stationary afterglow" technique of Puckett and Lineberger[26] involves the production of ions by pulsed photoionization. Ions which diffuse to the walls are sampled by time-resolved mass spectrometry, and rate constants are obtained from the observed decay rates of the ions involved. Treatment of the data has to take account of the natures of the diffusion processes which the ions undergo en route to the wall.

III. Mechanism of Clustering

It has been pointed out[20] that an ion-molecule clustering reaction is a process very similar to the combination of two atoms or two free radicals. One would expect an initial combination step, with no activation energy, brought about by ion-permanent dipole or ion-induced dipole attraction between the reactants. The energy thus liberated in the reaction complex could then be lost by collision with a third body, and we can usefully consider clustering to be an example of an "energy-transfer" process, with a mechanism similar to that proposed[27,28] for radical combination:

$$\mathrm{I} + \mathrm{A} \underset{k_d}{\overset{k_c}{\rightleftharpoons}} \mathrm{I{\cdot}A^*} \qquad \begin{matrix}\text{combination}\\ \text{decomposition}\end{matrix} \tag{2}$$

$$\mathrm{I{\cdot}A^*} + \mathrm{M} \underset{k_a}{\overset{k_s}{\rightleftharpoons}} \mathrm{I{\cdot}A} + \mathrm{M} \qquad \begin{matrix}\text{stabilization}\\ \text{activation}\end{matrix} \tag{3}$$

When third-order kinetics are observed experimentally, we can say, in the usual way, that $k_d \gg k_s[\mathrm{M}]$, and hence we obtain rate equations of the form:

$$\text{forward rate} = k_f[\mathrm{I}][\mathrm{A}][\mathrm{M}] = \frac{k_c k_s}{k_d}[\mathrm{I}][\mathrm{A}][\mathrm{M}] \tag{4}$$

$$\text{reverse rate} = k_r[\mathrm{I{\cdot}A}][\mathrm{M}] = k_a[\mathrm{I{\cdot}A}][\mathrm{M}] \tag{5}$$

where k_f and k_r represent the forward and reverse rate constants, respectively.

Considering the individual rate constants which combine to give k_f, we expect, as discussed above, that k_c should contain no activation energy term and that it should thus be independent of temperature to a first approximation. Stabilization should depend on the identity of M; k_s may have some slight temperature dependence also, if the excess energy to be lost is distributed according to Maxwell–Boltzmann statistics.

Applying simple RRK theory to the decomposition step, we see that k_d will depend upon the dissociation energy of the complex, $D°$(I–A), and the internal energy, nRT. It has been shown[20] that if $D° \gg nRT$, then

$$k_d \propto (nRT/D)^{s-1} \tag{6}$$

where s is related to the number of vibrational degrees of freedom in the cluster.

Hence, overall, if we disregard any temperature dependence of k_c and k_s, we obtain the relationship:

$$k_f \propto T^{(1-s)} \tag{7}$$

Thus the simple theory predicts a negative temperature dependence—an apparent "negative activation energy"—for k_f in most cases. Such a dependence is observed experimentally in many systems,[20] but although results have often been expressed in the form of an Arrhenius plot for convenience, they cannot of course be interpreted in such a simple way.

The discussion of the more sophisticated theories of the mechanism of clustering will be postponed until the experimental data have been considered in detail. It should, however, be noted at this stage that an alternative mechanism, analogous to the "radical–molecule complex" pathway proposed[28] for radical reactions, would also account for the observed reaction products and for the rate law. In such a case, the initial combination produces the species I·M*, which then undergoes "switching" with A:

$$\mathrm{I} + \mathrm{M} \rightleftharpoons \mathrm{I{\cdot}M^*} \tag{8}$$

$$\mathrm{I{\cdot}M^*} + \mathrm{A} \rightleftharpoons \mathrm{I{\cdot}A} + \mathrm{M} \tag{9}$$

Such a mechanism should be most important when I and A are small, perhaps atomic, species and M is a larger molecule with more degrees of freedom.[28] If such a process occurs, we can expect it to have an effect on the observed magnitude and temperature dependence of k_f.

IV. Clustering in the Rare Gases

Ion–molecule clustering has been observed in samples of all the rare gases, both in their pure states and with an excess of some second gas as third body. Mixed clusters have also been observed. Rate constants for the formation of dimer ions have been measured in a variety of experimental situations including flames,[29] drift tubes,[30] high-pressure ion sources,[31] afterglows,[8,32,33] and electron density decay studies.[34] The available rate constant data are listed in Table I.

All the methods give k_f values which are within an order of magnitude of 1(−31) at 300 K, while the data obtained at other temperatures[32,35,36] largely display the negative temperature dependence discussed in section III. Paradoxically, this is not the verification of the simple energy-transfer mechanism that it at first appears to be, because for a diatomic cluster we would expect s in eq 7 to have a value of one, making k_f independent of T. It would be necessary to invoke possible temperature dependences of k_c and k_s to explain the data on an energy-transfer basis.

However, as noted in section III, there is the possibility of a competing radical–molecule complex mechanism for atomic reactants. Also, Mahan[37] has been able, by assuming a charge-transfer mechanism, to calculate theoretical k_f values which are in good agreement with the experimental data as regards both magnitude and temperature dependence. The calculation will be more fully discussed in section XVII below.

TABLE I. Rate Constants of Clustering Reactions in the Rare Gases

I	A	M	T, °K	$10^{31}k_f$, molecule^{-2} cm^6 sec^{-1}
He^+	He	He	76	1.7^{36}
			300	0.63,^{34} 0.84,^{b} 0.35,^{c} 1.10,^{d} 1.06,^{33} 1.08,^{30} 0.64,^{e} 0.68^{f}
Ne^+	He	He	300	0.07,^{g} 0.21^{h}
	(Ne + He)^{a}	He	300	3.0^{h}
$(Ne{\cdot}He)^+$	Ne	He	300	0.02^{i}
Ne^+	Ne	Ne	195	0.09^{j}
			300	0.7,^{30} 0.42,^{g} 0.79,^{k} 0.44,^{l} 0.15^{j}
			331	0.73^{m}
			523	0.27^{j}
Ar^+	(Ar + Ne)^{a}	Ne	300	3.0^{n}
	Ar	He	82	16^{32}
			290	1.3^{32}
			300	0.92,^{n} 0.8^{o}
		Ar	293	0.84^{29}
			296	2.07^{p}
			298	4.4,^{8} 2^{q}
			300	1.5,^{c} 0.6,^{31} 2.5,^{k} 3.0,^{r} 2.3,^{s} 3.0,^{t} 0.7^{u}
			331	3.85^{m}
Kr^+	(Kr + Ne)	Ne	300	0.6^{n}
	Kr	He	300	0.64^{v}
		Kr	180	2.70^{35}
			300	2.3^{w}, 2.74^{35}
			510	1.65^{35}
Xe^+	Xe	He	300	1.12^{v}
		Xe	300	3.57,^{35} 1.8,^{x} 2.0^{y}

[a] In these cases the total rate of disappearance of I was measured. [b] H. J. Oskam and V. R. Mittelstadt, *Phys. Rev.*, **132**, 1435 (1963). [c] C. B. Kretschmer and H. L. Petersen, *J. Appl. Phys.*, **34**, 3209 (1963). [d] R. Hackam and J. J. Lennon, *Proc. Phys. Soc., London*, **84**, 133 (1964). [e] D. Smith and M. J. Copsey, *J. Phys. B*, 1, 650 (1968). [f] D. Smith, C. V. Goodall, and M. J. Copsey, *ibid.*, 1, 660 (1968). [g] G. F. Sauter, R. A. Gerber and H. J. Oskam, *Physica (Utrecht)*, **32**, 1921 (1966). [h] G. E. Veatch and H. J. Oskam, *Phys. Rev. A*, **2**, 1422 (1970). [i] Products are Ne_2^+ + 2He. See footnote *g* above. [j] R. Hackam, *Br. J. Appl. Phys.*, 17, 197 (1966). [k] D. Smith and P. R. Cromey, *J. Phys. B*, 1, 638 (1968). [l] A. P. Vitols and H. J. Oskam, *Phys. Rev. A*, **5**, 2618 (1972). [m] J. P. Gaur and L. M. Chanin, *Phys. Rev.*, **182**, 167 (1969). [n] H. J. Oskam, *Philips Res. Rep.*, 13, 335 (1958). [o] G. E. Veatch and H. J. Oskam, *Phys. Rev. A*, 1, 1498 (1970). [p] W. F. Liu and D. C. Conway, *J. Chem. Phys.*, **60**, 784 (1974); the authors find that the $^2P_{1/2}$ state of Ar^+ does not react. [q] Intermediate between second and third order: D. Hyatt and P. F. Knewstubb, *J. Chem. Soc., Faraday Trans. 1*, 68, 202 (1972). [r] J. C. Cronin and M. C. Sexton, *Br. J. Appl. Phys.*, 1, 889 (1968). [s] W. Peterson and E. C. Beaty, *Bull. Am. Phys. Soc.*, **14**, 260 (1969). [t] P. Kebarle and M. Yoshida, unpublished result quoted in ref 2. [u] U. A. Arifov, S. L. Pozharov, and I. G. Chernov, *High Energy Chem. (Engl. Transl.)*, **5**, 1 (1971). [v] C. L. Chen, *Phys. Rev.*, 131, 2550 (1963). [w] A. K. Bhattacharya, *Phys. Rev. A*, 1, 1196 (1970). [x] A. K. Bhattacharya, *Appl. Phys. Lett.*, 17, 521 (1970). [y] A. P. Vitols and H. J. Oskam, *Phys. Rev. A*, 8, 1860 (1973).

No direct equilibrium studies have been made for any of the rare gas clusters. However, indirect estimates of the various bond dissociation energies have been made using a variety of techniques. Beam studies[38] indicate a value of 193–232 kJ mol^{-1} for $D°$(He^+–He). Appearance potential data[39] have led to the estimate that $D°$(Ar^+–N_2) and $D°$(Ar^+–Ar) are both ≥63 kJ mol^{-1}, while measurements of the threshold of photoionization in argon[40] have raised this lower limit to 101 for Ar_2^+. Work in a high-pressure ion source[31] has led to an estimate that $D°$(Ar^+–Ar) lies in the range 144–192 kJ mol^{-1}, with a similar value expected for Ne_2^+. These values were obtained by an indirect thermochemical method. Drift tube measurements[41] give values of 102 and 110 for $D°$(Ar^+–

TABLE II. Rates of Clustering Reactions Involving Ions of Nitrogen

I	A	M	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	Ref
N_2^+	N_2	He	82	1.2(−28)	32
			280	1.9(−29)	32
			300	5.6(−30)	*a*
		N_2	298	8.5(−29)	58
				8(−29)	8
			300	5(−29)	*b*
				8(−29)	60
				6.2(−29)	*c*
N^+	N_2	He	82	7.2(−29)	32
			280	8.6(−30)	32
			300	4.6(−29)	*a*
		N_2	300	3(−29)	*d*
				1.8(−29)	*b*
				5(−29)	60
N_2^+	N	N_2	300	2.5(−29)	*e*
e^-	N_2	N_2	300	3.5(−32)[f]	77

[a] T. D. Mark and H. J. Oskam, *Phys. Rev. A*, **4**, 1445 (1971). [b] J. T. Moseley, Ph.D. Thesis, Georgia Institute of Technology, 1968; quoted in ref 32. [c] I. Dzidic, A. Good, and P. Kebarle, *Can. J. Chem.*, **48**, 664 (1970). [d] L. G. McKnight, K. B. McAfee, and D. P. Sipler, *Phys. Rev.*, **164**, 62 (1967). [e] J. W. Dreyer and D. Perner, *Chem. Phys. Lett.*, **12**, 299 (1971). [f] Reactions of this type are discussed in section V.C.

N_2) and $D°(Ar^+–Ar)$, respectively, in line with earlier appearance potential data giving[42] 110 and 105 kJ mol^{-1}. Clearly, more work is needed to establish reliable values for these bond strengths. No measurements have been reported for Kr_2^+ or Xe_2^+.

A number of theoretical calculations have been performed to estimate the bond strengths of the clusters. Values of 205[43] and 230[44] have been calculated as the lower limits of $D°(He^+–He)$, while Mulliken[45] has selected 134 kJ mol^{-1} as the best value for $D°(Ar^+–Ar)$.

The ion He_3^+ has been detected in a drift tube at 76 K[36] and in mass spectrometers,[46–49] but no quantitative data have been reported.

V. Clustering in Homonuclear Diatomic Gases

A. Hydrogen

There has been little published work on the possible clustering reactions of pure hydrogen. Drift-tube studies have led to k_f values of 3.2(−29)[50] and 3.05(−29) molecule^{-2} cm^6 sec^{-1} [51] at 300 K for the reaction:

$$H^+ + 2H_2 \rightleftharpoons H_3^+ + H_2 \qquad (10)$$

The corresponding deuterium reaction had a rate constant of 3.0(−29).[50,51] Beam studies of the binding energies of these clusters[52] have given values of 386–415 kJ mol^{-1} for the proton affinity of H_2 and 396–424 for the deuteron affinity of D_2. Values of this magnitude imply chemical rather than electrostatic bonding. Theoretical studies[53] suggest an equilateral triangular structure for H_3^+, the length of each side being 0.088 nm, and the calculated bond strength 460 kJ mol^{-1}.

Larger clusters, in the series $H^+(H_2)_n$, have been detected in a qualitative investigation.[54] The $n = 7$ cluster was the major ion observed, but the precise thermodynamic state of the ions was not clear. The exothermicity of the reaction whereby H_3^+ reacts to give H_5^+ has been estimated as 21.3 kJ mol^{-1} [55]; k_f was 4.5(−31) for D_5^+ formation at 296 K. A more detailed investigation[56] of the H_3^+/H_5^+ and H_5^+/H_7^+ equilibria has yielded values of respectively −8.4 and +5.9 kJ mol^{-1} for $\Delta G°$(298 K), −40.6 and −7.5 kJ mol^{-1} for $\Delta H°$(298 K), and −107 and −45 J K^{-1} mol^{-1} for $\Delta S°$.

B. Nitrogen

After an initial period of controversy, during which nitrogen ion clustering data were variously interpreted in terms of second-[57] and third-order[8,58] kinetics, it now appears to have been conclusively established that N_4^+ is produced by a reaction of the type

$$N_2^+ + N_2 + M \rightleftharpoons N_4^+ + M \qquad (11)$$

with no second-order component apparent even at pressures of above 1 Torr at room temperature. Saturation leading to second-order kinetics has, however, been reported[59] for total pressures (M = He) of greater than 0.8 Torr at 80 K.

The reported rate constants are listed in Table II. Results obtained in pure nitrogen, using the pulsed-beam technique over the temperature range 300–420 K,[60] indicated an apparent "activation energy" of −9.6 kJ mol^{-1}, while a value of −15 was estimated from drift data.[8] The rate constant with He as third body is lower than that in pure nitrogen at the same temperature by a factor of about 5.[32,60] This would be expected as a result of the greater ability of the N_2 molecule to take up the excess energy in collisions with $(N_4^+)^*$.

An apparent equilibrium constant of 5.7 × 10^4 atm^{-1} was reported[8] for eq 11 at 298 K. Subsequent work,[60] however, failed to detect any residual N_2^+ at temperatures as high as 420 K. This was in agreement with the data of Varney, whose extrapolated drift-tube results[61] indicated a K_p value of about 8 × 10^6 at 420 K and gave an estimated $D°(N_2^+–N_2)$ value of 84 kJ mol^{-1}.

The bond dissociation energy has also been estimated by other means. Appearance potential data[42] gave a value of 121 (±30), and lower limits of 50[62] and 45[63] kJ mol^{-1} were also reported.

More recently, direct studies of the equilibrium have been made using a high-pressure ion source[64] and a drift tube.[41] In the temperature range 400–600 K, the measurement of log K_p as a function of temperature, followed by suitable extrapolation of the data, led to a value of 3 × 10^{12} for K_p at 298 K,[64] together with values of −95.4 and −71.1 kJ mol^{-1} for $\Delta H°$(298 K) and $\Delta G°$(298 K), respectively. The drift-tube data gave a best value of 102 for $D°(N_2^+–N_2)$.[41] As $D°$ and $-\Delta H°$ are approximately comparable, the two sets of data are in good agreement. The drift-tube work gave a value of −67.7 J K^{-1} mol^{-1} for $\Delta S°$ at 723 K.

An alternative route for the formation of N_4^+ has been suggested by work using a monoenergetic electron beam.[42,63] This involves the initial formation of an excited neutral molecule, which can undergo subsequent associative ionization:

$$N_2 + e^- \rightarrow N_2^* + e^- \qquad (12)$$

$$N_2^* + N_2 \rightarrow N_4^+ + e^- \qquad (13)$$

However, this process is unlikely to be important at the higher pressures used in the equilibrium studies[41,64] for which collisional deactivation may be expected to be very rapid.

An SCF-MO calculation for the N_4^+ ion has suggested that it may be linear,[65] with a calculated $N_2^+–N_2$ bond length of 0.204 nm. However, as the calculated $D°(N_2^+–N_2)$ value of 145 kJ mol^{-1} is rather large when compared with the experimental values, this conclusion can only be regarded as tentative.

The ions N_6^+ and N_8^+ have been observed in a flowing afterglow at 82 K,[32] but no quantitative data have been reported.

The mixed cluster $N_2^+·O_2$ has been studied in the temperature range 177–249 K,[66] and the bond dissociation energy was measured as 23.1 kJ mol^{-1}; values of −23.8 kJ mol^{-1} and −79 J K^{-1} mol^{-1} were obtained for $\Delta H°$ and $\Delta S°$ at

200 K, giving a $\Delta G°(200\ K)$ value of −8.0 kJ mol^{-1}. This cluster is clearly much more weakly bonded than is N_4^+.

A second clustering series is found to occur in nitrogen, leading to the formation of the N_3^+ ion. The process is almost certainly third order:

$$N^+ + N_2 + M \rightleftharpoons N_3^+ + M \qquad (14)$$

but this has not been conclusively established.[60] The measured rate constants, calculated on the assumption that the reaction does obey third-order kinetics, are listed in Table II. On this basis, with nitrogen as third body, it is possible to obtain an apparent "activation energy" of −3.3 kJ mol^{-1} [60] for k_f in eq 14, but the same data were also consistent with a temperature-independent second-order rate constant of 1.3(−12) molecule^{-1} cm^3 sec^{-1}. The bond dissociation energy for N_3^+ has been shown[63] to be ≥293, and this large value does suggest the possibility that the lifetime of $(N_3^+)^*$ may be long enough to cause the reaction to be second order at pressures of the order of 3 Torr. The cluster ions up to and including N_9^+ have been detected,[32] but no quantitative data are available for these larger species.

An alternative mechanism has been proposed[63,67] for the formation of N_3^+ at low pressures. This involves the $^4\Sigma_u^+$ state of N_2^+, which is 305 kJ mol^{-1} above the ground $^2\Sigma_g^+$ state[68]:

$$N_2^+(^4\Sigma_u^+) + N_2 \rightarrow N_3^+ + N \qquad (15)$$

However, this species would not be present to any significant extent at pressures of the order of several Torr; indeed, it has been shown[60] that the sum of the ion intensities of the species N^+ and N_3^+ is a constant fraction of the total ion intensity in pure nitrogen, even at very long reaction times. A crossover reaction such as eq 15 is therefore probably ruled out as a significant contributor to the mechanism at higher pressures.

C. Oxygen

1. Positive Ion Clustering

The formation of O_4^+ [69] and higher clusters[70] from O_2^+ was initially investigated by Yang and Conway, who employed total oxygen pressures of 1–4 Torr and ion-residence times of about 1 msec to obtain K_p values for the various equilibria involved. More recent work in the same laboratory[71] has extended the measurements up to total pressures of 12 Torr in the temperature range 77–362 K. Values of $D°$ and, by extrapolation, $\Delta H°(298\ K)$ and $\Delta S°(298\ K)$ were obtained, and the most recent values are given in Table III. Clearly, $D°$ and $-\Delta H°(298\ K)$ are equivalent to within the limits of reasonable experimental error. Values of $\Delta G°(298\ K)$ calculated from the experimental data are also included in this table and show that clusters larger than O_4^+ will not be observed at room temperature.

This conclusion is in agreement with data obtained in a pulsed-beam ion source.[20] The clustering of oxygen was investigated in the pure gas[20] and in oxygen contaminated with traces of water vapor.[72] No oxygen cluster larger than O_4^+ was detected at 300 K, even at pressures of several Torr. The equilibrium constant for the process

$$O_2^+ + 2O_2 \rightleftharpoons O_4^+ + O_2 \qquad (16)$$

was in good agreement with the data of Conway and coworkers.[69,71] One would expect further clustering only at much lower temperatures, and indeed the formation of O_6^+ has been observed in flowing-afterglow studies at 82 K.[73]

TABLE III. Thermodynamic Properties of Oxygen Cluster Ions (After Conway and Janik[71])

Product species	$D°$, kJ mol^{-1}	$-\Delta S°$, J K^{-1} mol^{-1}	$-\Delta H°$, kJ mol^{-1}	$\Delta G°(298\ K)$, kJ mol^{-1}
O_4^+	43.9	105	45.2	−12.8
O_6^+	27.2	133	28.8	+12.5
O_8^+	10.7	82.8	10.6	+14.0
O_{10}^+	10.2	100	10.3	+19.6
O_{12}^+	8.4	71.1	7.7	+12.8

The forward reaction in eq 16 has been shown experimentally to be third order,[20] although it appeared to change to second-order behavior at pressures above 1.6 Torr at 82 K.[59] It was possible to measure both k_f and k_r, the latter being obtained indirectly via the measured values of k_f and K_p. Rate constants obtained in this and other work are given in Table IV, which also includes data on mixed clustering involving the O_2^+ ion. Most of the data were obtained by flowing-afterglow measurements.[73]

The k_f value for eq 16 was shown to have an apparent "activation energy" of the order of −6 kJ mol^{-1}.[20] The formation of O_4^+ with He as third body proceeded with a rate constant smaller by a factor of 6 than that when O_2 was third body.[74] This observation tallies with that for the nitrogen system discussed in section V.B. The subsequent reaction to give O_6^+, also with He as third body, was found to be an order of magnitude slower than O_4^+ formation at 82 K.[73]

No third-order rate constants involving the species O^+ have been reported at room temperature. The O_3^+ ion has been observed in the mass spectrum of ozone,[75] but the charge-transfer process

$$O^+ + O_2 \rightarrow O_2^+ + O \qquad (17)$$

is exothermic by about 200 kJ mol^{-1},[68] in contrast to the situation in nitrogen, and so clustering would not be expected in this case. The reaction between O^+ and N_2 has been observed in a flowing-afterglow experiment[32] to be third order at 80 K, as listed in Table IV, but the exact mechanism is unclear as no N_2O^+ was observed. At room temperature, the same system leads to the second-order formation of NO^+.

2. Negative Ion Clustering

The clustering of oxygen negative ions has also been investigated and the experimental kinetic data are listed in Table V. We can regard the initial associative ionization of O_2 as the first step in the series of reactions leading to O_{2n}^-. This reaction has been extensively studied[76,77] and has been shown to be third order and to behave as a typical ion–molecule clustering reaction, with the expected variations of k_f with third body.[76] Results obtained at different temperatures[78–81] seem to indicate a positive temperature dependence for k_f.

The rate constant for the formation of O_3^- has a measured "apparent activation energy" of −8 kJ mol^{-1},[82] and the process is third order.[83,84] However, in drift-tube work, where the ions are not at thermal energies, a charge exchange reaction

$$O^- + O_2 \rightarrow O_2^- + O \qquad (18)$$

has been reported.[7,85] The rate constant of this reaction varied sharply with field strength, changing from 2.5(−14) at E/N = 63(−17) V cm^2 to 5(−11) at E/N = 300(−17).[85]

The rate constant for the formation of O_4^- is seen to be an order of magnitude smaller than that for formation of O_4^+ with the same third body, but no general trends are apparent from a comparison of the kinetic data for O_2^+ and O_2^-. The two reported values of k_f for the reaction between O_2^- and CO_2[86,87] differ widely and lie on either side of the reported value for the corresponding O_2^+ reaction[73] even if allowance is made for the lower temperature prevailing in this last ex-

TABLE IV. Rate Constants for Oxygen Positive-Ion Clustering Reactions

I	A	M	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	k_r, molecule^{-1} cm^3 sec^{-1}	Ref
O^+	N_2	He	82	5.4(−29)		32
O_2^+	O_2	He	82	3.1(−29)		32
			200	2.4(−30)		73
			300	5(−31)	3.6(−14)	74
		O_2	298	2.8(−30)	2.8(−13)	20
			300	2.5(−30)	1.8(−13)	74
				1.5(−30)		162
				2.6(−30)		*a*
			307	2.4(−30)		72
	H_2	He	82	7.4(−31)		73
	N_2	He	82	1.9(−29)		73
		N_2	300	8(−31)	2(−11)	74
	CO_2	He	200	2.3(−29)		73
	N_2O	He	200	5.2(−29)		73
	SO_2	He	200	6(−29)		73
	H_2O	He	295	9(−29)		156
			300	8.5(−29)		73
				8.7(−29)		74
		Ar	295	2.0(−28)		156
			300	1.7(−28)		74
				1.2(−28)		*b*
		N_2	295	2.8(−28)		156
			300	2.5(−28)		74
		O_2	300	1.9(−28)		*c*
				2.3(−28)		74
			307	1(−28)		72
O_4^+	O_2	He	82	5(−30)		73
		O_2	300	7(−32)		*a*
	N_2	He	82	1(−29)		73
$O_2^+ \cdot N_2$	N_2	He	82	1(−29)		73
O_6^+	O_2	O_2	90	2.5(−29)		*a*

[a] J. D. Payzant, A. J. Cunningham, and P. Kebarle, *J. Chem. Phys.*, **59**, 5615 (1973). [b] R. C. Bolden and N. D. Twiddy, *J. Chem. Soc., Discuss. Faraday Soc.*, **53**, 192 (1973). [c] C. J. Howard, H. W. Rundle, and F. Kaufman, *Bull. Am. Phys. Soc.*, 16, 213 (1971).

periment. There is a similar wide discrepancy between the data for the O^-/CO_2 system.[86,88]

High-pressure studies of the formation of O_4^- in pure oxygen[89] indicate that $-\Delta H^\circ$(298 K) for the forward reaction, which will be approximately equal to $D^\circ(O_2^- - O_2)$, has a value of 56.7 kJ mol^{-1}. An SCF-MO calculation[65] yielded a value of 35.5 kJ mol^{-1}. Equilibrium studies have also been made of the clustering series involving the ions $O_2^-(H_2O)_n$,[82,90,91] $O_2^-(CH_3OH)_n$,[92] and $O_2^-(CH_3CN)_n$.[92] The thermodynamic data obtained are listed in Table VI. The results indicate that methanol is bound slightly more strongly than H_2O in the initial solvation step, but that thereafter hydration is energetically preferred; CH_3CN is bound less strongly.

3. General Comments

The flowing-afterglow method has been used[73] to investigate possible switching reactions of the type:

$$I{\cdot}A + B \rightarrow I{\cdot}B + A \qquad (19)$$

The occurrence of such a process implies that the reaction is exothermic and hence that $D^\circ(I-B) > D^\circ(I-A)$, if the reactants are at thermal energies. The results indicated that the value of $D^\circ(O_2^+-A)$ varied with A in the sequence $H_2O > SO_2 > N_2O > O_2 > N_2 > H_2$, while for $O_2^- - A$ the order was $NO > CO_2 > H_2O > O_2 > N_2O, N_2, CO$. Experimental and theoretical values of some of these bond dissociation energies are given in Table XXIII, and such experimental data as are available are in agreement with the quoted sequences.

TABLE V. Rate Constants for Oxygen Negative-Ion Clustering Reactions

I	A	M	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	k_r, molecule^{-1} cm^3 sec^{-1}	Ref
e^-	O_2	He	300	7.5(−32)		76
		N_2	300	1.1(−31)		76
			477	1.3(−31)		79
		O_2	77	<1(−30)		78
			113	7.2(−31)		80
			195	2.0(−30)		78
			200	1.5(−30)		80
			300	2.8(−30)		78
				2.1(−30)		76
				2.4(−30)		77
				2.0(−30)		79
				2.1(−30)		*a*
				5.6(−30)		*b*
				2.1(−30)		80
			370	3.1(−30)		78
		$(4N_2{:}1O_2)$	300	1.1(−31)		*a*
		H_2O	300	1.4(−29)		81
		CO_2	300	3.1(−30)		81
O^-	O_2	O_2	298	1.1(−30)		84
			300	9.0(−31)		83
				7.5(−31)		*c*
				7.8(−31)		*d*
				1.0(−30)		7
				1.2(−30)		*e*
				1.4(−30)		82
			310	9(−31)		85
	N_2	He	82	1.3(−30)		247
			200	4(−32)		73
	H_2O	O_2	300	1.0(−28)		*e*
	CO_2	He	200	2.6(−28)		73
			280	1.5(−28)		247
			300	1.5(−28)		86
		O_2	298	3.1(−28)		88
		CO_2	298	1.1(−27)		88
			300	9(−29)		86
	N_2O	N_2O	298	4.2(−29)		*f*
O_2^-	O_2	He	200	3.4(−31)		73
		O_2	298	3(−31)	7(−15)	84
			300	4(−31)	2.7(−14)	*e*
				3.5(−31)		*g*
				5.1(−31)		82
			315	3(−31)	2(−14)	*h*
	N_2	He	200	4(−32)		73
	CO	CO_2	298	<1(−30)		87
	CO_2	He	200	4.7(−29)		73
		O_2	300	2(−29)		86
		CO_2	298	1.2(−28)		87
			300	9(−30)		86
	H_2O	O_2	298	1.6(−28)		82
			300	3(−28)		*e*
$O_2^- \cdot H_2O$	H_2O	O_2	298	5.4(−28)	1.1(−14)	82
			300	4(−28)	7.1(−15)	*e*
$O_2^-(H_2O)_2$	H_2O	O_2	298	2.2(−11)^i	3.5(3)^i	82
O_3^-	N_2	N_2	300	<1.5(−31)		*j*
	H_2O	O_2	300	2.1(−28)		*e*

[a] M. N. Hirsch, P. N. Eisner, and J. A. Slevin, *Phys. Rev.*, **178**, 175 (1969). [b] D. Spence and G. J. Schultz, *Phys. Rev. A*, **5**, 724 (1972). [c] E. C. Beaty, L. M. Branscomb, and P. L. Patterson, *Bull. Am. Phys. Soc.*, **9**, 535 (1964). [d] J. H. Wealton and S. B. Woo, *Phys. Rev. Lett.*, **20**, 1137 (1968). [e] J. L. Pack and A. V. Phelps, *Bull. Am. Phys. Soc.*, 16, 214 (1971). [f] D. A. Parkes, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2103 (1972). [g] F. K. Truby, *Bull. Am. Phys. Soc.*, 16, 1341 (1971). [h] L. G. McKnight and J. M. Sawina, *Phys. Rev. A*, **4**, 1043 (1971). [i] k_f is second order and k_r first order. [j] E. E. Ferguson, *Can. J. Chem.*, **47**, 1815 (1969); products unidentified.

Theoretical investigations of the structures of $O_4^{\pm}$ have been performed using SCF-MO methods.[65] The derived $D^\circ(O_2^+-O_2)$ value of 48.8 kJ mol^{-1} is in good agreement

TABLE VI. Thermodynamic Data for the Equilibria: $O_2^-(X)_n + X \rightleftharpoons O_2^-(X)_{n+1}$

X	n	$-\Delta G°$ (298 K), kJ mol^{-1}	$-\Delta H°$ (298 K), kJ mol^{-1}	$-\Delta S°$ (298 K), J K^{-1} mol^{-1}	Ref
H_2O	0	12.5	18.4	20.1	90
	1	9.7	17.2	25.1	
	2	7.0	15.4	28.2	
CH_3OH	0	12.5	19.1	21.9	92
	1	8.1	15.5	24.8	
	2	5.2	13.5	27.9	
CH_3CN	0	11.2	16.4	17.4	92
	1	7.7	14.2	22.0	
	2	4.5	11.9	24.7	
	3	2.8	9.5	22.4	

with the experimental data given in Table III, whereas the calculated value for the negative ion, given above, is rather low. Unlike the N_4^+ species, both oxygen clusters are calculated to be nonlinear; "chair" configurations are predicted in each case. One terminal O–O bond is at an angle θ below the central O–O bond, while the other is in the same plane, at an angle θ above the central bond. The angle θ is calculated to be 67° for O_4^+ and 71° for O_4^-. The computed length of the central O–O bond is 0.203 nm for O_4^+ and 0.208 nm for O_4^-, the other bonds in each case being assumed to be equal in length to those in neutral oxygen.

VI. Clustering in Oxides of Nitrogen

A. Nitric Oxide

A great deal of work on the solvation of nitric oxide has been reported recently. Interest has derived largely from the possible role of NO^+ in the D region of the ionosphere. As it has the lowest ionization potential of any of the major neutral components of the upper atmosphere, nitric oxide should play an important part in the observed[93-95] conversion of the initially formed positive ions into hydrated proton clusters. Accordingly, most work has investigated the reactions of NO^+ with neutral NO[96-98] or with water.[99-102] The kinetic data for positive ions are listed in Table VII, which also includes results for clustering with other species.[103,104] The possible role of such clusters in the upper atmosphere has been discussed by Fehsenfeld and Ferguson.[105]

There is a clear discrepancy between the various k_f values reported for pure NO. The higher value of k_f[97,98] seems at present to be preferable, especially when the data with N_2 as third body[102] are also considered. The stationary-afterglow experiments[96] may be affected by wall processes[106] and the presence of significant amounts of non-ground-state species.

The data on the hydration of NO^+, on the other hand, display considerable consistency when results from the various laboratories are compared. The expected third-body effects are by and large displayed, with He the least efficient of the media used, though it is hard to find any a priori reason why N_2 should consistently prove more efficient as a third body than O_2, unless this is due to differences in polarizability (see section XVII). The excellent agreement found for k_f is not repeated in the reported k_r values. Many of these are obtained via observed K_p values, and the variations may reflect the problems of attaining true thermodynamic equilibrium in an ion source, as discussed in section II.B.

A number of "switching" reactions have been observed in systems involving NO^+ ions.[103] The data are insufficient to establish a sequence of bond strengths such as that obtained for O_2^+,[73] but the ion $NO^+\cdot CO_2$ has been seen to undergo switching with H_2O, NO, and NH_3, indicating that these three molecules are more strongly bound. All the rate constants were second order, with values ~10^{-9} molecule^{-1} cm^3 sec^{-1}.

The kinetic data involving the NO^- ion are given in Table VIII. Results for associative ionization of NO with a free electron,[107-109] which may be regarded as the first step of the clustering sequence, are also included. Parkes and Sugden[110] have suggested that these reported values for k_f may be too low, as a result of a competing detachment process. Only one study of the subsequent reaction giving $N_2O_2^-$ has been reported,[110] and the product ion was found to react giving NO_2^- as the ultimate product.

A feature of the data is the relative complexity of the reaction pathways. The system $NO^-/CO_2/N_2O$, for example, has at least three possible ionic products formed via third-order kinetics,[111] in addition to parallel second-order processes. The reactions are

$$NO^- + CO_2 + N_2O \rightarrow NO^-\cdot CO_2 + N_2O \quad (20)$$

$$\rightarrow CO_3^- + N_2 + NO \quad (21)$$

$$\rightarrow NO^-\cdot N_2O + CO_2 \quad (22)$$

and rate constants for eq 20 and eq 21 are given in Table VIII.

B. Nitrogen Dioxide

The clusters $NO_2^+(H_2O)$ and $NO_2^+(H_2O)_2$ have been reported in corona discharge experiments,[112] but most work has been done on the negative ion.

The kinetics of hydration of the NO_2^- ion have been studied by Puckett and Lineberger[96,113] and by Payzant et al.,[114] and the k_f and k_r values obtained are included in Table VIII for the reactions

$$NO_2^- + H_2O + M \rightleftharpoons NO_2^-(H_2O) + M \quad (23)$$

with He, Ar, NO, and O_2 as third body.

The data lead to a K_p value for eq 23 of 1.3 × 10^6 atm^{-1} at 300 K, while for the second hydration step K_p was measured as 1.62 × 10^{20}.[114]

Kebarle et al.[91,115] have also reported equilibrium data for the hydration series $NO_2^-(H_2O)_n$. The values of $-\Delta H°$(298 K) were 59.8, 53.9, and 43.5 kJ mol^{-1} for the formation of the n = 1, 2, and 3 clusters, respectively. The corresponding values of $-\Delta G°$(298 K) and $-\Delta S°$(298 K) were 33.5, 24.2, and 16.9 kJ mol^{-1} and 87.7, 99, and 88.7 J K^{-1} mol^{-1}, respectively.

C. Clustering around the NO_3^- Ion

The first hydration step of NO_3^- has been studied by Payzant et al.[114] using O_2 as third body. The kinetic data are included in Table VIII. Values of $-\Delta H°$, $-\Delta G°$, and $-\Delta S°$, all at 298 K, have been measured[115] and are respectively, in the usual units, 51.8, 27.8, and 79.9. Ionospheric studies[116] indicate that ions of the series $NO_3^-(H_2O)_n$, with n in the range 0–5, are the dominant negative ions in the region below 90 km altitude.

The only other reaction to have been studied is the solvation with HCl[117]:

$$NO_3^- + HCl + Ar \rightarrow NO_3^-\cdot HCl + Ar \quad (24)$$

The kinetic data are quoted in Table VIII.

VII. Clustering in Oxides of Carbon

The data from a single reported study of positive-ion clustering in pure CO[118] give k_f and k_r values of 1.43(−28) and 2.1(−12) at 340 K, with K_p having a value of 2.2 atm^{-1} at this temperature. Values of −117 and −20.6 kJ mol^{-1} were also reported for $\Delta H°$(340 K) and $\Delta G°$(340 K).

TABLE VII. Rate Constants for Nitric Oxide Positive-Ion Clustering Reactions

I	A	M	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	k_r, molecule^{-1} cm^3 sec^{-1}	Ref
NO^+	NO	NO	293	5(−30)	5(−16)	96
			300	3.3(−29)		97
				3(−29)		98
		N_2	300	8.7(−30)		102
	N_2	He	200	<5(−33)		103
		N_2	300	3.5(−31)		104
				2.4(−31)		*a*
	CO	CO	300	1.9(−30)		*a*
	O_2	He	200	<6(−34)		103
		Ar	200	<2(−32)		103
		O_2	300	<4(−32)		*a*
	CO_2	He	197	1.0(−29)		103
			235	7.2(−30)		103
			290	4(−30)		103
		Ar	196	3.1(−29)		103
			214	2.4(−29)		103
		N_2	200	2.5(−29)		103
		CO_2	300	2.4(−29)		*a*
	H_2O	NO	300	1.5(−28)		96
				1.6(−28)		99
		NO/H_2O^b	293	1.3(−28)		171
		He	300	3.6(−29)		100
		Ar	300	7.8(−29)		100
				1.6(−28)		100
				1.4(−28)		101
				1.8(−28)		102
		O_2	300	8.6(−29)		100
	N_2O	N_2O	300	2.5(−29)		*a*
	SO_2	M^c	300	2.5(−28)		*a*
	CH_3OH	M	300	8.0(−28)		*d*
$NO^+(H_2O)$	H_2O	NO	300	1.1(−27)	1.4(−14)	99
		NO/H_2O^b	293	1.2(−27)	<2(−13)	171
		He	300	3(−28)	<1(−13)	100
		Ar	300	8(−28)	<1(−13)	100
		N_2	300	1.0(−27)	<1(−13)	100
				1.2(−27)	1.7(−14)	101
				1(−27)	5(−14)	102
		O_2	300	8(−28)	1.0(−14)	100
$NO^+(CH_3OH)$	CH_3OH	M	300	1.9(−27)		*d*
$NO^+(H_2O)_2$	H_2O	NO	300	1.0(−27)	1.9(−12)	99
		NO/H_2O^b	293	3.6(−27)	<4(−12)	171
		He	300	4(−28)	2.7(−13)	100
		Ar	300	1.5(−27)	1(−12)	100
		N_2	300	2.0(−27)	1.3(−12)	100
				1.4(−27)	1.4(−12)	101
				1(−27)	3.4(−12)	102
		O_2	300	9(−28)	8(−13)	100
$NO^+(CH_3OH)_2$	CH_3OH	M	300	2(−27)		*d*

[a] J. A. Vanderhoff and J. M. Heimerl, *Bull. Am. Phys. Soc.*, **18**, 804 (1973). [b] NO/H_2O present in 1:1 ratio. [c] Identity of M not specified. [d] D. L. Turner and L. I. Bone, *J. Phys. Chem.*, **78**, 501 (1974); M was a mixture of varying proportions of NO and CH_3OH.

Third-order processes have also been detected in partly ionized samples of carbon suboxide[119] and involve the ion $C_5O_2^+$. A variety of products were observed, none of which, however, can be regarded as the result of clustering:

$$C_5O_2^+ + 2C_3O_2 \rightarrow C_6O_2^+ + 2CO + C_3O_2 \quad (25)$$

$$\rightarrow C_7O_2^+ + 4CO \quad (26)$$

$$\rightarrow C_8O_2^+ + 2CO + CO_2 \quad (27)$$

$$\rightarrow C_9O_2^+ + 2CO_2 \quad (28)$$

Studies on carbon dioxide in the same laboratory[120] have shown that clustering occurs, producing $C_2O_4^+$. However, the reaction is fourth order, with a rate constant, in pure CO_2, of 1(−43) molecule^{-3} cm^9 sec^{-1}. The authors attempt to explain this observation on the basis of a Langevin-type theory of ionic mobility. The same reaction has been observed[59,121] to "saturate" and show second-order kinetics at 277 K. An example of fourth-order clustering in benzene will be discussed in section XIV.F.

VIII. Solvation of Metal Ions

A. Alkali Metals

1. Hydration

There have been a number of studies by Kebarle and coworkers[91,122,123] of the thermodynamic properties of the equilibria

$$X^+(H_2O)_n + H_2O \rightleftharpoons X^+(H_2O)_{n+1} \quad (29)$$

TABLE VIII. Rate Constants for Negative-Ion Clustering Reactions in Oxides of Nitrogen

I	A	M	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	k_r, molecule^{-1} cm^3 sec^{-1}	Ref
e^-	NO	NO	298	2.2(−31)[a]		107
			300	1.3(−31)		108
				6.8(−32)		109
				1−2(−31)		110
NO^-	NO	NO	293	7.6(−30)[b]		110
	N_2O	Ar	193	7.1(−30)		*e*
		N_2O	300	8.5(−30)		*f*
	CO_2	Ar	193	3.6(−29)		*e*
		N_2O	300	1.5(−28)[c]		111
				1.0(−27)[d]		111
		CO_2	300	7.5(−29)		111
NO_2^-	H_2O	He	300	2.9(−29)	5.6(−16)	114
		Ar	300	6.0(−29)	1.1(−15)	114
		NO	300	1.2(−28)		96
				1.3(−28)		113
		O_2	300	8.4(−29)	1.6(−15)	114
$NO_2^-(H_2O)$	H_2O	O_2	300	3.8(−29)	5.8(−14)	114
NO_3^-	H_2O	O_2	300	7.5(−29)	1.4(−14)	114
	HCl	Ar	289	5(−28)		117

[a] k_f increased steadily above 10 Torr. [b] Total k_f for formation of NO_2^- and $N_2O_2^-$. [c] Rate constant for eq 20. [d] Rate constant for eq 21. [e] R. Marx, G. Mauclaire, F. C. Fehsenfeld, D. B. Dunkin, and E. E. Ferguson, *J. Chem. Phys.*, **58**, 3267 (1973). [f] A parallel second-order reaction giving $NO_2^- + N_2$ had a k_f value of 2.8(−14): D. A. Parkes, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2103 (1972).

where X is an alkali metal, and n has values of from 0 to 5. The usual van't Hoff treatment gave the thermodynamic data listed in Table IX. The smoothness of the general trends of these values gives no indication of the starting of a "second shell" of water molecules around the central ion. Such a shell would be expected to be accompanied by a discontinuity in the values of the thermodynamic properties. However, no ions containing more than six water molecules were observed, and it may be that this corresponded to the completion of the inner shell: certainly one would not expect alkali metals to exhibit coordination numbers of greater than 6. The magnitudes of $-\Delta G^\circ$ and $-\Delta H^\circ$ for a particular n value correlate fairly well with the ionization potentials of the alkali metals, which are in turn inversely proportional to the ionic radii.

Some calculations of the expected energies of these hydrated alkali metal ions have been carried out.[91,123,124] As the methods are generally applicable, they will be briefly discussed here.

If E_n is defined as the total energy difference between the cluster ion and the system in which the metal ion and the ligands are at infinite separation, then we have

$$E_n = E_{IPD} + E_{IID} + E_D + R_{DD} + R_E \qquad (30)$$

where E_{IPD} and E_{IID} represent ion-permanent and ion-induced dipole attraction energies, respectively, calculated using a point charge model.[125,126] E_D is the attraction energy due to dispersion forces calculated by the method of Muirhead-Gould and Laidler.[127] R_{DD} represents the permanent dipole repulsion between adjacent solvated water molecules, together with the various permanent-induced and induced-induced dipole repulsions. Finally, R_E is the electronic repulsion between the various molecules, calculated using a distance term and a proportionality constant obtained indirectly from rare gas data.[128] The appropriate Stokes radii[129] were used for the various central ions.

In practice, it was necessary to obtain R_E empirically from the experimental value of $-\Delta H^\circ$ with $n = 0$. The relative E_n values were then in good agreement with the experimental data. This agreement lends support to the supposed structure used in the calculations, in which the water molecules are arranged with their lone pairs toward X^+, the center of which lies on the extrapolated bisector of the H–O–H bond angle. These results are important because they show that a theory based on classical electrostatics can be quite successful in interpreting clustering data. Recent calculations[130,131] have used more sophisticated methods to evaluate the individual terms in eq 30 and give $-\Delta H^\circ$ values which are in good agreement with the experimental data, with respect to both magnitude and general trend.

Kinetic data on this hydration system are relatively sparse. Values of k_f were obtained in a drift tube[132] for the initial hydration step

$$X^+ + H_2O + M \rightarrow X^+{\cdot}H_2O + M \qquad (31)$$

where X was Na or K and M was He or H_2O. These data are included in Table X, together with data for the corresponding reaction for Cs^+.[133]

2. Other Solvation Data

Clustering of Li^+, Na^+, K^+, and Rb^+ with hydrogen and neon have all been reported,[134] although no quantitative information was obtained. Strong clustering was observed only for ions with six or fewer solvent molecules. Larger clusters were present in very low intensity, suggesting the possibility of a second shell starting at this point.

TABLE IX. Thermodynamic Properties of the Equilibria: $X^+(H_2O)_n + H_2O \rightleftharpoons X^+(H_2O)_{n+1}$

		n							
X		0	1	2	3	4	5	IP(X)[a]	Ref
Li^+	$-\Delta G^\circ$[b]	107	79	55.6	31.4	18.8	10.4	520	123
	$-\Delta H^\circ$[b]	(142)[d]	108	86.6	68.6	58.2	50.6		
	$-\Delta S^\circ$[c]	117	97	104	125	132	136		
Na^+	$-\Delta G^\circ$	73.6	55.2	38.9	26.3	16.3	11.7	497	123
	$-\Delta H^\circ$	100	82.8	66.1	57.7	51.5	44.8		
	$-\Delta S^\circ$	88.6	92.6	91.0	106	118	111		
K^+	$-\Delta G^\circ$	47.6	37.2	26.4	18.4	13.4	9.6	418	122
	$-\Delta H^\circ$	74.9	67.4	55.2	49.4	44.8	41.8		
	$-\Delta S^\circ$	91.3	102	98	105	107	108		
Rb^+	$-\Delta G^\circ$	40.1	29.3	20.9	15.9	11.7		403	123
	$-\Delta H^\circ$	66.5	56.9	51.1	46.9	43.9			
	$-\Delta S^\circ$	88.9	92.6	101	104	108			
Cs^+	$-\Delta G^\circ$	33.0	24.7	17.6	12.6			375	123
	$-\Delta H^\circ$	57.3	52.3	46.9	44.3				
	$-\Delta S^\circ$	81.6	92.5	97.0	105				

[a] Taken from ref 68; expressed in kJ mol^{-1}. [b] In kJ mol^{-1} at 298 K. [c] In J K^{-1} mol^{-1} at 298 K. [d] Obtained by extrapolation.

TABLE X. Rate Constants for Metal Solvation Reactions

I	A	M	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	k_r, molecule^{-1} cm^3 sec^{-1}	Ref
Li^+	Ar	Ar	319	1.8(−31)	2.0–3.2(−13)[a]	137
	N_2	He	296	8.0(−31)		141
		N_2	300	2(−30)		135
	CO_2	He	296	1.6(−29)		141
	SO_2	He	296	1.8(−28)		141
	NH_3	He	296	2.1(−28)		141
	CH_4	He	296	5.1(−30)		141
	CH_3F	He	296	8.4(−28)		141
	CH_3Cl	He	296	6.7(−28)		141
	CH_3Br	He	296	8.0(−28)		141
	CF_4	He	296	3.5(−29)		141
	CF_3H	He	296	5.9(−28)		141
	CF_3Br	He	296	8.2(−28)		141
	CF_2Cl_2	He	296	1.8(−27)		141
	$CHFCl_2$	He	296	3.2(−27)		141
	CHF_2Cl	He	296	1.4(−27)		141
	C_2H_4	He	296	1.9(−28)		141
	C_2H_6	He	296	2.3(−28)		141
	C_2H_3F	He	296	3.5(−27)		141
	C_2H_3Cl	He	296	~5(−27)		141
	C_2H_3Br	He	296	~8.4(−27)		141
	$(1,1)C_2H_2F_2$	He	296	2.5(−27)[b]		141
		Ar	296	4.0(−27)[b]		141
Na^+	O_2	O_2	310	5(−32)	8(−13)	140
	H_2O	He	300	4.7(−30)		132
		H_2O	300	1.0(−28)		132
	CO_2	CO_2	310	2(−29)	1(−14)[c]	140
$Na^+\cdot CO_2$	CO_2	CO_2	310	5(−29)	5(−13)[c]	140
K^+	O_2	Ar	300	<2(−31)		*d*
	H_2O	He	300	2.6(−30)		132
		H_2O	300	4.5(−29)		132
	CO_2	CO_2	310	4(−30)	2.5(−13)[e]	139
Cs^+	H_2O	N_2	300	2(−29)		133
Mg^+	O_2	Ar	300	2.5(−30)		143
Mg^{2+}	Ar	He	296	3.1(−30)		144
	N_2	He	296	1.9(−29)		144
	CO	He	296	4.7(−29)		144
	CO_2	He	296	3.1(−27)		144
Ca^+	O_2	He	296	~2(−30)		144
		Ar	300	6.6(−30)		143
	CO	He	296	2.7(−30)		144
Ca^{2+}	Ar	He	296	~1(−30)		144
	N_2	He	296	6.2(−30)		144
	O_2	He	296	8.9(−30)		144
	H_2O	He	296	~5(−28)		144
	CO	He	296	2.0(−29)		144
	CO_2	He	296	1.1(−27)		144
	N_2O	He	296	2.5(−27)		144
Ba^+	CO_2	He	296	2.8(−30)		144
Ba^{2+}	N_2	He	296	~1.6(−30)		144
	O_2	He	296	3(−30)		144
	H_2O	He	296	1.1(−28)		144
	CO	He	296	~5(−30)		144
	CO_2	He	296	1.1(−28)		144
	N_2O	He	296	~1.9(−28)		144
Fe^+	O_2	Ar	300	1.0(−30)		143
Hg^+	Hg	He	400	1.7(−31)		145
		Hg	400	1(−31)		145

[a] For E/N values of 9 to 24(−17) V cm^2. [b] Mixed order at higher pressures. [c] E/N value 12(−17) V cm^2. [d] E. E. Ferguson and F. C. Fehsenfeld, *J. Geophys. Res.*, 73, 6215 (1968). [e] For E/N values of 6 to 21(−17) V cm^2.

The clustering of Li^+ with the rare gases, O_2, N_2, NO, and CO_2 has been observed in drift tubes;[135–138] solvation of Na^+ and K^+ with CO_2 has also been reported.[139,140]

The bond strengths of the species containing an alkali metal ion and a single rare gas molecule have recently been measured.[136] Values of <6.8, 12.6, and 24.2 kJ mol^{-1} were obtained for $D°(Li^+–X)$ in the cases X = He, Ne, and Ar, respectively. Similarly, $D°(Na^+–X)$ was <10.6, 16.4, and 18.4, for X = Ne, Ar, and Kr; $D°(K^+–X)$ was 10.6 and 11.6 for X = Ar and Kr, and $D°(Cs^+–Ar)$ was 8.7 kJ mol^{-1}.

An extensive study of clustering around the Li^+ ion has been carried out by Spears and Ferguson.[141] Their data, to-

TABLE XI. Thermodynamic Data[a] for the Equilibria: $Pb^+(H_2O)_n + H_2O \rightleftharpoons Pb^+(H_2O)_{n+1}$

n	$-\Delta G°$(298 K), kJ mol^{-1}	$-\Delta H°$, kJ mol^{-1}	$-\Delta S°$, J K^{-1} mol^{-1}
0	48.9	93.6	149
1	39.0	70.5	106
2	25.9	51.0	84.5
3	19.3	45.2	87.0
4	13.8	41.8	93.2
5	10.5	40.2	98.8

[a] From ref 146.

gether with rate constants observed in the work discussed above, are listed in Table X. In addition to the tabulated data, Spears and Ferguson also reported that the clusterings of Li^+ with $H_2C_3H_2$, H_3CC_2H, and C_3H_8 were "mixed" second- and third-order processes. Clustering with c-C_4F_8, (1,2)$C_2F_4Cl_2$, C_2F_6, C_4H_{10}, (1,1)$C_2H_4F_2$, and C_2F_3Cl were all observed to be second order at 0.25 Torr, although the observed rate constants differed when He was replaced by Ar as "third body". Presumably the size of these solvating species results in a longer lived activated complex.

The Cs^+ ion did not undergo any detectable reaction with N_2, O_2, or Ar at 310 K,[132] indicating a k_f value in each case of <3(−34).

B. Other Metal Ions

The role of metallic ions in the upper atmosphere has recently been reviewed,[142] and most of the reported data have been obtained with this topic in mind. Flowing-afterglow methods have yielded most of the data for alkaline earths, both singly[143,144] and doubly[144] charged and for the other ions[145] listed in Table X. In three cases, it is possible to compare k_f values and, as might be expected, the doubly charged ions react more rapidly with particular solvent molecules than do the corresponding monovalent ions.

The hydration of the monovalent lead ion has been studied[146] in the temperature range 275–420 K. The data are given in Table XI and show the familiar smooth trend with increasing cluster size. The same is true of the $D°$ values reported[147] for $Bi^+(H_2O)_n$. For values of n from 1 to 6 respectively, $D°$ was measured as 95.2, 73.8, 58.5, 50.1, 43.8, and 40.5 kJ mol^{-1}. The $Bi^+(NH_3)_n$ series had $D°$ values of 148, 96.8, and 56.0 kJ mol^{-1}, for values of n in the range 1 to 3. The high strength of bonding for the first two NH_3 molecules could not be explained on electrostatic grounds alone.

Free energy measurements have been reported[144] for a number of equilibria of the type

$$Ca^{2+}(X)_n + X + He \rightleftharpoons Ca^{2+}(X)_{n+1} + He \qquad (32)$$

Values of −32 and −19 kJ mol^{-1} were obtained for $\Delta G°$(298 K) for the case X = O_2 and for values of n of 1 and 5, respectively. Values of −19 and −34 were found for n = 6 and X = N_2 and CO_2, respectively. For the equilibrium

$$Ca^{2+}\cdot CaCO_3(CO_2)_4 + CO_2 + He \rightleftharpoons Ca^{2+}\cdot CaCO_3(CO_2)_5 + He \qquad (33)$$

the free energy change was −25 kJ mol^{-1}.

TABLE XII. Thermodynamic Data for the Halide Equilibria: $X^-(H_2O)_n + H_2O \rightleftharpoons X^-(H_2O)_{n+1}$ (from Arshadi et al.[148])

		n				
X		0	1	2	3	4
F	$-\Delta G°$[a]	75.5	46.0	31.8	23.0	29.7
	$-\Delta H°$[a]	97.5	69.5	57.3	56.5	55.2
	$-\Delta S°$[b]	72.8	78.2	85.4	112[c]	86.5[c]
Cl	$-\Delta G°$	34.3	27.2	18.8	14.2	
	$-\Delta H°$	54.8	53.1	49.0	46.4	
	$-\Delta S°$	69.0	87.0	97.1	108	
Br	$-\Delta G°$	29.3	23.0	17.1	12.1	
	$-\Delta H°$	52.7	51.5	48.1	45.6	
	$-\Delta S°$	77.0	95.8	104	112	
I	$-\Delta G°$	22.6	17.6	12.9		
	$-\Delta H°$	42.7	41.0	39.3		
	$-\Delta S°$	68.2	79.5	89.1		

[a] In kJ mol^{-1} at 298 K. [b] In J K^{-1} mol^{-1} at 298 K. [c] These quantities have been corrected to allow for apparent typographical errors in ref 148.

TABLE XIII. Thermodynamic Data[a] for the Equilibria: $X^-(CH_3CN)_n + CH_3CN \rightleftharpoons X^-(CH_3CN)_{n+1}$

		n				
X		0	1	2	3	4
F	$-\Delta G°$[b]	50.2	35.5	26.8	18.8	13.0
	$-\Delta H°$[b]	66.8	53.9	48.8	43.5	22.2
	$-\Delta S°$[c]	56.0	61.9	74.8	81.9	30.9
Cl	$-\Delta G°$	38.5	27.6	19.2	12.5	
	$-\Delta H°$	56.0	51.0	44.3	25.9	
	$-\Delta S°$	59.8	79.0	84.2	45.2	
Br	$-\Delta G°$	33.5	24.3	15.1	9.2	
	$-\Delta H°$	53.9	49.3	41.8	23.0	
	$-\Delta S°$	69.0	85.3	90.6	45.5	
I	$-\Delta G°$	26.8	18.0	11.3		
	$-\Delta H°$	49.7	43.9	38.9		
	$-\Delta S°$	76.0	87.0	92.5		

[a] From ref 152. [b] In kJ mol^{-1} at 298 K. [c] In J K^{-1} mol^{-1} at 298 K.

IX. Clustering around Halide Ions

Thermodynamic data for the equilibria

$$X^-(H_2O)_n + H_2O \rightleftharpoons X^-(H_2O)_{n+1} \qquad (34)$$

have been reported by Kebarle and coworkers[91,125,148,149] for values of n of up to 4 in the cases X = F, Cl, Br, and I. The data are listed in Table XII. The observed trends are similar to those already discussed for the alkali metal ions[150] and calculated $-\Delta H°$ values[130,131] are in good agreement with the data.

The only reported kinetic studies of this system, for the case where X = Cl and n = 0, have led to k_f values of 3.4(−29) at 293 K (M = NO)[96,113] and 1(−29) at 308 K, with M = O_2.[151] The reactions of F^- with He as third body have been studied at 300 K;[141] k_f values of 5.5(−28), 1.3(−29), and 2.9(−29) were observed for SO_2, NH_3, and CO_2 "solvents", respectively. The $F^-(SO_2)_2$ ion was also observed.

The equilibria

$$X^-(CH_3CN)_n + CH_3CN \rightleftharpoons X^-(CH_3CN)_{n+1} \qquad (35)$$

have also been studied.[152] Table XIII gives the reported data, and comparison of $-\Delta H°$ values between Tables XII and XIII indicates a rather complex variation of the solvation "preferences" of the halide ions at different stages of solvation. Only for F^-, where hydration is always energetically preferred, is the situation clear-cut. For the other ions, a slight initial tendency to prefer solvation with CH_3CN changes to a distinct preference for hydration at $n \geq 2$.

The effect of acidity of solvent on the thermodynamics of the equilibrium

$$Cl^- + RH \rightleftharpoons Cl^-\cdot RH \qquad (36)$$

TABLE XIV. Effect[a] of Acidity on the Equilibria: $Cl^-(RH)_n + RH \rightleftharpoons Cl^-(RH)_{n+1}$

RH	n	$-\Delta G°$ (298 K), kJ mol^{-1}	$-\Delta H°$ (298 K), kJ mol^{-1}	$-\Delta S°$ (298 K), J K^{-1} mol^{-1}
H_2O	0	34.3	54.8	68.8
	1	26.8	50.2	79.0
CH_3OH	0	41.0	59.0	61.9
	1	30.1	54.3	81.5
$(CH_3)_3COH$	0	46.5	59.3	43.1
	1	32.2	56.0	80.3
CH_3Cl	0	45.2	63.5	61.9
C_6H_5OH	0	61.9	81.0	64.8
	1	47.2	77.3	102
CH_3COOH	0	66.0	90.3	80.5
HCOOH	0	97.8	155	166
C_6H_6	0	~14.2	~23	~30.5
$C_6H_5NH_2$	0	46.0	72.3	76.9
	1	33.9	62.7	97.4

[a] From ref 2 and 148.

has been investigated.[149] The data, which are given in Table XIV, indicate a distinct correlation between acidity and the magnitudes of $-\Delta H°$ and $-\Delta G°$.

X. Solvated Proton Clusters

The ions H_2O^+ and H_3O^+ appear as minor components of every conventional low-pressure mass spectrum. When higher gas pressures are used, it is found that larger ions representing more highly solvated protons are also present. As will be shown in section X.C, these can be most appropriately represented by the general formula $H_{2n+1}O_n^+$. This is meant to imply that no single proton can be identified as the original charge-bearing species; instead the charge is thought to be more evenly spread around the molecule.

Such clusters have been observed to occur among the ions produced in flames,[153] gas discharges,[154] field emission sources,[13,155] corona discharges,[112] stationary afterglows,[99] flowing afterglows,[156] α-particle ion sources,[16] and pulsed-beam ion sources,[60] among others. A number of these early studies measured the relative ion intensities for the various species at a single temperature either in the pure water system[16,157] or for the competitive solvation of water and methanol.[17] The latter work indicated an approximately equal preference for take-up of these solvents at low solvation numbers. Solvation with acetone and formic acid was also observed.[157]

It had been conclusively established by data from rocket-borne mass spectrometers[93-95] that hydrated proton clusters were the dominant positive ion species in the D region of the ionosphere, at altitudes of between 50 and 80 km. This observation, together with the obvious importance of clustering in solution chemistry, has been responsible for the large body of work on water clusters which has recently been reported.

A. Thermodynamics

The equilibria arising in the stepwise hydration of a proton may be represented by the equation

$$H_{2n+1}O_n^+ + H_2O \rightleftharpoons H_{2n+3}O_{n+1}^+ \quad (37)$$

The system has been studied by high-pressure mass spectrometry using α-particle and electron bombardment ion sources.[125,158] Data have been reported[24] for n values of from 1 to 7, over a temperature range of 288–873 K and a pressure range of 0.1–6 Torr. The thermodynamic information obtained via van't Hoff plots is summarized in Table XV, which also includes values reported subsequently from several different instruments.

TABLE XV. Thermodynamic Data for the Equilibria: $H_{2n+1}O_n^+ + H_2O \rightleftharpoons H_{2n+3}O_{n+1}^+$

n	Third body	$-\Delta G°$ (298 K), kJ mol^{-1}	$-\Delta H°$ (298 K), kJ mol^{-1}	$-\Delta S°$ (298 K), J K^{-1} mol^{-1}	Ref
1	H_2O	105	151	154	24
	D_2O[a]		135		159
	CH_4	32.2	29.3	−4.2	25
	CH_4	102	132	102	21
	C_3H_8	46.8	68	72	164
	C_3H_8	48.9	69	68	165
2	H_2O	56.9	93.3	121	24
	H_2O	41.8	83.6	130	166
	D_2O[a]		97		159
	CH_4	38.9	54.4	58.5	25
	CH_4	54.3	81.4	91.0	21
	C_3H_8	40.6	61.9	70.6	164
3	H_2O	35.6	71.1	118	24
	H_2O	34.3	67.7	112	166
	D_2O[a]		71		159
	CH_4	35.1	70.2	117	25
	CH_4	38.8	72.9	115	21
	C_3H_8	35.9	73.5	125	164
4	H_2O	23.0	64.0	137	24
	H_2O	21.8	61.8	133	166
	D_2O[a]		67		159
	CH_4	20.1	53.8	117	25
5	H_2O	16.3	54.4	127	24
	CH_4	14.2	35.5	71	25
6	H_2O	11.7	49.0	124	24
7	H_2O	9.2	43.1	127	24

[a] Results for fully deuterated clusters.

A study of the data indicates substantial agreement between the $\Delta H°$ values of Kebarle et al.[24] and De Paz et al.,[159] reflecting the similarities in the equilibrium distributions observed. Subsequent kinetic studies by Good et al.,[60,72] Cunningham et al.,[21] and Young et al.[160-162] are also in fair agreement with these equilibrium data. Despite this, there has been some discussion as to whether true thermodynamic equilibrium is achieved in practice. Friedman[23,159] has reported that a significant fraction of the clusters appeared to have greater than thermal energy, while Kebarle[22] and Field[25] have argued that this is merely a reflection of the expected Boltzmann energy distribution.

Nevertheless, Friedman is undoubtedly justified in warning of the possibility of spurious equilibria being observed. Data reported by Beggs and Field[25] for the methane–water system in the range 273–520 K have yielded K_p values for the equilibrium

$$H_3O^+ + H_2O \rightleftharpoons H_5O_2^+ \quad (38)$$

which are no less than ten orders of magnitude different from those of Kebarle.[24] It seems quite inconceivable that the data of Kebarle's and Friedman's groups, obtained in a total of five different instruments, could be in error by this amount, and one can only conclude that, for this stage of the hydration process, true equilibrium was not achieved in Beggs and Field's apparatus. It is noteworthy that their data,[25] as shown in Table XV, do not display the smooth decrease in $-\Delta G°$ and $-\Delta H°$ values which have otherwise been observed in this and all other clustering systems. Subsequent work in Field's laboratory on substantially the same instrument[163-165] has yielded K_p values which, though three orders of magnitude larger than the earliest result,[25] are still vastly different from the results in the other laboratories. In the C_3H_8/H_2O

TABLE XVI. Thermodynamic Data[a] for the Equilibria: $H^+(X)_n + X \rightleftharpoons H^+(X)_{n+1}$

X	n	$-\Delta G^\circ$ (298 K), kJ mol^{-1}	$-\Delta H^\circ$ (298 K), kJ mol^{-1}	$-\Delta S^\circ$ (298 K), J K^{-1} mol^{-1}
CH_3OH	1	24.0	33.1	30.5
	2	12.9	21.3	28.2
	3	7.5	16.1	28.9
	4	4.9	13.5	28.7
	5	3.2	12.5	31.1
	6	2.1	11.9	32.9
	7	1.4	12.0	35.7
CH_3OCH_3	1	21.9	30.7	29.6
	2	1.9	10.1	27.6

[a] From ref 169.

system,[164] however, the trends in $-\Delta G^\circ$ are more in accord with expectation.

For larger clusters, Field's earliest data[166] have been superseded by results for both the CH_4/H_2O[25] and C_3H_8/H_2O[164] systems which are in substantial agreement with those of Kebarle[24] for $n > 2$. It seems likely, then, that Field's data correspond to a state of thermal equilibrium for the larger clusters only. Possible reasons for an observed discrimination in favor of smaller clusters are (a) insufficient ion residence time (the ions are sampled before equilibrium is attained); (b) nonhomogeneity within the ion source, especially likely near the walls; (c) the breakdown of the larger clusters under the influence of the electric fields used for ion extraction; and (d) insufficient neutral gas pressure inside the ion source, causing collisional deactivation of the product clusters to be slow. In addition, Futrell (comment appended to ref 163) has pointed out that the proton transfer between H_3O^+ and C_3H_6, giving $C_3H_7^+$, is exothermic. It is therefore difficult to see how H_3O^+ could be formed in Field's C_3H_8/H_2O system unless excess energy was present in the reactant ions.

Further information comes from two recent theoretical determinations of $D^\circ(H_3O^+–H_2O)$. The reported values of 134.5[167] and 146.5[168] kJ mol^{-1} are in agreement with the data of Kebarle and Friedman.

This topic has been discussed at length because clearly the validity of all the thermodynamic data reported in this article depends upon the extent to which true thermal equilibrium is attained in the ion sources employed. In practice this can only be decided by the internal and external consistency of the data produced.

The smooth decrease in $-\Delta H^\circ$, observed by both Kebarle and Friedman, leads to the conclusion that there is no point at which a distinct "second shell" of water molecules begins. On the other hand, one cannot envisage up to eight waters being grouped around a single proton. The conclusion is, therefore, that the structures of the clusters are not of the spherical shell type; see section X.C.

The thermodynamics of proton solvation with organic molecules has been the subject of a recent investigation.[169] Equilibrium data for CH_3OH and CH_3OCH_3 are given in Table XVI. The sharp transition between the first and second solvation steps for CH_3OCH_3 is thought to be a result of the blocking of further hydrogen bonding by the surrounding methyl groups in the reactant ion $(CH_3)_2O{\cdot}H^+{\cdot}O(CH_3)_2$. Other data involving the solvation of a proton by organic molecules will be discussed in section XIV.

B. Kinetics

The first reported investigation of the kinetics of the reaction sequence

$$H_{2n+1}O_n^+ + H_2O + M \rightarrow H_{2n+3}O_{n+1}^+ + M \qquad (39)$$

employed the pulsed-beam technique discussed in section II.B, using N_2[60] or O_2[72] as third body. The mechanisms elucidated have been confirmed by later work.[74,156]

TABLE XVII. Kinetics of Production of Hydrated Proton Clusters in Moist Air

Eq no.	Reaction	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	Ref
(40)	$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$	298	8.5(−29)	58
			8(−29)	8
		300	8(−29)	60
(41)	$N_4^+ + H_2O \rightarrow H_2O^+ + 2N_2$	300	1.9(−9)[a]	60
(42)	$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	300	1.8(−9)[a]	60
		373	1.7(−9)[a]	170
(16)	$O_2^+ + 2O_2 \rightleftharpoons O_4^+ + O_2$	300	2.5(−30)	74
			1.5(−30)	162
		307	2.4(−30)	72
(43)	$O_2^+ + H_2O + O_2 \rightarrow O_2^+{\cdot}H_2O + O_2$	300	2.3(−28)	74
			2.9(−28)	162
		307	1(−28)	72
(44)	$O_4^+ + H_2O \rightarrow O_2^+{\cdot}H_2O + O_2$	295	2.2(−9)[a]	156
		300	1.5(−9)[a]	74
		307	1.3(−9)[a]	72
(45)	$O_2^+{\cdot}H_2O + H_2O + O_2 \rightarrow O_2^+(H_2O)_2 + O_2$	307	1.3(−27)	72
(46)[b]	$O_2^+{\cdot}H_2O + H_2O \rightarrow H_3O^+{\cdot}OH + O_2$	295	1.9(−9)[a]	156
		300	1.0(−9)[a]	74
		307	0.9(−9)[a]	72
(47)[b]	$O_2^+{\cdot}H_2O + H_2O \rightarrow H_3O^+ + OH + O_2$	295	⩽3(−10)[a]	156
		300	2(−10)[a]	74
		307	3(−10)[a]	72
(48)	$O_2^+(H_2O)_2 + H_2O \rightarrow H_5O_2^+{\cdot}OH + O_2$ $\rightarrow H_5O_2^+ + OH + O_2$	307	6.3(−11)[a]	72
(49)	$H_3O^+{\cdot}OH + H_2O \rightarrow H_5O_2^+ + OH$	295	3(−9)[a]	156
		300	1.4(−9)[a]	74
			1(−9)[a]	162
		307	⩾1(−9)[a]	72

[a] Second-order rate constants; in units of molecule^{-1} cm^3 sec^{-1}. [b] Reference 162 gives a value of 1(−9) for $k_{46} + k_{47}$.

TABLE XVIII. Kinetic Data for Proton Hydration

I	A	M	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	k_r, molecule^{-1} cm^3 sec^{-1}	Ref
H_3O^+	H_2O	He	300	1.2(−27)		74
				7.2(−28)		*a*
		Ar	337	6(−28)	<5(−13)	160
		N_2	300	3.4(−27)	7(−26)	60
		M	300	7(−28)		*b*
		H_2O	300	1(−27)		*c*
				1.1(−27)		*d*
		CH_4	398	1.3(−27)	3.2(−20)	21
			496	4.6(−28)	2.0(−17)	21
			672	1.7(−28)	2.8(−14)	21
			805	7.2(−29)	3.9(−13)	21
$H_5O_2^+$	H_2O	Ar	337	6(−28)	1(−13)	160
		N_2	300	2.3(−27)	7(−18)	60
		O_2	307	2(−27)	6.1(−18)	72
			310	1.7(−27)		162
		CH_4	398	9.8(−28)	1.9(−14)	21
			496	2.2(−28)	5.4(−13)	21
$H_7O_3^+$	H_2O	Ar	337	2(−28)	3(−14)	160
		N_2	300	2.4(−27)	4(−14)	60
		O_2	307	2(−27)	4(−14)	72
			310	1(−27)		162
		CH_4	398	4.2(−28)	2.3(−12)	21
$H_9O_4^+$	H_2O	O_2	307	9(−28)	6(−12)	60
			310	2(−29)		162

[a] R. C. Bolden and N. D. Twiddy, *J. Chem. Soc., Faraday Discuss.*, **53**, 192 (1973). [b] $H_2/O_2/N_2$ in ratio 4:1:4 made up the third body: A. N. Hayhurst and N. R. Telford, *Proc. R. Soc. London, Ser. A*, **322**, 483 (1971). [c] J. A. Burt, Ph.D. Thesis, York University, Toronto, 1968; quoted in footnote *b*. [d] J. F. Paulson, 1970; private communication quoted in footnote *b*.

The production of clusters from an N_2^+ precursor occurs in a relatively straightforward way. Table XVII lists the reactions involved, up to the point at which the first water cluster, in this case H_3O^+, is formed. The initial association of N_2^+ to give N_4^+ was discussed above; the product ion then undergoes dissociative charge transfer, leading rapidly to H_2O^+. The rate constant observed for the subsequent formation of H_3O^+ was in good agreement with earlier data.[170] The rest of the reaction mechanism, together with the measured rate constant values, is listed in Table XVIII. Equilibrium was observed for delay times of greater than 600 μsec, for the experimental conditions of 0.5–3.5 Torr N_2, 0.3–7 mTorr H_2O, at 300 K. The major ion at equilibrium was $H_9O_4^+$; lesser amounts of $H_7O_3^+$ and $H_5O_2^+$ were also present.

The formation of water clusters from an O_2^+ precursor proved to be more complex[72,105] as a result of the lower ionization potentials of O_2^+ and O_4^+ when compared with the corresponding nitrogen ions.[68] Thus neither ion could undergo exothermic charge transfer with water. Instead, the reaction was shown to proceed via $O_2^+{\cdot}H_2O$, formed by a switching reaction (direct formation by eq 43 being relatively unimportant under the experimental conditions of 1–3.3 Torr O_2 and 3–20 mTorr H_2O). All the contributing reactions are listed in Table XVII, but the major route accounting for the formation of the water clusters is thought to be that involving eq 16, 44, 46, and 49. Up to 25% of the reaction may, however, proceed via eq 47, to H_3O^+, at room temperature. Equations 45–47 all involve the $O_2^+(H_2O)_2{}^*$ intermediate, the identity of the products depending upon the rapidity and effectiveness of collisional deactivation. Trace amounts of ions with *m/e* values corresponding to $H_3O^+{\cdot}OH$ and $H_5O_2^+{\cdot}OH$ were observed in mass analysis of the O_2/H_2O system.[72]

Another possible ionospheric precursor of hydrated protons is the ion NO^+. This has an IP even lower than that of O_2^+. The result is that, as shown in Table VII, NO^+ can undergo hydration by up to three water molecules. Only at this point is the switching reaction energetically feasible:

$$NO^+(H_2O)_3 + H_2O \rightarrow H_7O_3^+ + HNO_2 \qquad (50)$$

The various studies of this system have led to k_{50} values of 7(−11),[99,101] 8(−11),[100] and 3(−10),[102] all at around 300 K, and of >6(−10) at 273 K.[171] The large spread in these values makes further work desirable.

Another important reaction in this particular mechanism is the switching process:

$$NO^+{\cdot}NO + H_2O \rightarrow NO^+{\cdot}H_2O + NO \qquad (51)$$

This is rapid, with k_{51} measured as 4(−10)[106] and 1(−9).[102] The former result is a little suspect, however, as a rate constant of 3(−13) was measured for the reverse of eq 51, suggesting the presence of substantial numbers of ions with excess energy. Direct hydration of NO^+ is likely, in any case, to be more important than eq 51 under ionospheric conditions, where the concentration of neutral NO is low.

Despite the complexity of the mechanisms, O_2^+ and NO^+ are regarded as being the most likely precursors of the ionospheric hydrated protons. N_2^+ or N_4^+ would be expected to charge exchange with O_2 or NO rather than water, which will have a lower partial pressure.

Kinetic data for the subsequent hydration reactions undergone by the proton clusters in all these systems are given in Table XVIII. The expected variations of k_f with third body are observed, Ar being less efficient than O_2 or N_2. The value of k_f does not appear to decrease significantly as the cluster size increases. As far as the ionospheric occurrence of these species is concerned, the possible exothermic charge exchange with NO must be taken into account for most ions. Recombination with free electrons is also extremely rapid, with rate constants as high as 1(−6) molecule^{-1} cm^3 sec^{-1} in many cases.[172]

Taking all these factors into account, the reported data for the O_2/H_2O system have been shown[173] to account substantially for the observed ionospheric intensities of water clusters as observed by Narcisi.[93-95]

Kinetic data for the formation of $H_5O_2^+$ from organic ions will be dealt with in section XIV.

C. Structure

The absence of evidence for the appearance of a "second shell" of solvated water molecules during the growth of the clusters[24] has led to the expectation that some kind of chain structure may be involved, with successive water molecules attaching themselves by means of their lone pairs to give a type of dative-covalent structure in which neither the initial proton nor the H_3O^+ group preserves its separate identity. On this basis, we would expect the positive charge to be fairly uniformly spread out through the molecule.

Theoretical investigations have been carried out in two laboratories, employing a CNDO/2 method to elucidate the structure of the clusters. The method of Daly and Burton[174] is to treat each molecule of water and each H_3O^+ ion as if it retains its original size and shape, considering only the bonds between these basic entities. This is less likely to yield a true picture of the situation than is the method of De Paz et al.[175] in which each atom is considered separately and which computes structural details, such as bond lengths and angles, which have to be assumed in the less detailed method.

The detailed calculations[175] consistently predict nonplanar structures for the ions, even down to H_3O^+, which is generally regarded as having a fast enough rate of inversion to be considered planar. Thus the results represent structural isomers of the ions, and averaging out between these and their mirror images is to be expected in practice.

For $H_5O_2^+$, the structure $H_2O{\cdot}H{\cdot}OH_2$ (disregarding the bond lengths and angles, which are fully reported in ref 175) was found to be the most stable. For $H_7O_3^+$, the structure $H_2O\cdot H\cdot OH\cdot H\cdot OH_2$ was found to be about 65 kJ mol^{-1} more stable than that with the three waters placed symmetrically about a central proton. For this ion, the protons in the O–H–O linkages were found to have charges of about +0.37, while the other protons all had charges of about +0.23. The central oxygen had a charge of −0.36, while the other two each had −0.29. Similar conclusions, leading to a structure of $H_2O\cdot H\cdot OH\cdot H\cdot OH\cdot H\cdot OH_2$, were reached for $H_9O_4^+$. This is in contrast with the earlier Eigen structure[176,177] in which three water molecules surrounded a central H_3O^+ ion.

A subsequent theoretical study[178] has formulated general rules for the clustering of both H_3O^+ and OH^- with water. A general energetic preference for chain structures was found, but with a tendency toward branching whenever possible. Inter-oxygen distances were found to increase with successive hydration, and there was a general tendency for bridging protons to occupy asymmetric positions.

The linear structures predicted by these studies have led Ferguson[121] to postulate linear structures for the ions $O_2^+(H_2O)_2$ and $NO^+(H_2O)_4$ which are precursors of hydrated protons in air. Certainly it is difficult otherwise to account for the ease with which the rearrangements take place.

Experimental diffraction studies have been reported for the ions H_3O^+ [179] and $H_5O_2^+$.[180] H_3O^+ was found to be a flat pyramid with three unequal bond lengths and angles; this presumably resulted from distortion in the $H_3O^+\cdot CH_3\cdot C_6H_4\cdot SO_3^-$ crystal used and cannot be applied directly to free gaseous H_3O^+.

Recently reported ir investigations of the $H_5O_2^+$ ion[181,182] suggested a planar structure containing similar O–H–O linkages to those of De Paz et al.[175] The H_3O^+ [183] and $H_9O_4^+$ [184] ions have also been studied by ir methods.

D. Other Data for Hydrated Proton Clusters

There have been a number of estimates made of $\Delta H_f(H_3O^+)$ based on a variety of thermodynamic calculations. Reported values include 598[185,186] and <635 kJ mol^{-1}.[187] The proton affinity of H_2O has been determined by a variety of methods. Crystal lattice studies have given values of 778[188,189] and 710 kJ mol^{-1}.[190] Classical methods, such as the measurement of energy thresholds for selected endothermic reactions, give values of 634[191] and 685[185] for H_2O, and 702[192] and 695 kJ mol^{-1} [193] for D_2O. The appearance potentials of H_3O^+, $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ have been measured by field ionization[194] as 848, 965, <1105, and <1115 kJ mol^{-1}, respectively.

It is of interest to compare the bond strengths in the larger clusters with the strength of hydrogen bonding in pure water. The latter has been measured, from ir work,[195] as ~19 kJ mol^{-1}, while theoretical studies give values of 20[196] and 25.[197] Kebarle et al.[24] found a value of 43 kJ mol^{-1} for $D^\circ(H_{15}O_7^+-H_2O)$. In other words the terminal water molecules are attached more strongly than in hydrogen bonding, but the difference is not very great. One might expect the D° value to approach the hydrogen-bond strength asymptotically as the positive charge becomes more spread out in clusters of increasing size.

The total heat of solvation of the proton, leading to the fully dissolved ion $H^+(H_2O)_\infty$, has been estimated[198] as 1085 kJ mol^{-1}. From the data of Kebarle et al.,[24] $\Sigma\Delta H^\circ$ for solvation up to $H_{17}O_8^+$ has a value of −1160 kJ mol^{-1}, taking 640 as the value of $-\Delta H^\circ$ for the formation of H_3O^+.[68] The larger value given by Kebarle's experiment perhaps arises because both ionic and hydrogen-bonding effects are being observed. If these are additive, the "ionic component" of $\Sigma\Delta H^\circ$ reduces to 1020 kJ mol^{-1}, taking the hydrogen bond strength as 20 kJ mol^{-1} for each of the seven water molecules which are added to H_3O^+.

TABLE XIX. Thermodynamic Data for the Equilibria: $H_{2n-1}O_n^- + H_2O \rightleftharpoons H_{2n+1}O_{n+1}^-$

n	$-\Delta G^\circ$ (298 K), kJ mol^{-1}	$-\Delta H^\circ$exptl, kJ mol^{-1}	$-\Delta H^\circ$calcd, kJ mol^{-1}	$-\Delta S^\circ$, J K^{-1} mol^{-1}	Ref
1	70.7	94.1		79.9	90[a]
		146			202[a]
	78.4	104.5		86.9	115
			149		178
			102		[b]
2	44.8	68.6		80.8	90[a]
		96			202[a]
	48.2	74.8		88.6	115
			108		178
3	32.3	63.3		104	90[a]
		(75)[c]			202[a]
		(63.1)[c]			115
			81.1		178
4	22.8	59.4		123	90[a]
			74.4		178
5	17.7	59.0		139	90[a]

[a] These data were obtained using fully deuterated ions. [b] W. P. Kraemer and G. H. F. Diercksen, *Theor. Chim. Acta*, 23, 398 (1972); I thank a referee for drawing attention to this work. [c] Estimated values.

Finally, a recent study by Henderson and Schmeltekopf[199] is of interest as an example of a possible new technique in the study of clusters, with special application to aeronomy. The photochemically induced break-up of hydrated proton clusters was studied by sampling the ions produced in 0.1 Torr H_2O, mass-analyzing them, and allowing a beam of chosen m/e to intersect with a beam of photons of 580–610 nm wavelength. Upper limits were set for the cross-sections of decompositions of the type:

$$H_{2n+1}O_n^+ + h\nu \rightarrow H_{2(n-m)+1}O_{n-m}^+ + mH_2O \qquad (52)$$

Reactions involving the loss of one, two, or three water molecules were observed.

XI. Solvated Hydroxyl Ions

The electron affinity of the OH radical has been calculated, from experimental measurements on OH^- and OD^-, to be 174 kJ mol^{-1}.[200] Using this value, Golub and Steiner[201] investigated the electron detachment process

$$H_3O_2^- \rightarrow OH + H_2O + e^- \qquad (53)$$

and estimated that $D^\circ(OH^--H_2O) < 115$ kJ mol^{-1} by an amount equal to the kinetic energies of the products.

Subsequently, more intensive investigations of the equilibria

$$H_{2n-1}O_n^- + H_2O \rightleftharpoons H_{2n+1}O_{n+1}^- \qquad (54)$$

have been reported;[90,202] in both these cases the fully deuterated species were used to give unequivocal mass analysis, but this should have had little effect on the thermodynamic parameters. A subsequent study[115] using OH^- itself is also included in Table XIX.

A considerable discrepancy is apparent between the experimental data of Kebarle et al.[90,115] and De Paz et al.,[202] especially for the initial clustering step. The data of Golub and Steiner,[201] discussed above, seem more consistent with Kebarle's values.

The structures of the clusters have been investigated by the CNDO/2 method discussed in section X.C.[175] As in the

TABLE XX. Thermodynamic Data for the Equilibria: $NH_4^+(X)_n + X \rightleftharpoons NH_4^+(X)_{n+1}$

n	X	$-\Delta G°$ (298 K), kJ mol^{-1}	$-\Delta H°$ (298 K), kJ mol^{-1}	$-\Delta S°$ (298 K), J K^{-1} mol^{-1}	Ref
0	NH_3	(73.2)[a]	(113)[a]	(134)[a]	209
	NH_3	71.5	104	109	210
	H_2O	47.7	72.3	79.4	210
	CH_4	−1.06	3.59	15.5	214
1	NH_3	37.6	71.1	112	209
	NH_3	37.2	73.2	120.5[b]	210
	H_2O	34.3	61.4	91.5	210
2	NH_3	27.0	74.4	159	208
	NH_3	26.8	69.0	142	209
	NH_3	25.5	57.5	109	210
	H_2O	24.7	56.0	105	210
3	NH_3	16.0	66.4	169	208
	NH_3	15.9	60.7	151	209
	NH_3	15.5	52.2	125	210
	H_2O	17.1	51.0	114	210
4	NH_3	0.8	31.4	105	209
	H_2O	12.5	40.5	93.6	210

[a] By extrapolation. [b] This is a corrected value; that in ref 210 appears to be in error.

case of the hydrated proton, linear clusters were indicated, with $H_5O_3^-$ and $H_7O_4^-$ having the respective structures HO·H·OH·H·OH and HO·H·OH·H·OH·H·OH. The charge was again fairly evenly spread; for example, in $H_7O_4^-$ each O atom had a charge of ∼−0.5, there was a charge of +0.3 on H atoms in O–H–O linkages, and the normally bonded H atoms were approximately electroneutral. More recently, ab initio calculations have also predicted this type of structure.[178] Unfortunately, this work and the other calculated $-\Delta H°$ values presented in Table XIX display the same discrepancies as have already been noted for the experimental data.

The enthalpy changes in the reaction

$$OH^- + HX \rightleftharpoons OH^-\cdot HX \quad (55)$$

can be calculated from the enthalpy changes in the process:

$$X^- + H_2O \rightleftharpoons X^-\cdot H_2O \quad (56)$$

Such a calculation has been reported for the case where X is a halogen.[90,148]

XII. Solvation of Ammonium Ions

A. Clustering in Pure Ammonia

Early work on liquid-phase systems suggested[203,204] that the heat of solvation of the NH_4^+ ion in pure NH_3 should be greater than that in water by up to 50 kJ mol^{-1}; the latter quantity has been measured as −330 kJ mol^{-1}.[205] Thermodynamic properties of the NH_4^+ ion over the temperature range 200–1000 K have been reported by Altschuler.[206]

The sequence of clustering equilibria

$$NH_4^+(NH_3)_n + NH_3 \rightleftharpoons NH_4^+(NH_3)_{n+1} \quad (57)$$

have been investigated by Kebarle and coworkers.[207-210] Data are available for n values in the range 0–4,[209] for temperatures of up to 720 K,[210] while K_p values at 300 K have been measured for n = 3 to 7 at pressures of up to 200 Torr.[207] The collected values of thermodynamic properties are listed in Table XX. The data are not in complete agreement, but are sufficiently so to illustrate an interesting feature of this particular system. Whereas all the previous equilibria dealt with in this article have shown smooth decreases in $-\Delta G°$ and $-\Delta H°$, the data here seem to show a discontinuity at n = 4, where the values are much lower than would have been expected. Unfortunately, no data of this type are available for higher n values, but reported[207] approximate K_p values at 300 K are 3.4, 1.8, 1.5, 1.2, and 0.9 atm^{-1} for n = 3 to 7, respectively. Thus K_p appears to vary smoothly again following the point of discontinuity.

TABLE XXI. Thermodynamic Data for Clustering of $NH_4^+(NH_3)_n(H_2O)_w$ (Ref 210)

Reactant n	Reactant w	Product n	Product w	$-\Delta G°$ (298 K), kJ mol^{-1}	$-\Delta H°$ (298 K), kJ mol^{-1}	$-\Delta S°$ (298 K), J K^{-1} mol^{-1}
1	0	1	1	28.9	53.9	84.8
0	1	1	1	48.5	76.9	96.2
2	0	2	1	20.9	51.8	103
1	1	2	1	31.8	71.5	133
1	1	1	2	22.2	53.2	105
0	2	1	2	38.5	76.2	127
3	0	3	1	14.2	48.8	117
2	1	3	1	19.7	62.7	144
2	1	2	2	14.7	48.8	116
1	2	2	2	23.4	65.6	142
1	2	1	3	15.5	51.0	119
0	3	1	3	28.9	72.4	147

These data seem to indicate[209] that at this point a second shell of solvated NH_3 molecules begins. It was suggested that a pyramidal NH_3 molecule would add on to each vertex of the tetrahedral NH_4^+ ion. Subsequent additions of NH_3 would then be at much greater distances from the central ion. The value of $-\Delta H°$ for n = 4, for example, is only a little greater than that expected in a hydrogen bond. The observed heat of solvation in going from NH_4^+ to $NH_4^+(NH_3)_4$ adds up to −313 kJ mol^{-1};[209] comparison with the expected total heat of solvation of −380 (discussed above) indicates the small contribution of the second and subsequent shells to this property.

A kinetic study[211] has shown that k_f for the reaction

$$NH_4^+ + NH_3 + O_2 \rightarrow NH_4^+\cdot NH_3 + O_2 \quad (58)$$

has a value of 1.8(−27) at 300 K. Data with NO as third body will be given in subsection C below.

B. Clustering in the Presence of Water

Early work by Hogg and Kebarle[207] on the competitive solvation of NH_4^+ with water and ammonia showed that NH_3 was preferentially taken up for $n \leq 3$, i.e., in the inner solvation shell, but that thereafter water was energetically preferred.

A recent study[210] reports data for both competitive solvation and hydration of the NH_4^+ ion. The reaction

$$NH_4^+(H_2O)_n + H_2O \rightleftharpoons NH_4^+(H_2O)_{n+1} \quad (59)$$

was investigated for n values of 0 to 4. The results are included in Table XX and confirm the earlier qualitative conclusions based on competitive clustering. Payzant et al.[210] also report a large body of data for the equilibria

$$NH_4^+(NH_3)_n(H_2O)_w + H_2O \rightleftharpoons NH_4^+(NH_3)_n(H_2O)_{w+1} \quad (60)$$

$$NH_4^+(NH_3)_n(H_2O)_w + NH_3 \rightleftharpoons NH_4^+(NH_3)_{n+1}(H_2O)_w \quad (61)$$

and this is given in Table XXI. The general tendency to take up NH_3 preferentially is clear from the $-\Delta H°$ values.

Kinetically, the only investigation of hydrated NH_4^+ has been a study by Fehsenfeld and Ferguson[212] of the reactions

$$NO^+(H_2O)_n + NH_3 \rightarrow NH_4^+(H_2O)_{n-1} + HNO_2 \quad (62)$$

The measured rate constant for n = 1, at 295 K, was 1(−9) molecule^{-1} cm^3 sec^{-1}, and similar values were found for n = 2 and 3.

TABLE XXII. Clustering in Nitric Oxide/Ammonia Mixtures (Ref 213)

Reaction	k_f, molecule^{-2} cm^6 sec^{-1}	k_r, molecule^{-1} cm^3 sec^{-1}
$NO^+ + 2NO \rightleftharpoons NO^+{\cdot}NO + NO$	5(−30)	9(−16)
$NO^+{\cdot}NO + NH_3 \rightarrow NO^+{\cdot}NH_3 + NO$	1.3(−9)[a]	
$NO^+ + NH_3 + NO \rightarrow NO^+{\cdot}NH_3 + NO$	5.4(−28)	
$NO^+{\cdot}NH_3 + NH_3 \rightarrow NH_4^+ + (NO + NH_2)$	9.1(−10)[a]	
$NH_4^+ + NH_3 + NO \rightarrow NH_4^+{\cdot}NH_3 + NO$	1.0(−27)	
$NH_4^+{\cdot}NH_3 + NH_3 + NO \rightleftharpoons NH_4^+(NH_3)_2 + NO$	2.7(−27)	2.4(−15)
$NH_4^+(NH_3)_2 + NH_3 + NO \rightleftharpoons NH_4^+(NH_3)_3 + NO$	2.4(−27)	1.2(−12)

[a] Second order; same units as for k_r.

C. Clustering in Nitric Oxide/Ammonia Mixtures

A kinetic study of positive ion clustering in the NO/NH_3 system has been reported.[213] The initial steps involve clustering of NH_3 around the NO^+ precursor. Switching then occurs, as in the NO/H_2O system, and this is followed by the clustering of NH_3 around NH_4^+. The complete scheme is given in Table XXII. Unfortunately, the data do not extend up to $NH_4^+(NH_3)_4$. It would be of interest to see what effect the postulated "second-shell" inception at this point would have on the value of k_f.

XIII. *The Solvation of CN^-*

A gas-phase study of the formation of the CN^- monohydrate ion has yielded[115] values of 57.7, 32.8 (both in kJ mol^{-1}), and 82.9 J K^{-1} mol^{-1} for $-\Delta H^\circ$, $-\Delta G^\circ$(300 K), and $-\Delta S^\circ$, respectively. An approximately linear correspondence between $D^\circ(H^+{-}X^-)$ and $-\Delta H^\circ$ for the first hydration step of X^- was found for X = OH, halide, CN, NO_2, and NO_3.

XIV. *Clustering around Organic Ions*

Many ionic equilibria involving organic species have been studied, notably by Field and coworkers. The present article will deal only with those systems having most relevance to the general themes which have been discussed above. In particular, the rather sparse kinetic data will be considered.

A. Clustering Reactions in Methane

Early work[14] by Field and coworkers identified the ion $C_2H_8^+$ in the mass spectrum of methane at high pressure. A third-order process involving CH_3^+, which proceeded via clustering and subsequent fragmentation, was also postulated:

$$CH_3^+ + CH_4 \rightleftharpoons (C_2H_7^+)^* \xrightarrow{CH_4} CH_5^+ + C_2H_6 \tag{63}$$

This was calculated to be exothermic by ≤120 kJ mol^{-1}. This is not an orthodox clustering reaction, but Bennett and Field[214] have observed an equilibrium for the corresponding reaction of the CF_3^+ ion, giving rise to $CF_3^+{\cdot}CH_4$. The values of ΔG°(298 K), ΔH°, and ΔS° were +1.1, −4.55, and −18.8, respectively, in the usual units. Very similar data were reported for the formation of $H_3S^+{\cdot}CH_4$. The values of the same parameters in this case were +1.55, −8.87, and −18.1.

Field and Beggs[215] have subsequently found true clustering in pure methane at between 0.1 and 1 Torr and temperatures of 77–300 K. The equilibria

$$CH_5^+ + CH_4 \rightleftharpoons C_2H_9^+ \tag{64}$$

$$C_2H_5^+ + CH_4 \rightleftharpoons C_3H_9^+ \tag{65}$$

$$C_2H_9^+ + CH_4 \rightleftharpoons C_3H_{13}^+ \tag{66}$$

were studied and ΔG°(298 K) values of −1.9, +0.43, and +2.9 kJ mol^{-1} were obtained for the three reactions. The corresponding values of $-\Delta H^\circ$ were 17.3, 9.99, and 6.14 kJ mol^{-1}, and of $-\Delta S^\circ$ were 51.8, 35.9, and 30.1 J K^{-1} mol^{-1}.

Work on the methane/water system, which gives rise to the hydrated proton sequence,[25] has been discussed in section X.A. Subsequent work at low temperatures[216] has detected the solvation of the H_3O^+ ion by methane molecules:

$$H_3O^+ + CH_4 \rightleftharpoons H_3O^+{\cdot}CH_4 \tag{67}$$

$$H_3O^+{\cdot}CH_4 + CH_4 \rightleftharpoons H_3O^+(CH_4)_2 \tag{68}$$

The quantitative details were: $-\Delta G^\circ$(298 K) = 7.9 and 5.0 kJ mol^{-1}, $-\Delta H^\circ$ = 33.4 and 14.2 kJ mol^{-1}, and $-\Delta S^\circ$ = 85.3 and 33.8 J K^{-1} mol^{-1}.

Bromo- and iodomethane have recently been observed[217] to undergo dimerization to give $(CH_3X)_2^+$. The corresponding ion was not observed in chloromethane.

B. Clustering in Ethylene and Derivatives

The earliest observations of clustering in ethylene used either the pure gas[218,219] or a xenon-sensitized sample.[220–223] The system has been reinvestigated by Tiernan and coworkers.[224,225] It was shown[221] that the $C_2H_4^+$ ion underwent an initial two-body reaction, giving the excited dimer, which could then react to give a variety of possible products:

$$C_2H_4^+ + C_2H_4 \rightleftharpoons (C_4H_8^+)^* \xrightarrow{M} C_4H_8^+ + M \tag{69}$$

$$\rightarrow C_3H_5^+ + CH_3 \tag{70}$$

$$\rightarrow C_4H_7^+ + H \tag{71}$$

In pure ethylene, the main process was that in eq 70, in the range 5–200 Torr.[220] Ions of general formula $C_nH_{2n-1}^+$ were observed up to $C_{15}H_{29}^+$, the upper mass limit of the instrument employed, indicating the importance of reactions like eq 71. The ion $C_{14}H_{28}^+$ was also seen. When a mixture of 1% C_2H_4 in Xe was studied,[220] the $C_nH_{2n}^+$ chain was present with a greatly enhanced intensity, showing the greater contribution of eq 69. The rate constant of eq 69 in pure ethylene has been measured[218] as 2(−27) molecule^{-2} cm^6 sec^{-1}.

The subsequent reaction

$$C_3H_5^+ + 2C_2H_4 \rightarrow C_5H_9^+ + C_2H_4 \tag{72}$$

has also been investigated,[226] and it was found that it was this process, rather than the decomposition of excited $C_6H_{12}^+$, which was the main precursor of $C_5H_9^+$ in the system. The corresponding reaction of $C_3H_5^+$ with C_2D_4 has been studied.[227] The rate constant was found to depend on repeller voltage and on the source of the $C_3H_5^+$. At 0.64 eV, rate constants of 8.4, 14.1, 6.2, and 3.6(−25) were observed for cyclopropyl bromide, allyl bromide, 2-bromopropene, and 1-bromopropene precursors, respectively.

Several studies of partially halogenated ethylenes have been carried out. Thus, for the reaction

$$C_2H_3X^+ + 2C_2H_3X \rightarrow \text{products} \tag{73}$$

rate constants of 1.2(−25),[228] 1(−25),[229] and 5.5(−26)[229] were obtained for X = F, Cl, and Br, respectively. However, the products were not the dimers, but fragments such as $C_3H_4X^+$, $C_4H_5X^+$, and $C_3H_3X_2^+$, so these were not clustering reactions. Similarly, $C_3H_5^+$ reacts with C_2H_3F to give $C_5H_7^+$ with a third-order rate constant of 8.8(−25) at 0.64 eV.[227]

True clustering has recently been reported[230] for the dimerization of $CF_2CH_2^+$ to give $C_4F_4H_4^+$. Ion-cyclotron resonance studies at 300 K gave values of $10^{25}k_f$, for the third bodies indicated, of 1.7 (He), 2.3 (Ne), 4.3 (Ar), 5.4 (Kr), 5.8 (Xe), 4.8 (N_2), 5.0 (CO), and 12.0 (CF_2CH_2).

In ethylene with added nitric oxide, the clustering of $C_4H_8^+$ with an NO molecule has been observed.[222] This is followed by third-order fragmentation:

$$C_4H_8^+\cdot NO + 2NO \rightarrow C_2H_5(NO)_2^+ + C_2H_3NO \qquad (74)$$

This is clustering of a sort, but is clearly more complex than the solvation-type reactions we have largely been dealing with.

C. Clustering in Other Aliphatic Hydrocarbons

The formation of the dimer ion $(C_3H_8)_2^+$ in pure propane has been reported,[231] although no quantitative data have been obtained. Ion–molecule reactions in ethane/water systems have been shown[232] to give rise to $C_2H_4^+(H_2O)_n$ and $C_3H_7^+(H_2O)_n$ clusters with n values of up to 4 in both cases.

The latter series of clusters have also been studied in the propane/water system.[164] For n values of 0, 1, and 2, respectively, the reported thermodynamic parameters were: $-\Delta G°(298\ K)$ = 38.5, 40.5, and 35.5 kJ mol^{-1}; $-\Delta H°$ = 73.5, 56.4, and 62.2 kJ mol^{-1}; and $-\Delta S°$ = 116, 53.1, and 89.9 J K^{-1} mol^{-1}. No clear pattern is discernible from these data.

An interesting route for the formation of $H_5O_2^+$ has been reported by Sieck and Searles[187] in a photoionization source at 300 K. The reaction

$$RH_2^+ + 2H_2O \rightarrow H_5O_2^+ + RH \qquad (75)$$

was observed for a number of hydrocarbons. For smaller molecules, the reaction was experimentally second order. Thus, both the $C_2H_6^+$ and the $C_3H_8^+$ ions were seen to undergo reaction with a single molecule of water, leading to the formation of H_3O^+ in each case. The rate constants of these reactions were 1.2(−9) and 1.4(−9) molecule^{-1} cm^3 sec^{-1}, respectively.

The larger hydrocarbons studied[187] all underwent third-order switching as described by eq 75. The ions studied, with their corresponding rate constants, were: n-$C_4H_{10}^+$, 4(−25); i-$C_4H_{10}^+$, 1.2(−25); c-$C_5H_{10}^+$, 5(−26); n-$C_5H_{12}^+$, 4.6(−26); n-$C_6H_{14}^+$, 3.6(−26); i-$C_6H_{14}^+$, 1.5(−26); c-$C_6H_{12}^+$, 5(−27). These are not, of course, clustering reactions as such, but they are important as precursors of clusters in view of their great rapidity.

D. Clustering in Amines

Clustering reactions are known[233] to occur in pure samples of methyl-, dimethyl- and trimethylamine; at pressures of up to 0.5-Torr the series $H^+(CH_3NH_2)_n$, $H^+(CH_3NHCH_3)_n$, and $H^+\{(CH_3)_3N\}_n$ have been observed with maximum n values of 4, 3, and 2, respectively.

The gas-phase proton-exchange equilibria of ammonia and of aliphatic and aromatic amines have been studied and have yielded information on basicities,[234,235] hydrogen bonding,[235] and proton-induced cyclization.[235]

E. Clustering in Other Aliphatic Compounds

The first associated dimer ion to be reported was $(C_2H_5I)_2^+$,[236] but no quantitative data are available for this ion. Ethanol has been found to give rise to clusters of the type $H^+(C_2H_5OH)_n$ with n values of up to 4.[237] In pure gaseous acetone, the clusters $H^+(CH_3COCH_3)_n$[157,238] and $CH_3^+(CH_3COCH_3)_n$[238] were found with n up to 4, while $CH_3CO^+(CH_3COCH_3)_n$ was present with n up to 3,[238] all at pressures of up to 0.6 Torr. The $H^+(HCOOH)$ cluster has also been reported,[157] as have $H^+(CH_3OH)_n$ and $H^+(CH_3OCH_3)_n$;[169] see section X.A.

A number of rate constants have been measured in a time-of-flight mass spectrometer[239] for clustering in trioxane:

$$H^+(CH_2O) + 2(CH_2O)_3 \rightarrow H^+(CH_2O)_4 + (CH_2O)_3 \qquad (76)$$

$$H^+(CH_2O)_2 + 2(CH_2O)_3 \rightarrow H^+(CH_2O)_5 + (CH_2O)_3 \qquad (77)$$

$$H^+(CH_2O)_3 + 2(CH_2O)_3 \rightarrow H^+(CH_2O)_6 + (CH_2O)_3 \qquad (78)$$

The k_f values for these reactions were respectively 6.28(−24), 9.9(−25), and 1.17(−23) molecule^{-2} cm^6 sec^{-1}. The precursor ions in eq 76 and 77 are products of the electron-impact decomposition of neutral trioxane, but unfortunately the authors do not discuss possible structures for these fragments. The addition of a further molecule of trioxane to the product ion is second order in all three cases, but owing to a typographical error in Table 1 of ref 239, it is not possible to quote rate constant values for these processes.

F. Clustering in Aromatic Compounds

Wexler and Pobo have studied the clustering of C_6 hydrocarbons in drift tubes[240] and report that clustering was observed for aromatics but not for aliphatics. Thus, $C_6H_{12}^+$ underwent partial decomposition:

$$C_6H_{12}^+ + 2C_6H_{12} \rightarrow C_{18}H_{34}^+ + H_2 \qquad (79)$$

However, $C_6H_6^+$ underwent fourth-order clustering[241] at field strengths of from 10 to 54 V cm^{-1}. The suggested reaction scheme was

$$(C_6H_6^+)^\ddagger + C_6H_6 \rightarrow (C_6H_6^+)^* + C_6H_6^* \qquad (80)$$

$$(C_6H_6^+)^* + C_6H_6 \rightleftharpoons (C_{12}H_{12}^+)^* \qquad (81)$$

$$(C_{12}H_{12}^+)^* + C_6H_6 \rightarrow C_{12}H_{12}^+ + C_6H_6 \qquad (82)$$

The initial excess energy presumably derives from the applied field. Equation 80 can perhaps be regarded as an abortive attempt to undergo reaction 81, which fails because of the excess of energy in the cluster. This is not very convincing, however, and a very recent study has observed third-order clustering for benzene with a variety of third bodies.[230] The reported values of $10^{27}k_f$ at 300 K were, for the formation of $C_{12}H_{12}^+$ using the third body indicated, 4 (He), 0 ± 6 (Ne), 7 (Ar), 11 (Kr), 16 (Xe), and 120 (C_6H_6). These data cast doubt on the fourth-order mechanism.

An equilibrium study of the dimerization reaction leading to $C_{12}H_{12}^+$ has led[242] to values of −63 kJ mol^{-1}, −33 kJ mol^{-1}, and −97 J K^{-1} mol^{-1} for $\Delta H°(298\ K)$, $\Delta G°(298\ K)$, and $\Delta S°$, respectively.

XV. Clustering in Boron Compounds

No quantitative information is available for boron clusters, but the ions $BCl^-(H_2O)_n$, for n from 1 to 6, and $B_2Cl^-(H_2O)_n$, for n from 1 to 7, have been reported.[243]

XVI. Clustering in Silicon and Germanium Compounds

A large body of data on the ion–molecule reactions of inorganic hydrides has been reported by Lampe and coworkers.

Most of these reactions are second order, but in the study of CH_4/SiH_4 mixtures in a modified time-of-flight mass spectrometer, Beggs and Lampe[11] observed the reaction

$$CH_4^+ + SiH_4 + M \rightarrow SiH_5^+ + CH_3 + M \quad (83)$$

which had a rate constant of 2.0(−26) molecule^{-2} cm^6 sec^{-1}. The third body was necessary to prevent decomposition into SiH_3^+. Other SiH_4-derived ions have been seen to undergo orthodox clustering. Yu et al.[244] studied the reactions

$$Si^+ + 2SiH_4 \rightarrow Si_2H_4^+ + SiH_4 \quad (84)$$

$$SiH^+ + 2SiH_4 \rightarrow Si_2H_5^+ + SiH_4 \quad (85)$$

$$SiH_2^+ + 2SiH_4 \rightarrow Si_2H_6^+ + SiH_4 \quad (86)$$

$$SiH_3^+ + 2SiH_4 \rightarrow Si_2H_7^+ + SiH_4 \quad (87)$$

and measured rate constant values of 1.0(−26), 1.1(−26), 7(−26), and 1.44(−26) molecule^{-2} cm^6 sec^{-1}, respectively.

A similar series of reactions has been reported for GeH_4 from the same laboratory.[245] However, $Ge_2H_6^+$ was not observed, suggesting that the reaction analogous to eq 86 did not occur. The reactions with Ge^+, GeH^+, and GeH_3^+ precursors had rate constants of 1.4(−26), 1.3(−26), and 1.8(−26) molecule^{-2} cm^6 sec^{-1}, respectively.

XVII. Theories of Third-Order Ion-Molecule Reaction

A. General Langevin Theory of Two-Body Reactions

As shown in section III, we can consider ion-molecule clustering in terms of an energy-transfer mechanism, represented by eq 2 and 3. Three of the four processes involved, those of combination, stabilization, and activation, were two-body reactions. It is therefore necessary to begin a discussion of the theory of clustering by considering the theoretical treatments which have been applied to such reactions.

The classical theory giving the energies of interaction between ions and molecules was developed from standard electrostatic relations by Langevin[246] and has been applied to the special case of ion-molecule reaction by Gioumousis and Stevenson.[247] It has been extended by Walton[248] and Gupta et al.[170] to take account of a possible permanent dipole moment in the neutral molecule, assuming that the effect of such a dipole would be additive to the ion-induced-dipole attraction. Thus the potential energy of interaction, V, between an ion I and a molecule A can be shown to be

$$V = -\left(\frac{\alpha_A e^2}{2} + \frac{\mu_A{}^2 e^2}{3kT}\right)\frac{1}{r^4} \quad (88)$$

where e is the unit of electronic charge, α_A and μ_A are respectively the polarizability and permanent dipole moment of the molecule A, and r is the distance of separation. The negative sign indicates the attractive nature of the interaction.

For reaction to occur, this energy V must be $\geq \frac{1}{2}mv^2$, the kinetic energy of the system, where m is the reduced mass and v the relative velocity of I and A. This condition will only be fulfilled when $r \leq r_c$, where r_c is some critical distance of separation equivalent to the radius of the reaction cross-section. Thus, when $r = r_c$

$$r_c = \left[\left(\frac{\alpha_A e^2}{2} + \frac{\mu_A{}^2 e^2}{3kT}\right)\left(\frac{2}{mv^2}\right)\right]^{1/4} \quad (89)$$

The microscopic cross-section, q, is given by $2\pi r_c{}^2$ and hence[248]

$$k = qv = 2\pi r_c{}^2 v = 2\pi e\left(\frac{\alpha_A}{m} + \frac{2\mu_A{}^2}{3mkT}\right)^{1/2} \quad (90)$$

This expression was found to correlate well with data obtained for simple second-order reactions, although there was evidence[248] that, when $\mu_A \neq 0$, better agreement could sometimes be obtained with a square-well potential model in which

$$k_{\text{well}} = k_{90}(1/\pi)^2 \quad (91)$$

An expression similar to eq 90 was derived by Gupta et al.[170] However, rather than summing at the potential energy stage, the method in this case was to calculate separate rate constants for ion-induced dipole and ion-permanent dipole effects before performing the addition. The final equation

$$k = 2\pi e\left[\left(\frac{\alpha_A}{m}\right)^{1/2} + \left(\frac{2\mu_A{}^2}{mkT}\right)^{1/2}\right] \quad (92)$$

thus differs slightly from eq 90. Thus k_{90} and k_{92} will show slight numerical differences, but the general trends will be similar. Of the two, Walton's method[248] is probably preferable.

I am grateful to a referee for drawing my attention to a recent, more sophisticated treatment of the role of dipole effects.[249] Both methods discussed above assume a "locking-in" of ionic charge and dipole; i.e., the dipole is treated as though it were in the electrically most favorable orientation with respect to the ionic charge. Thus the effect of the dipole moment tends to be overestimated. Su and Bowers[249] have allowed for the thermal rotational energy of the dipolar molecule, which they therefore assume to be oriented at an angle θ to the electrically most favored position. The angle θ is dependent on the intermolecular distance. This treatment has yielded a closer correspondence between experimental and calculated rate constants than that achieved by the simpler theories.

B. Empirical Third-Order Reaction Rate Theory

An empirical theory of third-order ion-molecule reaction was proposed by Bohme,[32,250] who considered all the data then available (1969) and concluded that the rate constant for clustering was related to the number of atoms in the product ion, N, by the expression

$$k_f = 10^{-32.5}N^{6.24} \quad (93)$$

The observed scatter was at most ± one order of magnitude. Subsequent data also appear to fit eq 93 within the quoted limits, right up to $H^+(CH_2O)_6$, the largest product ion (N = 25) for which kinetic data are available.[239]

This observation may be rationalized by considering the possible decomposition of the excited species I·A* in eq 3. Clearly, the probability that this will occur before stabilization will decrease as the number of degrees of freedom available for storing the energy increases. However, the rate of decomposition will also depend on the amount of energy which needs to be stored in this way; in other words, k_d will vary as the exothermicity of the combination reaction, which is approximately equivalent to $D°$(I-A), varies. This helps to account for the observed scatter. A comment by Keller and Niles[251] carries this approach one step further by showing how observed k_f values may be correlated with both cluster mass and the polarizability of A.

C. Classical Theory

The effects of both cluster size and energy release have been taken into account in a classical semiempirical treat-

TABLE XXIII. Calculated and Experimental Bond Strengths of Ion·Molecule Clusters, I·A

I	A	M	T, °K	k_f, molecule^{-2} cm^6 sec^{-1}	Ref	Dcalcd°,^{a} kJ mol^{-1}	Dexptl°, kJ mol^{-1}	Ref
N_2^+	N_2	N_2	300	8.3(−29)	60	115	95.4	64
O_2^+	O_2	O_2	300	2.8(−30)	20	46	43.9	71
	H_2	He	82	7.4(−31)	73	7	<20^b	73
	H_2O	He	300	8.5(−29)	73	109	110^b	72
O_4^+	O_2	He	82	5(−30)	73	27	27.2	71
H_3O^+	H_2O	N_2	300	3.7(−27)	60	169	151	24
$H_5O_2^+$	H_2O	N_2	300	2.3(−27)	60	81	92.9	24
$H_7O_3^+$	H_2O	N_2	300	2.4(−27)	60	63	72.1	24
$H_9O_4^+$	H_2O	O_2	307	9.0(−28)	72	54	64	24
CO^+	CO	CO	340	1.4(−28)	118	140	118^b	118

^{a} Calculated in ref 253 using eq 96. ^{b} Estimated from thermochemical data.

TABLE XXIV. Theoretical Values of Clustering Rate Constants in Pure Rare Gases (300 K)

	$10^{31}k_f$, molecule^{-2} cm^6 sec^{-1}				
Product ion	Exptl data^a	Mahan[37]	Niles, et al.[255]	Smirnov[256]	Dickenson et al.[257]
He_2^+	0.35–1.1	0.77	1.02	0.68	0.70
Ne_2^+	0.15–0.79	0.62	0.14	0.71	0.40
Ar_2^+	0.6–3.0	2.35	0.69	2.63	0.70
Kr_2^+	2.3–2.7	2.60	0.44	3.21	5.10
Xe_2^+	1.8–3.6	3.90	0.41	4.73	0.55

^{a} From Table I.

ment of clustering.[252,253] The relationship of the observed rate constant to the rate constants of the individual steps was shown in section III to be

$$k_f = k_c k_s / k_d \tag{4}$$

Equation 90 was used to evaluate k_c, while k_d was obtained from standard RRK theory[254] and was expressed as

$$k_d = A\left(\frac{rRT}{D + rRT}\right)^{s-1} \tag{94}$$

where A is a vibration frequency, D the bond dissociation energy of the cluster, r the number of square terms contributing to the internal energy of the molecule, and s related to the number of degrees of freedom in the excited complex.

The stabilization constant k_s was given by an equation of the same form as eq 90, but corrected by a factor f, to take account of the fraction of the total energy which had to be removed by collision with M. This gave

$$f = 1 - \frac{E_{\text{excess}}}{E_{\text{total}}} = \frac{rRT}{D + rRT} \tag{95}$$

A combination of these three expressions into eq 4 gave

$$k_f = \frac{4\pi^2 e^2}{A}\left(\alpha_A\alpha_M + \frac{2\mu_A{}^2\alpha_M}{3kT} + \frac{2\mu_M{}^2\alpha_A}{3kT} + \frac{4\mu_A{}^2\mu_M{}^2}{9k^2T^2}\right)^{1/2} \times \left(\frac{M_I + M_A + M_M}{M_I M_A M_M}\right)^{1/2}\left(\frac{D + rRT}{rRT}\right)^{s-2} \tag{96}$$

where M_X is the mass of species X. Reasonable values of A and s must be chosen, and the arbitrary nature of these quantities restricts the usefulness of the equation. However, it has been used with fair success to interpret the observed temperature dependence of k_f[252] and to predict $D°$ values for reactions with known k_f[253] (see Table XXIII).

D. Charge-Transfer Theory

A different mechanism has been proposed by Mahan[37] in a calculation of the rate constants for the formation of rare-gas dimer ions. He proposed that the initial step was a bimolecular resonant-charge-transfer reaction, having a rate constant k_{CT}:

$$Ar_I^+ + Ar_{II} \rightarrow Ar_I + Ar_{II}^+ \tag{97}$$

In order that these products may spend an appreciable time in proximity, the ion-induced-dipole attraction between them must be large enough to overcome the kinetic energy of the molecules:

$$\frac{\alpha_{Ar}e^2}{2r^4} \geq \frac{1}{2}mv^2 \tag{98}$$

For stabilized Ar_2^+ to be produced, there must be a third particle within a distance r_c, the limiting value of r in eq 98. Thus, in the limit

$$r_c = \left(\frac{\alpha_{Ar}e^2}{mv^2}\right)^{1/4} \tag{99}$$

and association occurs if $r < r_c$. Overall, one can say

$$k_f = k_{CT} \times \text{probability of finding third particle within } r_c = k_{CT}\frac{4\pi}{3}\int_0^\infty r_c(v)^3 f(v)\,dv \tag{100}$$

where f(v) is the Maxwell–Boltzmann distribution function at the reaction temperature. Integration leads to

$$k_f = \frac{4}{3}k_{CT}\pi^{1/2}2^{1/4}\Gamma\left(\frac{3}{4}\right)\left(\frac{\alpha e^2}{kT}\right)^{3/4} \tag{101}$$

This gives a predicted temperature dependence which varies from $T^{-5/4}$ at low temperatures to $T^{-1/4}$ at high temperatures. The k_f values obtained in this way are listed in Table XXIV.

Mahan's theory,[37] based as it is on a charge-transfer mechanism, is only likely to be directly applicable for cases in which I = A^+. In other systems, resonant charge transfer will not occur. Nevertheless, one could envisage the substitution of some other rate constant, say Walton's k_{90}, into Mahan's final equation, thus extending it to deal with other systems. In practice, however, results for larger molecules are too low by several orders of magnitude, perhaps because no account is taken of the ability of the intermediate to store energy and hence to undergo stabilization with particles at much greater r values.

E. Other Theories of Rare Gas Clustering

Because of the relative simplicity of rare gas clustering, this type of process has received more theoretical attention than any other. Niles and Robertson[255] employed a statistical mechanical method, developed from an earlier expression for the formation of He_2^+, to calculate k_f values for all the inert gases. They considered the final equilibrium

$$He^+ + 2He \rightleftharpoons He_2^+ + He \tag{102}$$

for which one can write

$$k_f = \frac{[He_2^+]}{[He^+][He]} k_r \qquad (103)$$

Writing in the partition functions gives

$$\frac{[He_2^+]}{[He^+][He]} = \frac{g_3}{g_1 g_2}\left(\frac{h^2}{2\pi MkT}\right)^{3/2}\left(\frac{8\pi^2 IkT}{h^2}\right) \times \exp(D/kT) \Big/ \left\{1 - \exp\left(\frac{-h\nu}{kT}\right)\right\} \qquad (104)$$

where g_1, g_2, and g_3 are the statistical weights of the ground states of He, He^+, and He_2^+, respectively; $M = m_{He^+} \cdot m_{He}/(m_{He^+} + m_{He})$; I is the moment of inertia of He_2^+; ν = vibrational frequency of He_2^+; D is the bond dissociation energy of He_2^+.

The rate of decomposition of He_2^+ will depend upon the total number of collisions between He_2^+ and He, denoted by z, upon the fraction F having sufficient energy to cause decomposition, and upon the fraction p of these which actually lead to decomposition. Thus

$$k_r = pFz \qquad (105)$$

Values of F and z are calculated, assuming Maxwell–Boltzmann statistics, from standard statistical-mechanical relations. Equations 104 and 105 are then substituted into eq 103, giving

$$k_f = p\left[4\pi hI(d)^2(3)^{1/2}\frac{g_3}{g_1 g_2}(M_{He})^{-2}\right] \times \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right]^{-1}\left[(D/kT) + 1\right] \qquad (106)$$

where d is the sum of the diameters of He and He_2^+. When this treatment is extended to the other inert gases, some terms will be constant in all cases. The general equation is

$$k_f T = (1.17 \times 10^{-47})(pDd^2/B_e M_X^2) \qquad (107)$$

where B_e is the rotational constant of the inert gas ion X_2^+ in its equilibrium position. The value of d may be obtained from measurements of ionic mobility in drift-tube experiments.

The calculated values of k_f for the rare gases are listed in Table XXIV. In principle the method could be extended to cover other clustering reactions by inserting the appropriate partition functions in eq 104. This might well have the effect of changing the predicted temperature dependence of k_f; in this particular case a T^{-1} dependence was obtained, as shown in eq 107.

Smirnov[256] obtained a $T^{-3/4}$ dependence for k_c, which was expressed in the form of a modified Langevin equation:

$$k_c \propto \left(\frac{\alpha e^2}{M}\right)^{1/2}\left(\frac{\alpha e^2}{T}\right)^{3/4} \qquad (108)$$

The proportionality constant was determined from a comparison with the experimental k_f values for He_2^+ formation. Smirnov's calculated data are given in Table XXIV. He also estimated a value of 1.5(−31) for k_f in the formation of Hg_2^+ with He as third body. This agrees quite well with the experimental result.[145]

Dickenson et al.[257] have employed a resonance theory treatment in which states having a rotational quantum number, J, greater than zero are also considered. The result is an expression which is basically similar to that of Niles and Robertson though rather more complex in its final form, as it involves a summation of reaction cross-sections for all values of J. The inclusion of these extra terms tends to give higher computed values of k_f, as shown in Table XXIV. Both methods fail to reproduce the observed trends of the experimental values in Table I, where k_f is seen to become larger as the atomic weight of the gas increases.

All the methods discussed lead to k_f values which are within an order of magnitude of the experimental k_f values also quoted in Table XXIV. However, while the methods of Mahan[37] and Smirnov[255] give results close to the range of experimental k_f values for all five gases, those of Niles and Robertson[256] and Dickenson et al.[257] are considerably in error for Kr_2^+ and Xe_2^+.

XVIII. Conclusion

Most of the experimental data reported here have been obtained within the last five years. Work is continuing in many laboratories to provide some of the quantitative data which are as yet unavailable. There are numbers of systems in which either kinetic or equilibrium data, or both, are still needed. It appears, however, that the presently available experimental techniques, in particular the "flowing-afterglow" and "pulsed-beam" methods, have been developed to the extent necessary for the provision of much of these missing data. Thus, progress in this aspect of the subject seems only a matter of time.

There remains, however, a lack of information about the true structures of cluster ions and the exact nature of the bonding involved. The theoretical treatments have so far been largely classical and empirical, lacking in generality.

The uses to which the data can be put have already been outlined. At present the information on ionospheric clustering seems to have overtaken the level of knowledge in other areas of the subject, and a full kinetic analysis of ionospheric chemistry must now await more data on recombination rates and other processes becoming available.

One may envisage an increasing interest, on the part of solution chemists, in the application of data of this kind to the solving of problems in the liquid phase. The possibilities of this area of study have scarcely begun to be realized.

XIX. References

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