PREFACE

The present volume is the second of four volumes planned for inorganic metal halates. The first, on *ALKALINE EARTH METAL HALATES*, was published in 1983 (1), and two more volumes, on copper and silver halates, and on transition and rare earth metal halates are in course of preparation.

The alkali and alkaline earth metal halates have an important place in the history of both theoretical and practical analytical chemistry. In 1848, Berthelot, in France, described the use of potassium iodate as a standard titrant for the determination of iodide, and the well established method for determining phenol with excess bromate-bromine reagent in acid solution was first described by Knop in 1845, and further developed by Koppeschaar in 1875. Important practical applications of halate chemistry include their use in pyrotechnics, and in the paper pulp industry for the generation of chloric dioxide blanching agent.

In spite of the long history on the chemistry of alkali metal halates, the reader will discover that there are still considerable uncertainties in the nature of solid phases and transition temperatures for a number of systems: e.g. we can cite the binary systems $LiIO_3$ - H_2O and HIO_3 - H_2O. Hopefully, this volume will serve as a guide for future studies on these systems.

The literature of the solubilities of alkali metal halates was covered through the first half of 1984, and we believe this survey to be complete. In a few instances, relevant papers were not compiled since it was not possible to obtain either reprints or other reproductions of the original publication. We were, for example, unable to obtain the paper in Ref. (2), and this publication was omitted from this volume. A number of publications were not compiled or referred to in the critical evaluations for a variety of reasons. In Ref. (3), $KClO_3$ was stated to be "appreciably soluble" in liquid SO_2, and in Ref. (4) only partial phase diagrams were given for several ternary $NaClO_3$ systems with no numerical solubility data. Some publications dealing with solubilities in non-aqueous solvents were not compiled as the authors stated various alkali metal halates were "insoluble" (5-7) without providing numerical information.

To arrive at either *recommended* or *tentative* solubility values, we generally applied a statistical treatment similar to that recommended by Cohen-Adad (8) based on the thermodynamic treatment of saturated solutions and their equilibrated solid phases (8-10) as discussed in the *INTRODUCTION TO THE SOLUBILITY OF SOLIDS IN LIQUIDS* found in this volume. These thermodynamic treatments show that for binary systems, solubilities over the complete range of ice as the solid phase to the melting of the pure solute can be expressed by

$$Y = A/(T/K) + B\ \ell n\ (T/K) + C + D(T/K) \qquad [1]$$

The complex Y term in eq. [1] takes different forms depending upon the concentration units employed. In the present volume, the evaluators have analyzed solubilities based on mole fraction and mass units, and in terms of mole fraction units, the complex Y term (called Y_x throughout this volume) is given by (8-10).

$$Y_x = ln \left\{ \chi^{v(1-\chi)r}(v + r)^{v+r} / \left[r^r(1 + \chi)^{v+r} \right] \right\} \qquad [2]$$

where r is the solvation number in the solid phase, v is the number of ions produced upon dissolution, and χ is the mole fraction solubility. When sufficient data were available, the evaluators used eq. [2] in a four parameter fit to eq. [1]: note that for the ice polytherm, v = 0 and r = 1.

For solubilities expressed in mol kg^{-1} units, the evaluators used a simpler form of Y referred to as Y_m throughout this volume. Y_m is given by (see 8-11 and the INTRODUCTION to this volume):

$$Y_m = \ell n\ (m/m_0) - rM(m - m_0) \qquad [3]$$

where r is the solvation number of the solid, m is the molality of the saturated solution, m_0 is an arbitrarily selected reference molality (usually the molality at 298 K), and M is the molar mass of the solvent. When fitting the Y_m terms to eq. [1], the evaluators generally used a three parameter fit (i.e. the constants A, B and C were evaluated).

In fitting the solubility data for binary systems to the smoothing eq. [1], the evaluators rejected a number of data points based on the deviation from the standard error of estimate, σ: that is, when the difference between calculated and observed solubilities exceeded 2σ, the data point was rejected. For mole fraction solubilities, the standard error of estimate, σ_x is defined by:

$$\sigma_x = \left\{ \sum(x_{obsd} - x_{calcd})/(N - 4) \right\}^{1/2} \qquad [4]$$

where N is the number of data points associated with the particular polytherm being considered. A similar relation exists for the standard error of estimate for mol kg^{-1} solubilities, σ_m, but the evaluators used (N - 3) in the denominator since Y_m values were fitted to a three constant smoothing equation. In addition to reporting the standard errors σ_x and σ_m, the evaluators also reported the standard errors for the Y terms (Y_x and Y_m), denoted simply as σ_y in the evaluations.

For convenience of the users, the evaluators have prepared two computer programs written in *BASIC* to calculate the solubilities at any temperature. The programs called "CALC_X" and "CALC_M" are given on the pages following the references. Note that the user is requested to enter an initial estimate of the solubility to start the calculations. Since the Newton-Raphson iteration method is used, the user should be aware that a very poor initial estimate of the solubility may result in convergence at an incorrect answer. Finally, we should like to point out that both programs use double precision in the calculations (statement number 20 in both programs: DEFDBL A-H, O-Z). Using IBM-PC or compatibles with MS-BASIC, double precision is required to give at least 8-bit numerical precision.

Although an attempt has been made to locate all publications on the system under consideration through the first half of 1984, some omissions may have occurred. The editors will therefore be grateful to readers who will bring these omissions to their attention.

The editors would like to acknowledge the cooperation of the American Chemical Society and VAAP, the copyright agency of the USSR, for their permission to reproduce phase diagrams from their publications.

The editors gratefully acknowledge the advice and comments from members of IUPAC Commission V.8 (the Commission on Solubility Data), and in particular to Professors H. L. Clever, R. Cohen-Adad, J. W. Lorimer, and A. S. Kertes. We are also grateful to Dr. K. Loening of the Chemical Abstracts Service for providing Registry Numbers for numerous compounds.

One of us (H.M.) would also like to acknowledge the hospitality of Prof. H. L. Clever during his stay at the Solubility Research and Information Center at Emory University in Atlanta, GA, USA (1981-1982), and to Profs. Hideo Akaiwa (Gunma University) and Michihiro Fujii (Niigata University) for valuable comments and suggestions. We would also like to thank Ms. Karen Salomon for her help in translations. Finally the editors would like to thank Mrs. Shikako Miyamoto for her assistance with the tedious calculations of converting experimental solubility data in mass % units to S.I. units.

REFERENCES

1. Miyamoto, H.; Salomon, M. and Clever, H. L., eds. *IUPAC SOLUBILITY DATA SERIES VOLUME 14: ALKALINE EARTH METAL HALATES.* Pergamon Press, London, 1983.

2. Malyshev, A. A.; Kuz'menko, A. L.; Novikov, G. I.; Tomasheva, L. T. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1982, *25*, 380.

3. Perkins, H.; Taft, R. *J. Phys. Chem.* 1925, *29*, 1075.

4. Perel'man, F. M.; Korzhenyak, I. G. *Zh. Neorg. Khim.* 1963, *13*, 277.

5. Kolthoff, I. M.; Chantooni, M. K. *J. Phys. Chem.* 1973, *77*, 523.

6. Isbin, H. S.; Kobe, K. A. *J. Am. Chem. Soc.* 1945, *67*, 464,

7. Miravitlles, M. L. *Ann. Fis. Quim. (Madrid)* 1945, *41*, 120.

8. Cohen-Adad, R. *Pure and Appl. Chem.* 1985, *57*, 255.

9. Counioux, J. -J.; Tenu, R. *J. Chim. Phys.* 1981, *78*, 816.

10. Tenu, R.; Counioux, J.-J. *J. Chim. Phys.* 1981, *78*, 823.

REFERENCES (Continued)

11. Siekierski, S.; Mioduski, T.; Salomon, M., eds. *IUPAC SOLUBILITY DATA SERIES VOLUME 13: SCANDIUM YTTRIUM, LANTHANUM AND LANTHANIDE NITRATES.* Pergamon Press, London, 1983.

Hiroshi Miyamoto, Niigata, Japan
Mark Salomon, Fort Monmouth, NJ, USA
November, 1986

```
10  '  CALC_M
20  DEFDBL A-H,O-Z
30  '  PROGRAM TO CALCULATE mol/kg SOLUBILITIES FOR A SPECIFIED TEMPERATURE
40  '  BASED ON THE SMOOTHING EQUATION GIVEN IN THE PREFACE
50  '
60  DIM G$[80]
70  PRINT "ENTER PROBLEM IDENTIFYING INFORMATION"
80  INPUT G$
90  PRINT
100 PRINT "ENTER CONSTANTS IN  y = A/T + B log(T) + C "
110 PRINT
120 INPUT "CONSTANT A =  ",A
130 INPUT "CONSTANT B =  ",B
140 INPUT "CONSTANT C =  ",C
150 PRINT
160 PRINT "ENTER DATA TO IDENTIFY THE POLYTHERM"
170 PRINT
180 INPUT "MOLAR MASS OF SOLVENT =  ",W
190 INPUT "SOLVATION NUMBER OF SOLID PHASE =  ",R
200 INPUT "REFERENCE MOLALITY =  ",M0
210 INPUT "CHOOSE ITERATION LIMIT FOR CALCD mol/kg SOLUBILITIES:  ",MLIM
220 PRINT
230 LPRINT
240 LPRINT G$
250 LPRINT "CONSTANT A = ";A
260 LPRINT "CONSTANT B = ";B
270 LPRINT "CONSTANT C = ";C
280 LPRINT "MOLAR MASS OF SOLVENT = ";W
290 LPRINT "SOLVATION NUMBER = ";R
300 LPRINT "REFERENCE MOLALITY = ";M0
310 LPRINT "CONVERGERNCE LIMIT SET AT "; MLIM
320 LPRINT
330 '
340 '  START CALCULATIONS
350 '
360 I = 0
370 PRINT "ENTER TEMP AND AN INITIAL GUESS FOR THE MOLALITY"
380 INPUT "T/K =  ",T
390 INPUT "GUESS FOR THE MOLALITY IS:  ",MSTART
400 I = I + 1
410 '
420 '  NEWTON-RAPHSON ITERATION
430 '
440 F0 = A/T + B*LOG(T) + C + LOG(M0/MSTART) + R*W*(MSTART - M0)/1000
450 F1 = R*W/1000 - 1/MSTART
460 MNEW = MSTART - F0/F1
470 IF ABS(MSTART - MNEW) < MLIM THEN 500
480 MSTART = MNEW
490 GOTO 440
500 PRINT
510 PRINT "FOR T/K = ";T;" , SOLUBILITY (mol/kg) = ";MNEW
520 PRINT
530 LPRINT
540 LPRINT "FOR CALCULATION No. ";I
550 LPRINT "T/K = ";T;"  or t/C = ";T-273.15
560 LPRINT "SOLUBILITY = ";MNEW;"  mol/kg"
570 LPRINT
580 PRINT "DO YOU WANT TO CALCULATE A NEW SOLUBILITY AT A NEW TEMPERATURE?"
590 INPUT "ENTER Y/N:  ",C$
600 IF C$ = "Y" OR C$ = "y" THEN 370
610 END
```

```
10  REM CALC_X
20  DEFDBL A-H, O-Z
30  REM PROGRAM TO CALCULATE MOLE FRACTION SOLUBILITIES AT A GIVEN TEMP
40  REM BASED ON THE SMOOTHING EQUATION GIVEN IN THE PREFACE
50  DIM G$[80] , C(4)
60  REM
70  PRINT"READ PROBLEM IDENTIFYING INFORMATION (80 CHARACTERS MAX)"
80  INPUT G$
90  PRINT
100 INPUT"ENTER NUMB OF CONSTANTS IN SMOOTHING EQN (3 CONSTANTS MIN): ",NC
110 IF NC = 3 THEN C(4) = 0
120 PRINT
130 FOR I = 1 TO NC
140 PRINT"ENTER VALUE OF CONSTANT NUMBER ";I
150 INPUT C(I)
160 NEXT I
170 PRINT
180 PRINT"ENTER DATA IDENTIFYING THE POLYTHERM"
190 PRINT"NOTE THAT FOR THE ICE POLYTHERM, R = 1 and V = 0"
200 PRINT"WHERE R = SOLID PHASE SOLVATION NUMBER AND V = NUMBER OF IONS"
210 PRINT
220 INPUT"ENTER SOLVATION NUMBER R:  ",R
230 INPUT"ENTER NUMBER  OF IONS  V:  ",V
240 PRINT
250 PRINT"CHOOSE THE ITERATION LIMIT FOR CALCD MOLE FRACTION SOLUBILITY"
260 INPUT"ENTER ITERATION LIMIT :  ",XLIM
270 PRINT
280 LPRINT G$
290 LPRINT
300 LPRINT"SOLVATION NUMBER R = ";R
310 LPRINT"NUMBER  OF IONS  V = ";V
320 LPRINT
330 LPRINT "CONVERGENCE LIMIT FOR MOLE FRACTION SOLUBILITY SET AT  ";XLIM
340 LPRINT
350 FOR I = 1 TO NC
360 LPRINT"CONSTANT C(";I;") = ";C(I)
370 NEXT I
380 R1 = R + V
390 REM
400 PRINT
410 INPUT"ENTER TEMPERATURE IN DEGREES C:  ",TC
420 TK = TC + 273.15
430 NITER = 0
440 INPUT"ENTER AN APPROXIMATE VALUE FOR MOLE FRACTION SOLUBILITY: ",Y
450 IF R = 0 THEN R2 = 1
460 IF R = 0 THEN 480
470 R2 = R^R
480 Y3 = C(1)/TK + C(2) * LOG(TK) + C(3) + C(4)*TK
490 REM
500 REM ITERATION BY NEWTWON-RAPHSON METHOD
510 REM
520 Y5 = R2*EXP(Y3)/R1^R1
530 F0 = Y^V*(1-Y)^R/(1+Y)^R1 - Y5
540 NITER = NITER + 1
550 P1 = (1 + Y)^R1
560 P2 = -R*Y^V*(1-Y)^(R-1) + V*Y^(V-1)*(1-Y)^R
570 P3 = -Y^V*(1-Y)^R * R1 * (1+Y)^(R1-1)
580 F1 = (P1 * P2 + P3)/(1 + Y)^2
590 Y6 = Y - F0/F1
600 IF ABS (Y6 - Y) < XLIM THEN 630
610 Y = Y6
620 GOTO 530
630 LPRINT
640 LPRINT"FOR t = ";TC;" deg C, or  T = ";TK;" K"
650 LPRINT"CALCD MOL FRACTION SOLUBILITY = ";Y
660 PRINT
670 PRINT"FOR t = ";TC;" deg C, or  T = ";TK;" K"
680 PRINT"FOR ";NITER;" ITERATIONS"
690 PRINT"CALCD MOL FRACTION SOLUBILITY = ";Y
700 PRINT
710 PRINT"DO YOU WANT TO CALCULATE ANOTHER SOLUBILITY FOR A NEW TEMPERATURE?"
720 INPUT"ENTER Y/N:  ",C$
730 IF C$ = "Y" OR C$ = "y" THEN 410
740 END
```