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MONITORING AND MEASUREMENT OF OXYGEN CONCENTRATIONS IN LIQUID SODIUM

By

D. L. Smith

MASTER

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MONITORING AND MEASUREMENT OF OXYGEN CONCENTRATIONS IN LIQUID SODIUM

D. L. Smith

Materials Science Division
ARGONNE NATIONAL LABORATORY
Argonne, Illinois 60439

ABSTRACT

The measurement of oxygen concentrations in sodium at levels of interest for LMFBR applications has been reviewed. Additional data are presented to support the validity of the vanadium-equilibration method as a reference for determination of oxygen concentrations in sodium at levels ≤15 ppm. Operating experience with electrochemical oxygen meters that have a thoria-yttria electrolyte and a Na-Na_2O reference electrode is described. Meter lifetimes in excess of one year have generally been achieved for operating temperatures of 352 and 402°C, and fairly stable emfs have been observed for periods of several months.

INTRODUCTION

Accurate measurement of nonmetallic impurity-element concentrations in liquid sodium at levels of interest for Liquid-Metal Fast-Breeder Reactor (LMFBR) applications is essential for reliable interpretation and correlation of compatibility data on various reactor materials in sodium. Over the past twenty years the measurement of oxygen concentrations in sodium has received the most attention since this impurity was generally conceded to have the predominant effect on the corrosion of most LMFBR structural and fuel cladding materials. As a result, the state of technology for the analysis of oxygen in sodium at the part-per-million level has improved greatly during this period.

The methods that have been used most often for determiniation of oxygen concentrations in sodium for LMFBR applications are (a) the vacuum distillation technique[1], (b) the mercury amalgamation method[2], (c) oxygen solubility at cold-trap (Na-Na_2O equilibrium) temperature, (d) the vanadium-equilibrium method[3,4], and (e) electrochemical oxygen meters[5]. Of the five methods for determining oxygen concentrations in sodium, only the vacuum distillation and mercury amalgamation methods give an independent quantitative measure of the oxygen concentration. Both of these methods are tedious and susceptible to considerable error in the low part-per-million oxygen range. The other three techniques require either a knowledge of the temperature dependence of the oxygen solubility in sodium or an experimental calibration against a standard analysis. Much of the controversy surrounding accurate analysis of oxygen in sodium involves this latter point, i.e., calibration against a standard, since worldwide agreement on the standard solubility curve has not been attained. In the present paper, data for the solubility of oxygen in sodium are reviewed as they apply to monitoring and control of oxygen concentrations in sodium systems. Recent experience with the vanadium-equilibration method for measurement of oxygen concentrations in sodium and operating experience with electrochemical oxygen meters that utilize a Na-Na_2O reference electrode are presented.

OXYGEN SOLUBILITY IN SODIUM

A number of investigators have measured the solubility of oxygen in sodium and several reviews of the data have been published with recommended equations expressing the temperature dependence[4,6-8]. Figure 1 is a plot showing four recommended solubility

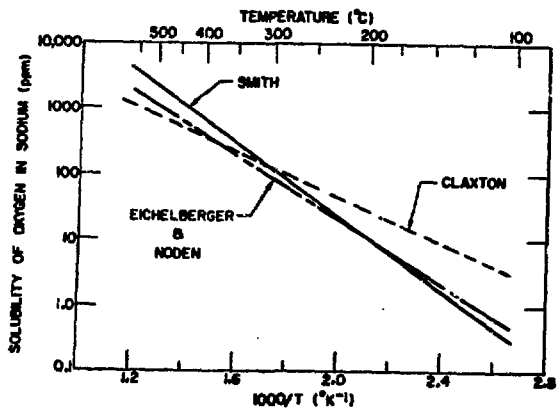

Fig. 1. Temperature Dependence for Solubility of Oxygen in Sodium from Four Investigations.

equations. Claxton's[6] correlation, based on the data of four investigators, results in an equation with heat of solution for solid Na_2O in liquid sodium of 8305 cal/mole. More recently Eichelberger[7] and Noden[8] have reviewed data of 7 and 12 investigators, respectively, and have arrived at nearly identical expressions with a heat of solution for Na_2O in sodium

of 11,200 cal/mole. Only selected data were used to obtain these recommended equations. On the basis of available literature data plus additional experimental data, the present author has also published a recommended expression for the solubility of oxygen in sodium[4]. Only the data that were obtained in a stainless steel system by Noden and Bagley[9] were considered valid in the temperature range 300-550°C. At temperatures below 300°C, only the vacuum distillation results of Rutkauskas[10] and those of the present author[4] were used. The expression obtained from the data in Fig. 2 is given by

$$\log C_{\underline{O}_{Na}} = 6.967 - 2809\ T^{-1}\ , \qquad (1)$$

where the oxygen concentration, $C_{\underline{O}_{Na}}$, is in parts per million and temperature is in °K. The heat of solution of Na_2O in sodium is 12,900 cal/mole.

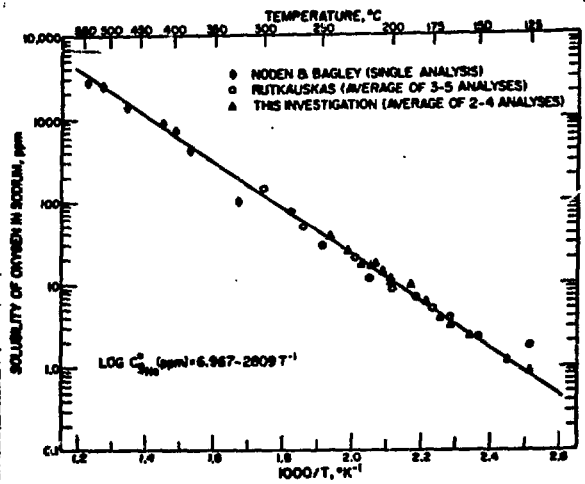

Fig. 2. Recommended Temperature Dependence for Solubility of Oxygen in Sodium Between 100 and 550°C.

This equation or slight modifications, thereof, has been established as the reference equation for LMFBR work in the U.S[11]. Oxygen distribution coefficients used in the vanadium-equilibration method discussed below are based on this equation. Although there are undoubtedly some who prefer other expressions, it has been beneficial for investigators at various laboratories to use the same reference equation. It should be noted that all three equations agree fairly well at ~300°C; however rather large descrepancies exist at higher and lower temperatures. For example, at 125°C Eq. 1 yields a value of 0.8 ppm oxygen compared to a value of ~4 ppm for the Claxton equation; a factor of 5 variation. This results in a significant difference in the reported oxygen concentration in a cold-trapped sodium system.

OXYGEN SOLUBILITY AT THE COLD-TRAP TEMPERATURE

Probably the oldest and most used method for establishing the oxygen concentrations in sodium systems has been by cold trapping. The cold trap utilizes the Na-Na_2O phase equilibrium at low temperatures to control the oxygen concentration in sodium. Direct comparisons from system to system can be made on the basis of the cold-trap temperature or quantitative oxygen concentrations can be derived from the oxygen-solubility curves at the cold-trap temperature. Although the concept is reliable, inability to achieve or maintain the necessary physico-chemical conditions has led to erroneous results in several cases. Since the concept relies on attainment of Na-Na_2O equilibrium, the method is reliable only when sufficient oxygen is available to establish the appropriate equilibrium. Therefore, the method establishes only a maximum concentration set by the Na-Na_2O equilibrium and is invalid if the oxygen is depleted. Kinetic limitations have also been the cause of erroneous results, particularly in cases where diffusion-type or bypass-type cold traps have been used. A more subtle concern relating to the accuracy of this method is in the measurement of the effective cold-trap (or saturation) temperature. Also, this type of determination is useful only at oxygen concentrations above the saturation value (~0.3 ppm) at the melting temperature.

VANADIUM-EQUILIBRATION METHOD

The vanadium-equilibrium method[3,4], which was recently developed, has received widespread use in the U.S[12-17]. The technique is based on (a) the elevated temperature equilibration of oxygen between two mutually insoluble metals, viz., vanadium and sodium, (b) measurement of the oxygen concentration in the vanadium, and (c) determination of the oxygen concentration in sodium from experimentally predetermined distribution-coefficient data. The major advantages of the vanadium-equilibration method relate to (a) its simplicity, which makes it quite versatile and inexpensive, (b) the amplification derived from the relatively large distribution coefficient, which results in high sensitivity at low concentrations (≤1 ppm oxygen in sodium), and (c) the fact that it provides a good reference, which results in reliable interlaboratory comparisons.

Theoretical expressions for the equilibrium dis-

tribution coefficients have been developed previously[18]. Values are based on free energy of formation for the most stable binary vanadium and sodium oxides, and the saturation curves for the binary vanadium- and sodium-oxygen systems. The experimentally measured distribution coefficients deviate somewhat from the calculated values for the V-O-Na system. These differences are attributed primarily to uncertainties in the thermodynamic data used in the calculations and to assumptions required for the simple calculation.

Questions have been raised in the literature concerning the attainment of equilibrium in the system[19]. Experimental data obtained in the present investigation overwhelmingly support the conclusion that equilibrium is attained under the conditions specified for the technique. The experimentally determined exposure times required for equilibration are in good agreement with calculated values based on solid state diffusion-controlled process, viz., oxygen diffusion in vanadium. Exposure times in sodium over two orders of magnitude longer than the specified minimum give the same oxygen concentration in vanadium as standard equilibrations, and oxygen concentrations in wires of various diameters give the same result when exposed simultaneously for periods sufficient to achieve equilibrium. Also, exposures of vanadium samples to sodium for shorter periods result in oxygen profiles that are in satisfactory agreement with profiles calculated from diffusion data. Vanadium samples previously injected with oxygen have been simultaneously exposed with standard specimens and equilibrated to identical concentrations lying between the original concentrations of the two specimens. Further evidence in Fig. 3 shows the systematic variation of the oxygen concentrations in vanadium with oxygen concentration in sodium determined by both vacuum-distillation analyses and from saturation values of a carefully controlled cold trap. Additional evidence supporting the reliability of the equilibration method is given below in the discussion of electrochemical-cell measurements.

ELECTROCHEMICAL OXYGEN METERS

Electrochemical oxygen meters provide an attractive online monitoring device for the measurement of oxygen concentrations in sodium. Over the past several years, considerable effort in the U.S. has been devoted to the development of reliable oxygen meters for liquid-sodium systems. A thoria-yttria electrolyte (7.5 and 15 wt% yttria) has been used in the meters. The performance of both UNC-type[20] meters

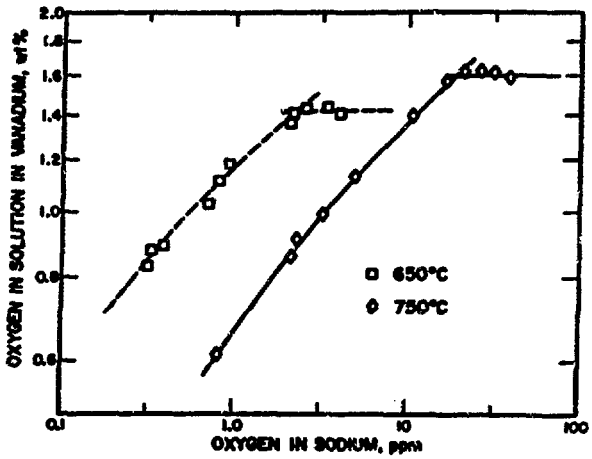

Fig. 3. Measured Oxygen Concentrations in Vanadium after Exposure to Sodium that Contained Various Oxygen Concentrations.

with Cu-Cu_2O reference electrodes and Westinghouse-type[21] meters with air reference electrodes has been investigated at several laboratories[12-15,22]. Major problems that have been encountered with both types of meters include: (a) limited lifetime caused by fracture of the electrolyte tube, (b) drift or instabilities of the emf with time, and (c) nontheoretical response of emf versus oxygen concentration. In attempts to better understand and eliminate these deficiencies, primarily the nontheoretical response, modified oxygen meters that utilize an Na-Na_2O reference electrode with both UNC- and Westinghouse-type electrolyte tubes have been constructed and operated at ANL. Errors in the calculated response of the meters arising from uncertainties in the standard free-energy data for the reference oxide relative to oxygen in sodium would be mitigated by use of the Na-Na_2O reference electrode. Possible electronic conductivity effects attributable to the high oxygen potential of the air reference electrode would also be reduced by use of the Na-Na_2O reference electrode. Much of the early work with UNC-type meters and modified meters utilizing similar electrolyte tubes with Na-Na_2O reference elctrodes has been reported previously[4]. Both types of meters responded to changes in oxygen concentration in sodium as determined by vacuum-distillation analyses, cold-trap temperature solubility, and vanadium-equilibration analyses; however, the experimental responses (~30-35 mV/decade in oxygen concentration) were considerably less than the theoretically predicted value of 62 mV/decade at 352°C. Similar results were also obtained

for cell temperatures of 402°C.

The operating characteristics of oxygen meters with a $Na-Na_2O$ reference electrode and a high-purity thoria-yttria electrolyte, viz., the type used in the Westinghouse oxygen meters, have been determined. Four different cells of this type have been constructed and operated for extended periods on laboratory-size (5-50 kg of sodium) loops. The reference electrode consists of ~250 mg of high-purity sodium to which ~15 mg of reagent grade sodium oxide was added. The operating history of the four meters is summarized in Table I. The maximum sodium temperature in the loop was typically between 450 and 750°C with the cell

Table I. Operating History of Four Electrochemical Oxygen Meters with $Na-Na_2O$ Reference Electrodes.

Cell No.	Loop	Max. Sodium Temp., °C	Cell Temp., °C	Number of Shutdowns	Cell Life days
1WN	HOSEA	550-700	352	1	94
2WN	HOSEA	550-800	302-402	6	422
3WN	FFTS-I	450-750	352-427	8	412
4WN	FFTS-II	500-750	377-452	3	452

operating at temperatures from 300 to 450°C. Three of the four meters were operated for periods of the order of 1 year and one meter is still operational with an accumulated lifetime of 14 months. All four meters were subjected to periodic shutdowns as indicated in the table. Failure of the first three electrolyte tubes occurred during flow transients associated with startups. The thermal shock resistance of the electrolyte tubes has not been quantitatively assessed; however, the tubes have survived thermal transients in excess of 100°C. Figure 4 shows a photograph of the fractured electrolyte tube from meter #3WN. The other tubes fractured in a similar manner.

Meters 1WN and 2WN were operated over a wide range of oxygen concentrations, primarily at a cell temperature of 352°C, with similar results. Figure 5 shows a plot of cell emf as a function of oxygen concentration in sodium for meter 2WN. The 402°C curve was obtained by operating the cell periodically at the higher temperature for short times, typically ≤1 day. The oxygen concentrations represented by the open symbols were determined from the cold-trap temperature, under carefully controlled conditions, and the oxygen solu-

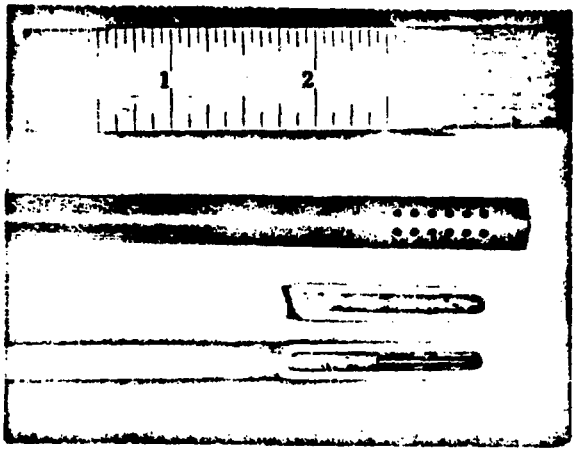

Fig. 4. Photograph of Fractured Thoria-Yttria Electrolyte Tube from Meter #3WN.

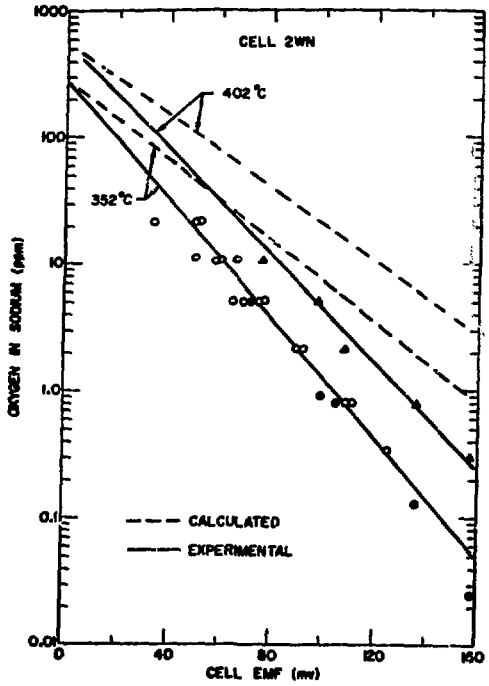

Fig. 5. Oxygen Meter emf as a Function of Oxygen Concentration in Sodium for an Electrochemical Cell with a $Na-Na_2O$ Reference Electrode. Oxygen concentration was determined from the solubility at the cold-trap temperature (open symbols) and the vanadium-equilibration method (closed symbols).

bility, i.e., Eq. 1. The solid symbols represent oxygen concentrations determined by the vanadium-equilibration method. Several of the points obtained by the latter method, including all data below 0.3 ppm oxygen, were obtained with the cold trap bypassed. The

consistency of the cold-trap solubility and the vanadium-equilibration method for oxygen datarmination ia demonstrated by the linearity of the cell data over a wide concentration range and reproducible results over long periods of time. However, as in the case of previous meter operating experience, the cell emf ia not in agreement with theoretical predictions. Results are also shown in Fig. 5 for the 402°C operating temperature. Similar results that were obtained with meter 1WN have not been included because of the relatively short lifetime. A linear plot of log $C_{\underline{O}_{Na}}$ versus emf was also obtained; however, the corresponding emf's were slightly lower.

Meters 3WN and 4WN were operated predominantly at 402°C on similar sodium systems in which the oxygen concentration was normally maintained at ∿1 ppm. Short excursions in the oxygen concentration occurred periodically. Figure 6 shows the responses of these meters

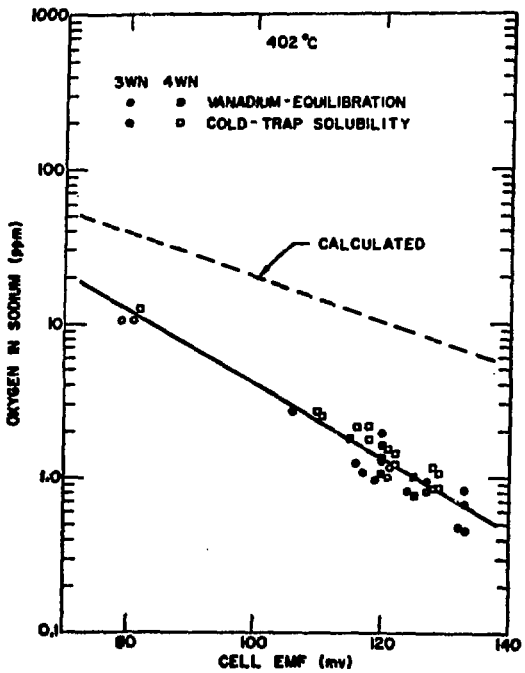

Fig. 6. Oxygen Meter emf as a Function of Oxygen Concentration in Sodium for Two Electrochemical Cells with Na-Na_2O Reference Electrodes.

during their lifetime. The solid symbols represent values obtained by vanadium-equilibration analyses and the open symbols are correlations with cold-trap temperatura solubility. The solid curve is the same as the 402°C curve in Fig. 5. The important observations are (a) the relatively good stability of the meters during their lifetime, (b) the good agreement in response of these meters with meter 2WN, and (c) the long operating lifetime.

The consistent variations of the oxygen-meter emfs with oxygen concentrations determined by the vanadium-equilibration method support the validity of this method for measuring oxygen concentrations in sodium. This observation is particularly impressive when one considers a range of nearly four orders of magnitude in oxygen concentration for meter 2WN. Extensive oxygen meter tests conducted at both Westinghouse[14] and Argonne[13] also demonstrate consistent variations in cell emf with oxygen concentration in sodium determined by the vanadium-equilibration method.

Two anomalies remain concerning the measurement of oxygen in sodium at low concentrations, viz., the nontheoretical behavior of the electrochemical oxygen meters and the strong concentration dependence of the distribution coefficient for oxygen between vanadium and sodium. Common to both of these factors is the temperature dependence of the solubility of oxygen in sodium. Therefore, variations in the heat of solution of Na_2O in sodium have been examined in an attempt to rationalize these questions. With the assumption that the electrochemical cells behave ideally and the necessary physico-chemical conditions are established in the sodium system, the data have been correlated to obtain a solubility equation with a heat of solution of 8700 cal/mole for Na_2O in sodium. If the solubility is fixed at a value of 120 ppm at 300°C, the temperature where best agreement of all data occurs, one obtains the expression

$$\log C'_{\underline{O}_{Na}} = 5.40 - 1900 \frac{1}{T} , \qquad (2)$$

where $C'_{\underline{O}_{Na}}$ is in parts per million and temperature is in °K. Figure 7 shows a plot of oxygen-meter data based on this equation. The oxygen concentrations determined from cold-trap solubility and the distribution coefficients for the vanadium-oxygen-sodium system were revised to conform with Eq. 2. Agreement between the experimental data and the theoretical curves is obtained for the three meters and both operating temperatures. Of course similar agreement would also be observed with other solubility curves if the heat of solution remained constant. However, when cell emf is plotted against oxygen concentration in the equilibrated vanadium samples, a linear relation (ln $C_{\underline{O}_V}$ vs emf) is not obtained. This indicates that

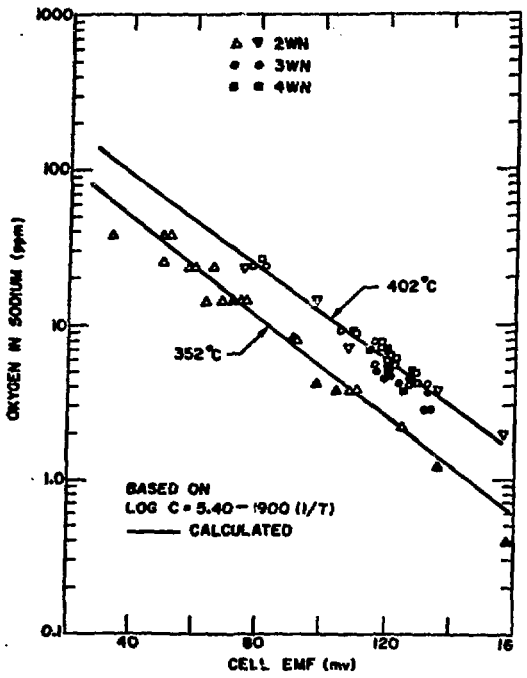

Fig. 7. Oxygen Meter Response Based on a Revised Equation for the Solubility of Oxygen in Sodium.

the distribution coefficient for oxygen between vanadium and sodium, based on Eq. 2, is still concentration dependent, although the concentration dependence is somewhat less than that obtained previously using Eq. 1. The two anomalies have not been completely reconciled; however, this does not detract from the use of the vanadium-equilibration method as a reference and electrochemical oxygen meters as monitors for oxygen activity or concentration in sodium.

SUMMARY

This report summarizes the results of an investigation on the measurement of oxygen concentrations in sodium at levels of interest for LMFBR applications. A review of solubility data for oxygen in sodium is given with the equation that is recommended and used in most LMFBR programs in this country. Additional data are presented to support the validity of the vanadium-equilibration method as a reference for determination of oxygen concentrations in sodium at levels ≤15 ppm. The fact that oxygen concentrations in sodium-exposed vanadium samples vary systematically with both the cold-trap temperature and electrochemical oxygen-meter emf demonstrates that the vanadium-equilibration method gives a reliable indication of oxygen concentration in the specified range.

Operating experience with electrochemical oxygen meters with a thoria-yttria electrolyte and a $Na-Na_2O$ reference electrode has been described. The oxygen meter characteristics include: (a) operating lifetimes generally in excess of one year under a variety of conditions, (b) fairly stable emfs for periods of several months, and (c) predictable behavior for oxygen concentrations in sodium between 0.1 and 20 ppm. Although consistent and reproducible results were obtained, the meters used in the present investigation did not respond theoretically to measured oxygen concentrations in sodium based on the recommended expression for the solubility of oxygen in sodium. When an alternate solubility expression was used as a basis for determination of oxygen concentrations in sodium, agreement between theoretical and observed emfs was obtained with meters at two operating temperatures, viz., 352 and 402°C. Since most laboratories obtain consistent and comparable results when the same solubility expression is used as a standard, a change of the reference equation is not recommended at this time. Further investigations in this area are required before any changes in the baseline data can be recommended. The more important consideration is the capability for valid interlaboratory comparisons attainable by use of an accepted standard.

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