[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Magnesium Bromide–Lithium Bromide–Water System

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RECEIVED SEPTEMBER 29, 1953

The ternary system magnesium bromide–lithium bromide–water has been investigated by thermal analysis from +20° to the ternary eutectic. No double salts are formed over the temperature range investigated, but the di-, tri- and pentahydrates of lithium bromide and the hexa- and decahydrates of magnesium bromide are found. The ternary eutectic occurs at a temperature of −78° and at a composition of 59.2% (by weight) water, 29.5% (by weight) lithium bromide and 11.3% (by weight) magnesium bromide. Isothermal sections were plotted at 0° and at −25°. The lithium bromide–water system which makes up one side of this ternary system has been investigated. A new hydrate of lithium bromide, existing at temperatures below −49°, was found. Evidence obtained indicates that this hydrate is probably the pentahydrate of lithium bromide. The eutectic point for this system was found to occur at a temperature of −67.5° and at a concentration of 39.3% (by weight) lithium bromide. The magnesium bromide–water system which makes up another side of the ternary system has also been studied. The terminal data obtained for this system are in good agreement with earlier solubility data obtained by Getman.[1,2] The eutectic point for this two-component system was found to occur at −44.0° and 36.8% (by weight) magnesium bromide.

The magnesium bromide–lithium bromide–water system was investigated from room temperature to the ternary eutectic temperature by the method of thermal analysis. Interest in this particular system stems from its desirable properties as an electrolyte for primary cells designed to operate at low temperature.

The binary system magnesium bromide–water, which makes up one side of this ternary system, has been described by Getman[1,2] from 100° to the eutectic temperature. Getman[1,2] in agreement with Panfiloff[3] and Menschutkin,[4] found two hydrates of magnesium bromide within this temperature range, *viz.*, the decahydrate and the hexahydrate.

Previous work, on the binary system lithium bromide–water, had been limited to solubility measurements from 0° to the higher temperatures. Bogorodski[5] investigated this system and reported the existence of the tri-, di- and monohydrates of lithium bromide. The composition and temperatures of transition between these hydrates were investigated, in a later study, by Hüttig and Reuscher.[6] These authors report the transition between lithium bromide trihydrate and lithium bromide dihydrate to take place at a temperature of +4° and at a composition of 59.18% (by weight) lithium bromide. The transition between the dihydrate and the monohydrate is given by Hüttig and Reuscher[6] to be 32° and a composition of 65.7% (by weight) lithium bromide; above 159° the anhydrous salt is stable.

The 25° isothermal equilibrium phase diagram for the ternary system magnesium bromide–lithium bromide-water has been described by Blidin.[7] This author reports no compound formation but he does report an area of solid solutions. However, in mixtures of anhydrous lithium bromide and magnesium bromide Ferrari and Colla[8] found by X-ray analysis, two series of mixed crystals, one being richer in magnesium bromide and the other being richer in lithium bromide with a very limited range of complete miscibility.

Voskresenskaya and Yanat'eva[9] investigated the closely related ternary phase system magnesium chloride–lithium chloride–water from 102° to the ternary eutectic temperature. The ternary eutectic temperature for the binary system lithium chloride–water was reported to be −66°.

Experimental

Since the temperature range of this system makes solubility measurements inconvenient, this investigation was carried out entirely by thermal analysis. The first step in this study was to investigate the two component systems magnesium bromide–water and lithium bromide–water. The three-dimensional phase diagram was then broken up into 25 two-dimensional sections for investigation: 10 passing through the water corner and extending to a plane cutting the H_2O–LiBr side at 59.48% and the H_2O–$MgBr_2$ side at 50.15% (KMNL, Fig. 3); 8 parallel to the LiBr–$MgBr_2$ side of the prism, between approximately 25% and 52% salt; and 7 running from the H_2O–$MgBr_2$ side, at approximately 59% and 48% LiBr.

Apparatus.—All freezing point determinations were made in a cryostat cell which consisted of an all-glass system composed of two sections connected by a 55/50 standard-taper, ground glass joint. The design facilitated the dismantling of the cell for cleaning purposes after a series of determinations. To eliminate the problem of supercooling a liquid-air cold finger was placed just below the ground glass joint. This cold finger was used to freeze a small amount of the solution under investigation which was in turn used to seed the main body of solution during a freezing point determination. The small amount of solution used for seeding was transferred for freezing to the cold finger and back again to the main body of solution for seeding by use of a glass tube 3 millimeters in diameter. This design made it possible to seed the sample with the correct solid phase at all times and also eliminated the concentration error involved by adding extraneous materials.

The upper part of the cryostat cell consisted of the inner member of the ground glass joint through which the stirrer, resistance thermometer or thermocouple well, and seeding rod was introduced. In addition the upper portion also contained a $^{14}/_{35}$ standard taper ground glass joint used for introducing the addition adapter. Accurately weighed amounts of a solution could be added to the cryostat cell by use of the addition adapter, which was designed to deliver the sample at the bottom of the cell and to avoid splashing on the walls which would introduce concentration errors. Agitation during a run was provided by a glass spiral stirrer attached to an eccentric on the shaft of a variable speed Cenco stirring motor resulting in vertical strokes of 3 centimeters. The optimum stirring speed was found to be approximately 100 strokes per minute.

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(1) F. Getman, *Rec. trav. chim.*, **54**, 866 (1935).

(2) F. Getman, *ibid.*, **57**, 847 (1938).

(3) J. Panfiloff, *J. Russ. Phys. Chem. Soc.*, **26**, 234 (1894).

(4) B. N. Menschutkin, *Z. anorg. Chem.*, **52**, 152 (1907).

(5) A. J. Bogorodski, *J. Russ. Phys. Chem. Soc.*, **26**, 209 (1894); **25**, 316 (1893).

(6) G. F. Hüttig and F. Reuscher, *Z. anorg. allgem. Chem.*, **137**, 155 (1924).

(7) V. P. Blidin, *J. Gen. Chem. U.S.S.R.*, **17**, 1590 (1947).

(8) A. Ferrari and C. Colla, *Atti. accad. Lincei*, **13**, 78 (1931).

(9) N. K. Voskresenskaya and O. K. Yanat'eva, *Bull. acad. soc. U.R.S.S.*, 99 (1937).

Temperature measurements were made by use of a copper–constantan thermocouple, and in certain areas of investigation where more sensitive measurements were necessary, by use of a glass enclosed platinum-resistance thermometer. The copper–constantan thermocouple was used in conjunction with the Leeds and Northrup Micromax recording potentiometer. Both the thermocouple and the resistance thermometer were calibrated against a standard resistance thermometer which had been calibrated at the National Bureau of Standards.

A Pyrex glass Dewar, constructed to fit around the lower portion of the cryostat cell, was used to insulate the cell from the coolant sufficiently so that a satisfactory cooling rate of approximately 1° per minute was obtained when liquid air was used as the cooling agent. The use of liquid air as the coolant resulted in a practically constant rate of cooling for a given run and eliminated tapering off of the cooling curve due to a decreasing cooling rate.

Reagents.—The lithium bromide used in this investigation was prepared from Mallinckrodt Analytical Reagent-grade lithium carbonate and Merck Reagent-grade hydrobromic acid. The lithium carbonate was washed several times in hot distilled water, then dissolved in a 40% solution of hydrobromic acid. The resulting acidified solution was concentrated, filtered and allowed to cool; crystals of lithium bromide dihydrate were deposited. These crystals were separated from the solvent by filtration and were recrystallized three times from double distilled water. The purity of the lithium bromide was checked by bromide analysis using the Fajans[10] method.

The magnesium bromide was a special, high purity material prepared by the Dow Chemical Company for this research.

Experimental Results

Compositions are reported in weight percentage. The following symbols will be used to represent the solid phases (which may be solid solutions) and invariant points involved: A, $MgBr_2 \cdot 10H_2O$; B, $MgBr_2 \cdot 6H_2O$; C, $LiBr \cdot 5H_2O$; D, $LiBr \cdot 3H_2O$; E, $LiBr \cdot 2H_2O$; F, ice; (a) $MgBr_2 \cdot 10H_3O$–$MgBr_2 \cdot 6H_2O$; (b) ice–$MgBr_2 \cdot 10H_2O$; (c) $LiBr \cdot 3H_2O$–$LiBr \cdot 2H_2O$; (d) $LiBr \cdot 5H_2O$–$LiBr \cdot 3H_2O$; (e) ice–$LiBr \cdot 5H_2O$; (f) $MgBr_2 \cdot 6H_2O$–$MgBr_2 \cdot 10H_2O$–$LiBr \cdot 3H_2O$; (g) $MgBr_2 \cdot 10H_2O$–$LiBr \cdot 3H_2O$–$LiBr \cdot 5H_2O$; (h) ice–$LiBr \cdot 5H_2O$–$MgBr_2 \cdot 10H_2O$ (ternary eutectic).

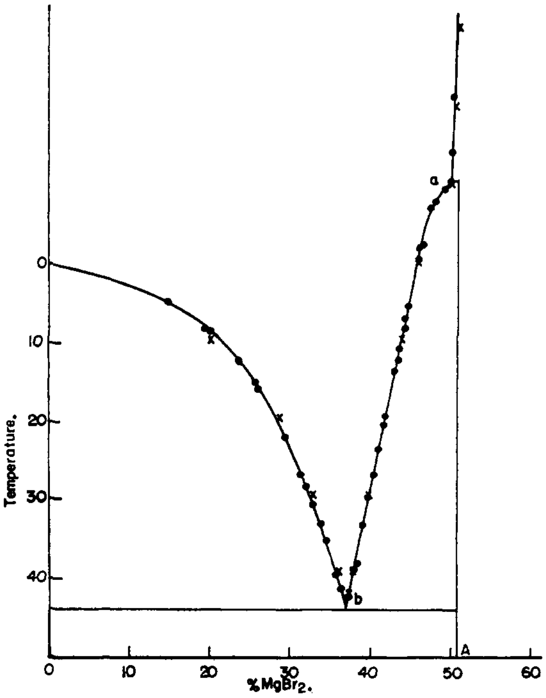

Fig. 1.—System $MgBr_2$–H_2O: ×, Getman; ●, this work; A = $MgBr_2 \cdot 10H_2O$.

The freezing point diagram for the binary system $MgBr_2$–H_2O is shown in Fig. 1. The results obtained agree well with Getman's data, included for comparison. The transition point *a*, between the hydrate $MgBr_2 \cdot 10H_2O$ and $MgBr_2 \cdot 6H_2O$, was determined by the intersection of the solubility curves to be at +10.5° with 49.7% $MgBr_2$; Getman reported 10.84°. The eutectic point b, similarly determined by intersection of the ice and $MgBr_2 \cdot 10H_2O$ curves, occurs, with 36.8%, $MgBr_2$, at −44.0° (−42.7° according to Getman).

The LiBr–H_2O system, shown in Fig. 2, has not previously been investigated at lower temperatures. The transition point c, between $LiBr \cdot 3H_2O$ and $LiBr \cdot 2H_2O$, was found to occur at +5.0° and 59.0% LiBr, in good agreement with Hüttig and Reuscher's data.

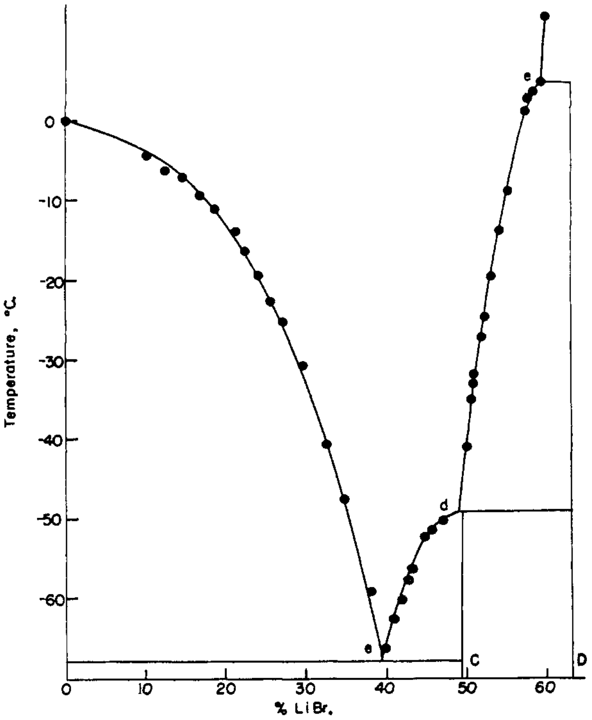

Fig. 2.—System LiBr–H_2O: C = $LiBr.5H_2O$; D = $LiBr \cdot 3H_2O$.

A new hydrate of LiBr was found at low temperature, with a solubility curve running from the eutectic e, at 67.5° and 39.3% LiBr, to the point d. From the shape of this solubility curve, the new phase seems to be an incongruently melting pentahydrate; the metastable maximum of the curve would then be expected at 49.1% LiBr, corresponding to $LiBr \cdot 5H_2O$. The transition point d, fixed by the intersection of the curves for this hydrate and $LiBr \cdot 3H_2O$, may be taken as −49° and 48.9% LiBr.

Additional evidence of this hydrate being the pentahydrate is the fact that a 50.05% (by weight)

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(10) K. Fajan and W. Steiner, *Z. physik. Chem.*, **125**, 309 (1927).

solution of lithium bromide completely solidifies at a temperature of −49.0°. If this were tetrahydrate, the solution would not solidify completely until the eutectic temperature (−67.5°) was reached. Further evidence in favor of the pentahydrate is obtained on comparing the closely related systems lithium chloride–water and lithium bromide–water. The mono-, di-, tri- and pentahydrates of lithium chloride are known, whereas to the present only the mono-, di- and trihydrates of lithium bromide have been reported.

The eutectic point (e) of this system was found, from the intersection of the salt and ice liquidus lines, to be at a temperature of −67.5° and at a concentration of 39.9% (by weight) lithium bromide.

The ternary phase system magnesium bromide–lithium bromide–water is represented by use of a right triangular prismatic diagram (Fig. 3). This diagram is arranged so that the concentrations are plotted on an equilateral triangle and the temperature upon an axis perpendicular to this triangle. The edges of the prism represent the state of the three components at different temperatures, and its sides show the temperature–concentration diagrams of the binary systems formed between each pair of the components of the ternary system.

This system of two salts and water can be classified as one in which there are no double salts formed, over the temperature range investigated, but each salt forms hydrates. Points b and e (Fig. 3) represent the eutectic points for the two component systems magnesium bromide–water and lithium bromide–water, respectively. The transition point between magnesium bromide decahydrate and magnesium bromide hexahydrate falls at point a. At d the transition between lithium bromide trihydrate and lithium bromide pentahydrate occurs whereas at c lithium bromide dihydrate is in equilibrium with the trihydrate.

The five surfaces sketched represent liquids saturated with the single solid phase as indicated. The lines along which two surfaces meet are ternary liquids saturated with two solids, and the points f, g, h represent liquids (condensed invari-

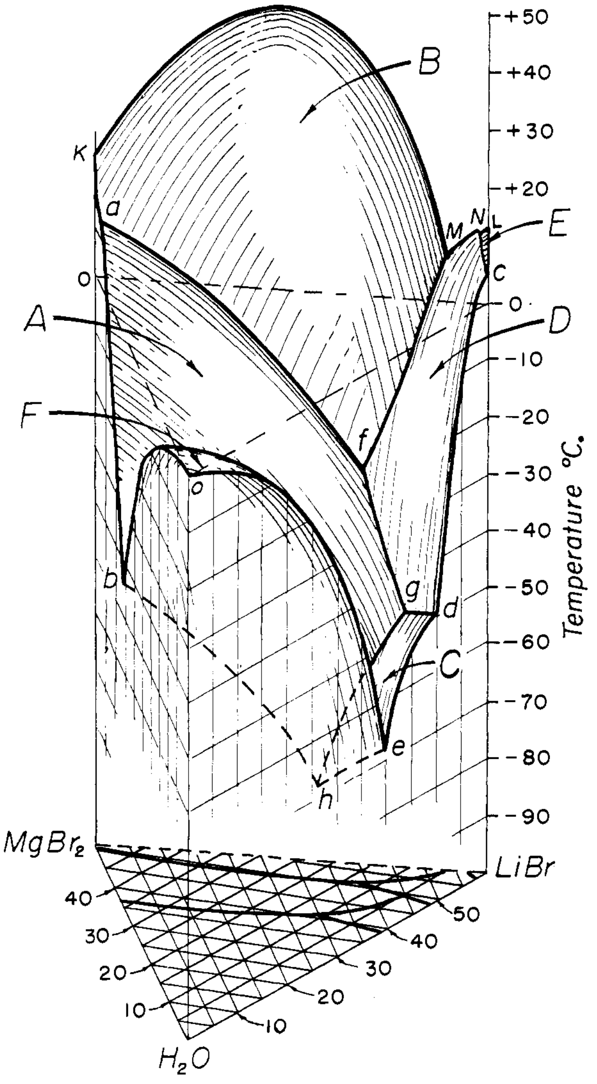

Fig. 3.—The $MgBr_2$–$LiBr$–H_2O phase system.

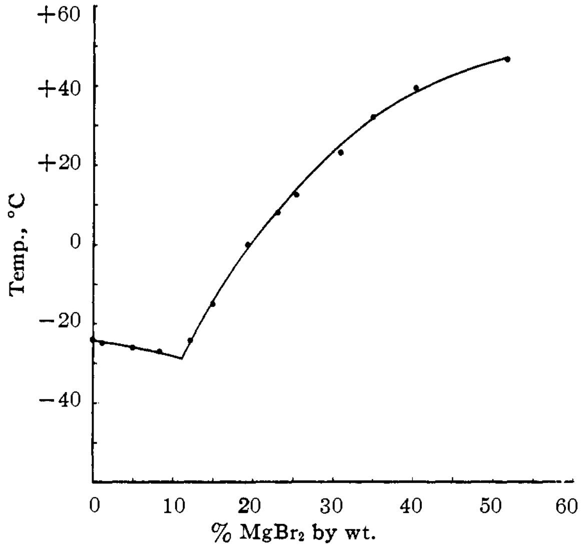

Fig. 4.—Two-dimensional section no. 19 along the 48% (by wt.) H_2O line.

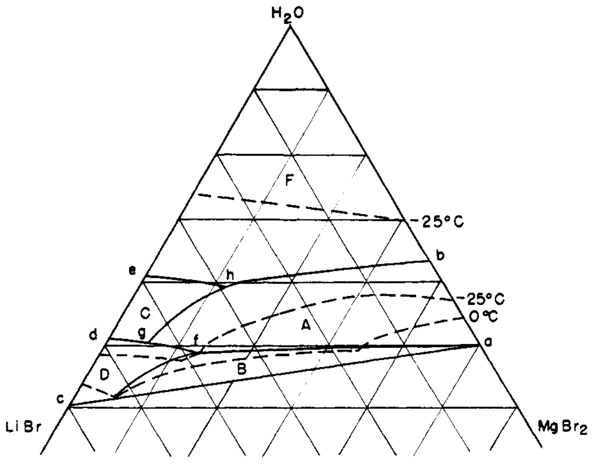

Fig. 5.—System $LiBr$–$MgBr_2$–H_2O, polytherm projection, including isothermal contours at 0° and −25°.

ants) saturated with three solids. Point h is the ternary eutectic, with ice, $MgBr_2 \cdot 10H_2O$ and $LiBr \cdot 5H_2O$ as its solids. The compositions and temperatures of these points are as follows

	Solid phase	Temp., °C.	$MgBr_2$, %	LiBr, %
f	A, B, D	−27.0	12.0	38.5
g	A, D, C	−50.0	4.8	44.2
h	A, C, F	−78.0	11.3	29.5

Projection of the ternary curves on the base of the prism yields a plot (Fig. 5) which gives a good comparison of the area that each of the five solid phases covers.

Within the temperature range of this investigation no double salt formation was found. The two-dimensional section No. 19 (Fig. 4), which is the 48.0% (by weight) water-line, clearly shows the absence of any double salt formation. This is in agreement with Blidin[7] who found no compound formation in the magnesium bromide–lithium bromide–water phase system at +25°. However, the ternary phase system magnesium chloride–lithium chloride–water, as investigated by Voskresenskaya and Yanat'eva,[9] does show a considerable area of double salt formation. The constitution of this double salt was found to be one mole lithium chloride to one mole of magnesium chloride and it was found to exist in the form of two hydrates.

Isothermal contours at 0° and −25° have been plotted from the freezing point data and are included in Fig. 5. The solid phases A, B and D are found in 0° contour and −25° contour includes the solid phases A, B, D and F.

No investigation for the existence of solid solutions was carried out.

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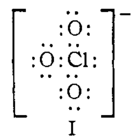
NOTES

Non-exchange of Chlorine between Chlorate and Perchlorate Ions[1]

By D. A. Lee

Received January 11, 1954

Taube and Dodgen[2] have studied the mechanism of interaction of chlorine oxidation states. They made no attempt to exchange chlorine between chlorate and perchlorate. The structure of perchlorate and chlorate ions are known to have Cl–O bonds which are shorter than the sum of the single-bond covalent radii for the atoms.[3] Pauling[4] attributes this bond shortening to double bond character. This picture provides a possible mechanism for an effective exchange of chlorine atoms between chlorate (I) and perchlorate (II) ions, by transfer of an oxygen atom.



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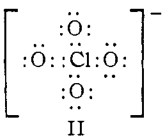

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Pitzer[5] states that bond shortening in these ions is not necessarily due to pi-bonding. This is also supported by the molecular orbital treatment of the structure of the perchlorate ion by Wolfsberg and Helmholz.[6] Since oxygen in perchlorate and chlorate does not exchange with oxygen in water[7] no intermediate involving water can be postulated. Therefore, a very slow oxygen transfer would be expected.

The experiments performed in this Laboratory show that there is no exchange of chlorine between chlorate and perchlorate ions in water solution at room temperature in two years. Also, there is no exchange in 0.1 N H_2SO_4 and 0.1 N NaOH in 19.5 hours. Increasing the temperature to 99° did not increase the exchange rate in one hour.

TABLE I

ACTIVITIES AFTER EQUILIBRATION

System	Equil., time	Act., c./min./γ AgCl	
		ClO_3^-	ClO_4^-
0.056 N $KCl^{36}O_3$ + 0.056 N $NaClO_4$ in water	2 min.	33.3	0.06
0.056 N $KCl^{36}O_3$ + 0.056 N $NaClO_4$ in water	19 hr. 45 min.	36.2	0.06
0.056 N $KCl^{36}O_3$ + 0.056 N $NaClO_4$ in 0.1 N H_2SO_4	19 hr. 34 min.	38.2	0.07
0.056 N $KCl^{36}O_3$ + 0.056 N $NaClO_4$ in 0.1 N NaOH	19 hr. 25 min.	35.9	0.02
0.056 N $KCl^{36}O_3$ + 0.056 N $NaClO_4$ in water	1 hr.[a]	47.0	0.00
0.056 N $KCl^{36}O_3$ + 0.056 N $NaClO_4$ in water	2 yr.	66.4[b]	1.04
0.056 N $KCl^{36}O_3$ + 0.056 N $NaClO_4$ in water with platinum black	2 yr.	66.1[b]	−0.03
0.056 N $KCl^{36}O_3$ + 0.056 N $NaClO_4$ in water with V_2O_5	2 yr.	65.0[b]	0.79

[a] 99°. [b] Higher activities are due to a different geometry in the counting apparatus.

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[1] This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] H. W. Dodgen and H. Taube, This Journal, **71**, 2501, 3330 (1949).

[3] R. G. Dickinson and E. A. Goodhue, *ibid.*, **43**, 2045 (1921); W. H. Zachariasen, *Z. Krist.*, **71**, 517 (1929); This Journal, **53**, 2123 (1931).

[4] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 227.

[5] K. S. Pitzer, This Journal, **70**, 2140 (1948).

[6] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[7] E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *J. Chem. Soc.* 131 (1940).