

in Table III then give about 184–187 kcal./mole for the heats of formation of 2-pentyl and 3-pentyl ions. This is not at all in agreement with a heat of formation derived from the appearance potential of what might be expected to be a *s*-pentyl fragment ion. For instance, we find that $A(C_5H_{11}^+)$ from 2-methylpentane is 10.61 v., using the curve matching procedure.¹⁵ This gives $\Delta H_f(C_5H_{11}^+) \leq 172$ kcal./mole, that is, about 14 kcal./mole lower than the value derived above for 2-pentyl ion. One possibility is that this fragment ion is a 2-pentyl ion in a configuration which contains some 14 kcal./mole less energy than that formed by direct ionization of a 2-pentyl radical. On this basis the vertical ionization potential would have to be at least 0.6 v. higher than the adiabatic value. It is also possible that in this dissociative ionization the 2-pentyl ion is isomerized to a *t*-pentyl ion, for which $\Delta H_f = 165$ kcal./mole, with an excess energy of about 7 kcal./mole. In view of the formation of

(15) Using the vanishing-current method, the appearance potential is 10.65 v. Koffel and Lad,¹¹ using the linear extrapolation method, also found 10.6 v. for this appearance potential. In this case the ionization efficiency curves for mass 71* and the xenon standard were found to be very nearly parallel when normalized to the peak height at 50 v. and plotted on a logarithmic scale. For curves of this type appearance potentials obtained by the linear extrapolation method can be quite close to those obtained by the other methods.

s-pentyl ions from normal alkanes,⁶ such a rearrangement is not unreasonable.

From the appearance potentials of $C_5H_{11}^+$ ions from *n*-heptane and *n*-octane, Stevenson⁶ obtained the relation $D(s-C_5H_{11}-H) + I(s-C_5H_{11}) = 10.88$ v. Assuming $D(s-C_5H_{11}-H) = 93$ kcal./mole, as above, this relation leads to an ionization potential of 6.85 v. This is about one volt lower than the vertical ionization potential found in this work, and is in fact, slightly lower than that found for *t*- C_5H_{11} radical. A re-measurement of the appearance potential for $C_5H_{11}^+$ from *n*-heptane in our instrument, however, gave 10.8 v.¹⁶ The difference between this and the 10.1 v. reported by Stevenson appears to be too large to be accounted for on the basis of different methods for evaluating the ionization threshold. No explanation for the difference can be offered at present. Although both of these values are consistent with a rearrangement of the pentyl ion from the original primary structure, the uncertainty is so great that no decision can be made at present as to whether the rearranged ion is a secondary or a tertiary ion.

(16) When normalized to the 50 v. peak height, the curves for $C_5H_{11}^+$ and xenon were parallel within 0.1 v. between 1% and 0.1% of the 50 v. peak height. Evaluation of the curves by the vanishing current method gave the same value, 10.8 v.

[CONTRIBUTION FROM THE RENSSELAER POLYTECHNIC INSTITUTE, TROY, N. Y.]

The Reaction of Carbon Suboxide with Oxygen Atoms

By H. VON WEYSENHOFF,¹ S. DONDES AND P. HARTECK

RECEIVED OCTOBER 27, 1961

The reaction of carbon suboxide C_3O_2 with oxygen atoms in a fast flowing gas system was investigated. Oxygen atoms were produced in a Wood discharge tube. Carbon suboxide was introduced into the atom gas stream through a small nozzle. In the reaction zone, a spherical flame occurred. The spectrum of this flame featured the "triplet" bands of carbon monoxide due to the transition $CO(d^3\Pi) \rightarrow CO(a^3\Pi)$. In addition, some of the Swan bands and the persistent CH bands were observed, the latter being attributed to minor impurities. The gas mixture evolving from the reaction was analyzed for CO and CO_2 by means of gas chromatography. The molar ratio CO/CO_2 was found to be about 14:1. No carbon deposit was formed at the walls. A reaction scheme is discussed which is consistent with the observed results. The experiments were carried out to confirm some features of the mechanism suggested in 1955 by Harteck and Dondes for the radiolysis of carbon monoxide and carbon dioxide.

Introduction

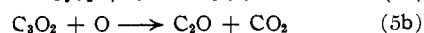
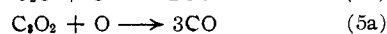
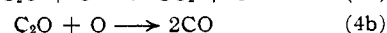
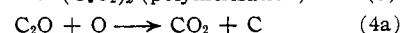
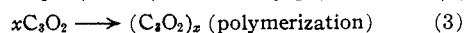
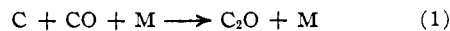
The mechanisms controlling the radiolysis of carbon monoxide, the radiolytic oxidation of carbon monoxide in the presence of oxygen and the surprising stability of carbon dioxide against ionizing radiation² can be understood if the typical features of these processes are assumed to depend on the intermediate presence of carbon suboxide species like C_2O or C_3O_2 .

Based on this assumption, Harteck and Dondes³ have proposed the following reaction scheme in which carbon atoms and oxygen atoms are supplied by direct radiative dissociation or by ion reactions in the systems mentioned.

(1) Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

(2) For comprehensive reference see: S. C. Lind, "Radiation Chemistry of Gases," Reinhold Publishing Co., New York, N. Y., 1961, pp. 112–123, 143–145.

(3) P. Harteck and S. Dondes, *J. Chem. Phys.*, **23**, 902 (1955); *ibid.*, **26**, 1727 (1957); *Z. Elektrochem.*, **64**, 983 (1960).



The reactions in irradiated pure CO will essentially follow equations 1, 2, 3 and 4a yielding suboxide polymers and CO_2 . The high G-value of 18–24² for the oxidation of CO in presence of oxygen and also the stability of CO_2 to ionizing radiation may be explained by means of chain reactions which are constituted by equations 1 and 4a, or 2 and 5b. This explanation implies, however, that one of these chain reactions is considerably faster than all competing and terminating reactions such as (4b) and including the three-body recombinations as well as the direct combi-

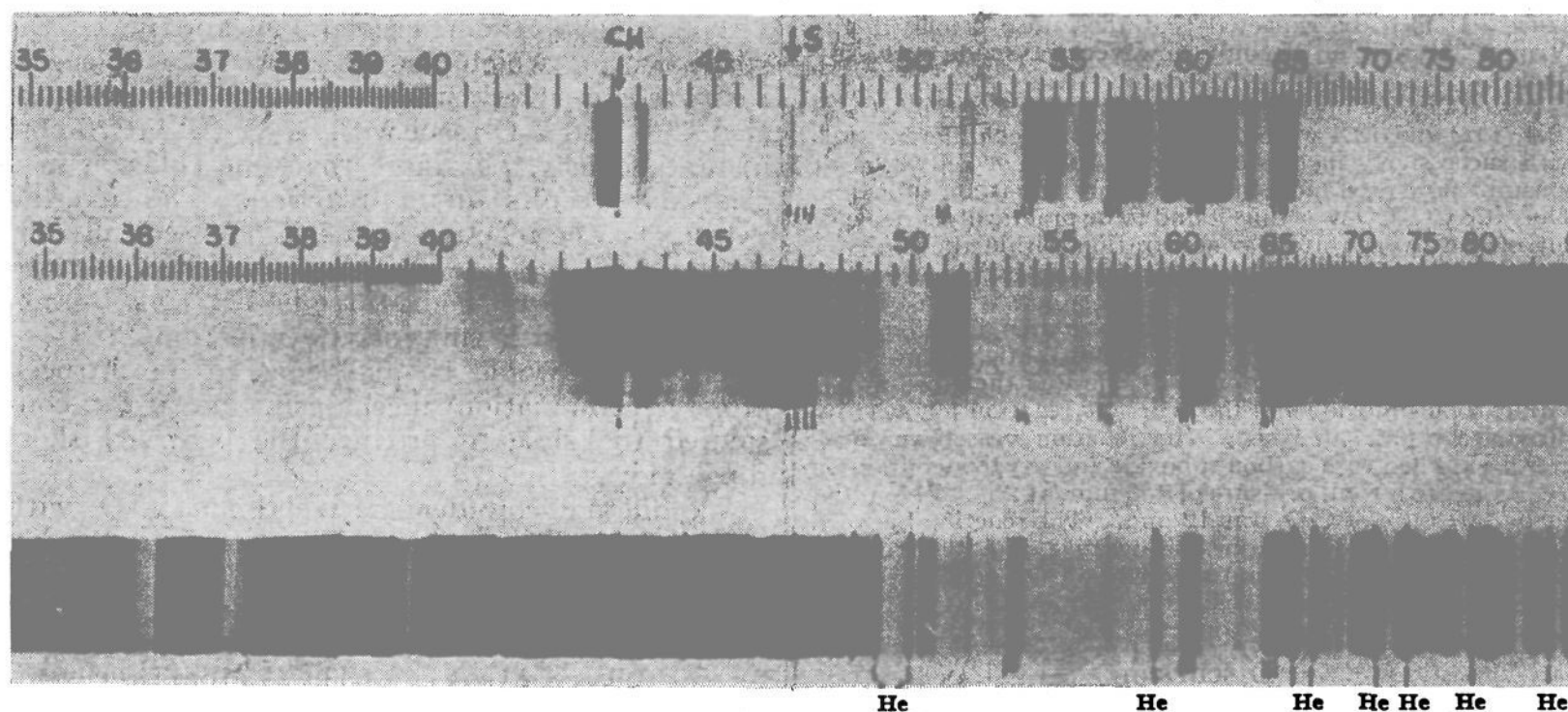
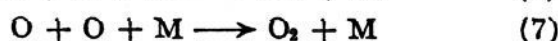


Fig. 1.—Top: flame spectrum on Kodak ID2 plate.

Fig. 2.—Middle: flame spectrum on Kodak IN plate.

Fig. 3.—Lower: discharge spectrum of helium with 1% of carbon monoxide on Kodak IN plate.

The triplet bands of the carbon monoxide are marked in all figures by triple lines ('''); S for Swan bands; CH for CH bands; the lines designated by He in Fig. 3 are helium lines from the discharge.



nation of CO and O.⁴ The lack of direct evidence for this mechanism has as yet prevented its general acceptance.

Therefore, the reaction of oxygen atoms with carbon suboxide C₃O₂ was studied under experimental conditions (pressure of about 2 mm. and relatively high O-atom concentration) in which the stepwise oxidation of C₃O₂ according to (5a,b) and (4a,b) could be observed. The results present strong support for the postulated mechanism, although no direct evidence could be obtained at the low pressures used for the three-body reactions 1 and 2 which initiate the chain reactions mentioned above. These reactions will, however, be sufficiently fast at the pressures of 1 atmosphere and higher which are used in all radiolysis experiments.^{2,3}

Experiments and Results

Reaction of C₃O₂ with O-atoms.—The reaction was carried out in a fast stream of oxygen atoms which was produced in a Wood discharge tube supplied by an a.c. current of 400 ma. at 2000 v. A mixture of 80% argon and 20% oxygen was used to obtain a high rate of dissociation into atoms at a low concentration of oxygen molecules. The oxygen was purified by distillation at liquid nitrogen temperature. The pumping velocity was 1.5 l./sec. at a pressure of about 2 mm. which was measured by a U-tube oil manometer. The reaction tube was of 20-cm. length and 42-mm. inner diameter. Carbon suboxide was blended into the gas stream through a nozzle which was mounted at the upstream end of the reaction tube with its orifice directed downstream. Perpendicular to the center of the reaction (flame) zone, a quartz window was mounted to observe radiation emitted from the reacting gases in the visible and ultraviolet region.

(4) A rate constant of $k = 8 \times 10^{-15} \times \exp(-3700/RT)$ cc./sec. has recently been reported for the second order reaction $\text{CO} + \text{O} \rightarrow \text{CO}_2 + h\nu$ by B. H. Mahan and R. B. Solo at the 139th meeting of the American Chemical Society, St. Louis, Mo., 1961 (see Abstract of Papers, p. 24R).

The carbon suboxide was prepared from malonic acid and phosphorus pentoxide and purified as described by Long, Murfin and Williams.⁵ A small fraction of the gas evolving from the reaction was collected by means of a Toepler pump and analyzed by gas chromatography with a Perkin-Elmer Vapor Fractometer using a charcoal column of 2-m. length at 45°. The molar ratio of CO to CO₂ was obtained by this analysis.

When the discharge was turned on, and no C₃O₂ mixed in, a weak background of the usual oxygen afterglow due to minor amounts of NO was seen extending through the entire system. As C₃O₂ was added this afterglow diminished gradually, indicating the consumption of oxygen atoms. At the same time, a yellowish reaction glow of spherical shape appeared in front of the nozzle increasing to a diameter of 3 cm. Spectrograms of the reaction glow were taken with a Hilger Medium Quartz Spectrograph on high speed Kodak IN and ID2 plates. A spectrogram of the flame, with a slight excess of oxygen atoms, is shown in Fig. 1. It was taken on a ID2 plate and was exposed for 1 hr. The bands at 4310 and 4350 Å. are CH bands. Other bands were identified⁶ as

- (1) Swan bands of C-C at 4737, 4715, 4698 and 4684 Å. These are relatively weak.
- (2) Triplet bands of CO: (d³Π) → (a³Π) at

6465, 6433, 6401 Å.; v' = 0 → v'' = 0	strong
6037, 6011, 5982 Å.; v' = 1 → v'' = 0	strongest
5671, 5648, 5624 Å.; v' = 2 → v'' = 0	weak
5351, 5331, 5308 Å.; v' = 3 → v'' = 0	weak
5071, 5053, 5033 Å.; v' = 4 → v'' = 0	weak
4823, 4807, 4787 Å.; v' = 5 → v'' = 0	very weak

Another spectrogram taken under the same conditions on an IN plate features strong additional bands between 7000 and 8000 Å. (Fig. 2). For comparison, a spectrogram of a discharge through helium with 2% CO⁷ was taken (Fig. 3). It shows the triplet bands listed above and bands at wave lengths beyond 6500 Å. which are not listed in Pierce and Gaydon but which agree well with those found in the C₃O₂-

(5) D. A. Long, F. S. Murfin and R. L. Williams, *Proc. Roy. Soc. (London)*, **A223**, 251 (1954).

(6) R. W. B. Pierce and A. G. Gaydon, "The Identification of Molecular Spectra," London, 1950.

(7) T. R. Merton and R. C. Johnson, *Proc. Roy. Soc. (London)*, **103**, 383 (1923).

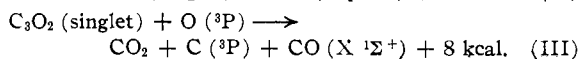
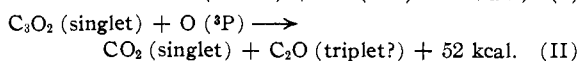
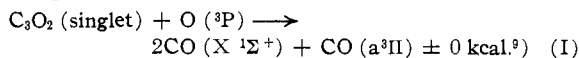
flame. It is to be expected that these also belong to the "triplet" system; no attempt, however, was made to classify them.

With an excess of oxygen atoms, the values of $\text{CO}/\text{CO}_2 = 12.4, 14.2$ and 13.4 were obtained from three different runs with successively increasing oxygen atom concentration at constant flow rate and constant supply of carbon suboxide. The ratio CO/CO_2 was thus found to be practically independent of the oxygen atom concentration within the limits of experimental error as long as there was an excess of oxygen atoms.⁸

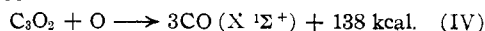
Reaction of C_3O_2 with Ozone.—It was thought to be valuable to see whether ozone would substantially enter the mechanism of these reactions. Ozone was therefore mixed with carbon suboxide and the course of reaction followed by chromatographic analysis. The reaction vessel was a 2-liter flask, filled with carbon suboxide and oxygen, containing 5% ozone, to a total pressure of 450 mm. at 25° . The initial partial pressure of C_3O_2 was 12 mm. The reaction between C_3O_2 and O_3 was found to be so slow that, after 30 hr., only half of the initial C_3O_2 had reacted to CO and CO_2 , which were formed in approximately equal amounts, in contrast to the reaction with oxygen atoms.

Discussion

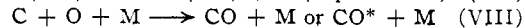
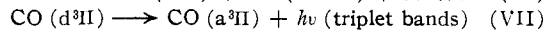
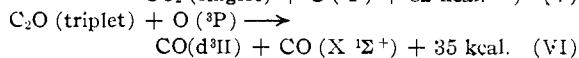
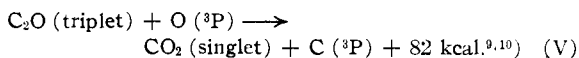
The results obtained on the reaction between C_3O_2 and oxygen atoms and consideration of energetic relations and spin conservation suggest the possibilities



The reaction



is not spin conservative and may, therefore, be considered to be slower than (I). The spin conservation indicates that the radical C_2O exists in a triplet state. Reaction II can be expected to be more favorable than reaction III because two bonds are to be broken in the latter reaction as compared to only one in the former. It can be seen that excitation of the CO to the ($d^3\Pi$) level is energetically impossible by reaction I unless the true heat of formation of C_3O_2 is much below the estimated value. It is, therefore, much more likely that the $\text{CO} (d^3\Pi)$, which accounts for the observed CO flame, is formed by reaction of C_2O and O as in reaction VI



(8) In another run in which the argon was replaced by helium, less oxygen atoms were produced. There was, therefore, a slight excess of C_3O_2 (this excess of C_3O_2 could be condensed in a trap past the reaction tube). The ratio CO/CO_2 was found to be in the order of 80 in this case.

(9) Heats of reaction are estimated values. It is assumed that the heats of formation from atoms of C_3O_2 and C_2O are about -630 and -300 kcal., respectively. These values are derived from the addition rule of chemical bonds, taking 174 kcal. for a $\text{C}=\text{O}$ bond in ketones (L. Pauling, "The Nature of Chemical Bond," 3rd Ed., Cornell Univ. Press, 1960, p. 189), and 125 kcal. for a $\text{C}=\text{C}$ bond in ketone (N. N. Semenov, "Some Problems of Chemical Kinetics," Vol. 4, Pergamon Press, 1958, p. 136, and adding about 30 kcal. to the value for C_3O_2 as a contribution of resonance structures (Pauling, *loc. cit.*, p. 267).

(10) There was no experimental evidence for the formation of the carbon atom in an excited state ($1D$ or $1S$).

The zone of the reaction glow and hence the space within which the reaction takes place is restricted to a very small volume. This indicates that C_3O_2 and C_2O react with oxygen atoms almost instantaneously, *i.e.*, more than one collision in a thousand results in a reaction. The over-all velocity of the reaction seems to be essentially determined by the rate of diffusion of the C_3O_2 into the oxygen stream. The three-body recombination of C and O with subsequent transition ($d^3\Pi$) \rightarrow ($a^3\Pi$), which would be analogous to the nitrogen atom recombination mechanism, must be considered too slow to produce the observed short range glow.

We did not consider the reaction of C_3O_2 with O_2 molecules, because as explained in the preceding section the reaction of C_3O_2 with O_2 molecule (containing 5% ozone) was exceedingly slow. We did not consider the reaction of C_2O with O_2 molecules for the following reasons. The O -atom concentration is larger under the experimental conditions of this paper than the concentration of the O_2 molecules. Since in all known cases O -atoms react much faster than O_2 molecules, this fact is certainly pertinent for the reaction with C_2O . The relative rates of reaction of O_2 molecule and O -atoms where (O_2) \gg (O) will be discussed in a later paper (in preparation) based on experiments on the irradiation of CO_2 and of $\text{CO} + \text{O}_2$ mixtures. In this work it has been found that in irradiation of CO_2 with ionizing radiation the addition of I_2 (which prevents the O -atom formation by ion recombination) hinders the reformation of CO_2 by reaction 4a. This could not be the case, if O_2 were to react fast with C_2O .

The origin of the Swan bands cannot be explained within the proposed scheme of reaction. They are believed to arise from impurities contained in the carbon suboxide. The same refers to the persistent CH -bands.

It can be seen from the observed molar ratio of CO and CO_2 (13.5 in the average) that reaction I is from 4 to 9 times faster than the competing reaction II depending on the relative velocities of the subsequent reactions, V and VI. The relatively low intensity of the glow (not more than 10^{16} quanta/sec) indicates that only a small fraction of all reactions of C_2O and O leads to the formation of the $\text{CO}(d^3\Pi)$ state according to reaction VI. It should be remarked that excitation to the ($d^3\Pi$) level (7.72 eV. above ground state) is extremely unusual in chemical reactions at lower temperatures even when radicals and atoms are involved.

With an oxygen atom concentration of about 5%, it can be estimated that less than one hundredth of the O -atoms react according to (VI) with subsequent emission. Based on this result and the observed ratio of CO/CO_2 , estimates of the relative rates of reactions I and II, and reactions V and VI are: $k_I/k_{II} \sim 9$ and $k_V/k_{VI} \sim 10$.

Carbon atoms resulting from reaction V seem to undergo recombination with either CO or O -atoms since no carbon deposit was found at the walls. No statement may be made as yet about the relative reaction rates of C_3O_2 and C_2O with oxygen atoms. It is true that the existence of the free radical C_2O is confirmed only by indirect

evidence, but this evidence has gained further support by the recent work of Bayes¹¹ on the photolysis of carbon suboxide.

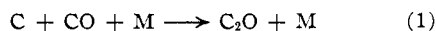
Conclusions.—The experimental results may be summarized by

(a) C_3O_2 reacts extremely fast with oxygen atoms with CO as a chief product. To a small fraction, however, C_2O and CO_2 are formed.

(b) The radical C_2O reacts in two alternative ways with oxygen atoms. The faster reaction yields C and CO_2 , whereas $2CO$, one in an excited triplet state, are formed to a smaller extent.

(c) Ozone reacts with C_3O_2 in a different way than oxygen atoms. The reaction with ozone is extremely slow.

These results strongly support the suboxide mechanism⁸ proposed for the radiolysis of carbon-oxygen systems. They also show that, of the two chain reactions 1, 4a; and 2, 5b, only the first



(11) K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).



can occur because of the very fast reaction of C_2O with O-atoms.

In irradiated CO, however, reaction 2 may also occur due to the high concentration of CO. A chain reaction will not take place in this case since the terminating reaction 3 dominates.

The chemical kinetics of the carbon suboxide reactions are of great importance not only for the radiolytic but also photochemical and combustion processes in carbon-oxygen systems. They must be taken into consideration in any study of the chemistry of planetary atmospheres containing substantial amounts of carbon monoxide and carbon dioxide.

Acknowledgments.—This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(30-3)-321, Task I. The authors would like to acknowledge the aid and encouragement of Dr. L. G. Bassett and also Dr. R. R. Reeves for experimental assistance.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY,³ P. O. BOX X, OAK RIDGE, TENNESSEE, AND UNIVERSITY OF MAINE, ORONO, MAINE]

The Evaluation of Thermodynamic Association Constants in Solutions with an Application to Molten Salt Solutions

BY J. BRAUNSTEIN,¹ M. BLANDER AND R. M. LINDGREN²

RECEIVED JUNE 29, 1961

The evaluation of thermodynamic association constants in solution is discussed and is applied to molten salt systems. The calculated association constants K_1 , K_2 and K_{12} for the formation of the species $AgCl$, $AgCl_2^-$ and Ag_2Cl^+ , respectively, in molten KNO_3 at 385° are 460 ± 15 , 169 ± 20 and $20 \pm 10 \left(\frac{\text{moles}}{\text{mole } KNO_3} \right)^{-1}$. A recalculation of the association constants, K_1 , for the species $CdCl^+$ and $PbCl^+$ from cryoscopic, polarographic and from solubility data in nitrate melts indicates that the greater part of the very large discrepancies in the published values of K_1 is a result of the incorrect analysis of the data.

Introduction

In this paper, the determination of thermodynamic association (formation) constants in solution is discussed. Although our methods of calculation are here applied to molten salt solutions only, they may be used with modifications for other types of solutions.

To be able to test theories of association a reliable determination of association constants is required. Many of the methods of evaluation used⁴⁻⁷ often lead to uncertainties in the values of the association constants which are greater than the uncertainties warranted by the precision of the data, particularly when a single method is used for different systems without regard for the relative

magnitude of the association constants. It is the purpose of this paper to discuss methods which eliminate the uncertainties caused merely by the imprecise manipulation of data. We shall discuss the evaluation of formation constants for associations of Ag^+ and Cl^- in molten KNO_3 at 385° from our published data⁸ supplemented with new data. As a further illustration we will show that the greater part of the very large apparent inconsistency in the published values for association constants for the formation of $CdCl^+$ and $PbCl^+$ in molten nitrates⁹⁻¹¹ may be removed by a new and improved analysis of the data.

No single method of calculation of association constants is possible, since each set of data or type of measurement requires a somewhat different analysis. We do, however, include the following guiding principles in our analysis which are not all included in the most common methods of calculation used.

A. The extrapolation function used in the evaluation of the association constants, the values of

(1) On sabbatical leave from the University of Maine (1960-1961) with the Reactor Chemistry Division of Oak Ridge National Laboratory.

(2) N.D.E.A. Fellow at the University of Maine.

(3) Operated for the United States Atomic Energy Commission by the Union Carbide Corporation.

(4) I. Leden, *Z. physik Chem.*, **A188**, 160 (1941).

(5) S. Fronaeus, *Acta. Chem. Scand.*, **4**, 72 (1950).

(6) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

(7) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Company, New York, N. Y., 1961.

(8) J. Braunstein and M. Blander, *J. Phys. Chem.*, **64**, 10 (1960).

(9) E. R. Van Artsdalen, *ibid.*, **60**, 172 (1956).

(10) J. H. Christie and R. A. Osteryoung, *J. Am. Chem. Soc.*, **82**, 1841 (1960).

(11) F. R. Duke and M. L. Iverson, *J. Phys. Chem.*, **62**, 417 (1958).