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## **SOLUBILITY DATA SERIES**

**Volume 31**

**ALKALI METAL  
ORTHOPHOSPHATES**

## SOLUBILITY DATA SERIES

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# SOLUBILITY DATA SERIES

*Editor-in-Chief*  
A. S. KERTES

Volume 31

## ALKALI METAL ORTHOPHOSPHATES

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## CONTENTS

Foreword	vii
Preface	x
Introduction: The Solubility of solids in liquids	xi
1. Lithium phosphate	
1.1 Evaluation of aqueous systems	1
1.2 Binary aqueous system	7
1.3 Ternary aqueous system	8
1.4 Multicomponent aqueous system	9
2. The Na <sub>2</sub> O-P <sub>2</sub> O <sub>5</sub> -H <sub>2</sub> O system	
2.1 Evaluation of aqueous systems	11
2.2 Ternary systems	16
2.3 Multicomponent systems	26
3. Sodium dihydrogenphosphate	
3.1 Evaluation of aqueous binary system	39
3.2 Binary aqueous system	43
4. Sodium dihydrogenphosphate	
4.1 Evaluation of aqueous multicomponent systems	47
4.2 Ternary aqueous systems with two saturating components	53
4.3 Multicomponent systems	80
4.4 Systems with one organic component	96
5. Disodium hydrogenphosphate	
5.1 Evaluation of aqueous systems	93
5.2 Binary aqueous system	103
5.3 Ternary aqueous system with one saturating component	107
5.4 Ternary aqueous systems with two saturating components	108
5.5 Multicomponent systems	119
5.6 Systems with one organic component	124
6. Trisodium phosphate	
6.1 Evaluation of aqueous systems	127
6.2 Binary aqueous system	131
6.3 Ternary aqueous systems with two saturating components	137
6.4 Multicomponent aqueous systems	155
6.5 System with one organic component	166
7. The K <sub>2</sub> O-P <sub>2</sub> O <sub>5</sub> -H <sub>2</sub> O system	
7.1 Evaluation of aqueous systems	169
7.2 Binary aqueous systems	172
7.3 Ternary systems	174
7.4 Multicomponent systems	184
8. Potassium dihydrogenphosphate	
8.1 Evaluation of aqueous systems	206
8.2 Binary aqueous system	213
8.3 Ternary aqueous systems with two saturating components	220
8.4 Multicomponent aqueous systems	262
8.5 Systems with one organic component	272
9. Dipotassium hydrogenphosphate	
9.1 Evaluation of aqueous systems	278
9.2 Binary aqueous system	280
9.3 Ternary aqueous systems with two saturating components	281
9.4 Multicomponent aqueous systems	291
10. Tripotassium phosphate	
10.1 Evaluation of aqueous systems	297
10.2 Binary aqueous system	294
10.3 Ternary aqueous systems	300
10.4 Multicomponent aqueous system	305

(continued next page)

11.	Rubidium dihydrogenphosphate	
11.1	Evaluation of aqueous systems	307
11.2	Binary aqueous system	312
11.3	Ternary aqueous systems	313
11.4	Multicomponent aqueous systems	315
12.	Cesium dihydrogenphosphate	
12.1	Evaluation of aqueous systems	318
12.2	Binary aqueous system	325
12.3	Ternary aqueous systems	326
12.4	Multicomponent aqueous systems	329
	System Index	334
	Registry Number Index	341
	Author Index	343
	Solubility Data Series: Published and Forthcoming Volumes	348

## FOREWORD

*If the knowledge is  
undigested or simply wrong,  
more is not better*

How to communicate and disseminate numerical data effectively in chemical science and technology has been a problem of serious and growing concern to IUPAC, the International Union of Pure and Applied Chemistry, for the last two decades. The steadily expanding volume of numerical information, the formulation of new interdisciplinary areas in which chemistry is a partner, and the links between these and existing traditional subdisciplines in chemistry, along with an increasing number of users, have been considered as urgent aspects of the information problem in general, and of the numerical data problem in particular.

Among the several numerical data projects initiated and operated by various IUPAC commissions, the *Solubility Data Project* is probably one of the most ambitious ones. It is concerned with preparing a comprehensive critical compilation of data on solubilities in all physical systems, of gases, liquids and solids. Both the basic and applied branches of almost all scientific disciplines require a knowledge of solubilities as a function of solvent, temperature and pressure. Solubility data are basic to the fundamental understanding of processes relevant to agronomy, biology, chemistry, geology and oceanography, medicine and pharmacology, and metallurgy and materials science. Knowledge of solubility is very frequently of great importance to such diverse practical applications as drug dosage and drug solubility in biological fluids, anesthesiology, corrosion by dissolution of metals, properties of glasses, ceramics, concretes and coatings, phase relations in the formation of minerals and alloys, the deposits of minerals and radioactive fission products from ocean waters, the composition of ground waters, and the requirements of oxygen and other gases in life support systems.

The widespread relevance of solubility data to many branches and disciplines of science, medicine, technology and engineering, and the difficulty of recovering solubility data from the literature, lead to the proliferation of published data in an ever increasing number of scientific and technical primary sources. The sheer volume of data has overcome the capacity of the classical secondary and tertiary services to respond effectively.

While the proportion of secondary services of the review article type is generally increasing due to the rapid growth of all forms of primary literature, the review articles become more limited in scope, more specialized. The disturbing phenomenon is that in some disciplines, certainly in chemistry, authors are reluctant to treat even those limited-in-scope reviews exhaustively. There is a trend to preselect the literature, sometimes under the pretext of reducing it to manageable size. The crucial problem with such preselection - as far as numerical data are concerned - is that there is no indication as to whether the material was excluded by design or by a less than thorough literature search. We are equally concerned that most current secondary sources, critical in character as they may be, give scant attention to numerical data.

On the other hand, tertiary sources - handbooks, reference books and other tabulated and graphical compilations - as they exist today are comprehensive but, as a rule, uncritical. They usually attempt to cover whole disciplines, and thus obviously are superficial in treatment. Since they command a wide market, we believe that their service to the advancement of science is at least questionable. Additionally, the change which is taking place in the generation of new and diversified numerical data, and the rate at which this is done, is not reflected in an increased third-level service. The emergence of new tertiary literature sources does not parallel the shift that has occurred in the primary literature.

With the status of current secondary and tertiary services being as briefly stated above, the innovative approach of the *Solubility Data Project* is that its compilation and critical evaluation work involve consolidation and reprocessing services when both activities are based on intellectual and scholarly reworking of information from primary sources. It comprises compact compilation, rationalization and simplification, and the fitting of isolated numerical data into a critically evaluated general framework.

The *Solubility Data Project* has developed a mechanism which involves a number of innovations in exploiting the literature fully, and which contains new elements of a more imaginative approach for transfer of reliable information from primary to secondary/tertiary sources. The fundamental trend of the *Solubility Data Project* is toward integration of secondary and tertiary services with the objective of producing in-depth critical analysis and evaluation which are characteristic to secondary services, in a scope as broad as conventional tertiary services.

Fundamental to the philosophy of the project is the recognition that the basic element of strength is the active participation of career scientists in it. Consolidating primary data, producing a truly critically-evaluated set of numerical data, and synthesizing data in a meaningful relationship are demands considered worthy of the efforts of top scientists. Career scientists, who themselves contribute to science by their involvement in active scientific research, are the backbone of the project. The scholarly work is commissioned to recognized authorities, involving a process of careful selection in the best tradition of IUPAC. This selection in turn is the key to the quality of the output. These top experts are expected to view their specific topics dispassionately, paying equal attention to their own contributions and to those of their peers. They digest literature data into a coherent story by weeding out what is wrong from what is believed to be right. To fulfill this task, the evaluator must cover all relevant open literature. No reference is excluded by design and every effort is made to detect every bit of relevant primary source. Poor quality or wrong data are mentioned and explicitly disqualified as such. In fact, it is only when the reliable data are presented alongside the unreliable data that proper justice can be done. The user is bound to have incomparably more confidence in a succinct evaluative commentary and a comprehensive review with a complete bibliography to both good and poor data.

It is the standard practice that the treatment of any given solute-solvent system consists of two essential parts: I. Critical Evaluation and Recommended Values, and II. Compiled Data Sheets.

The Critical Evaluation part gives the following information:

- (i) a verbal text of evaluation which discusses the numerical solubility information appearing in the primary sources located in the literature. The evaluation text concerns primarily the quality of data after consideration of the purity of the materials and their characterization, the experimental method employed and the uncertainties in control of physical parameters, the reproducibility of the data, the agreement of the worker's results on accepted test systems with standard values, and finally, the fitting of data, with suitable statistical tests, to mathematical functions;
- (ii) a set of recommended numerical data. Whenever possible, the set of recommended data includes weighted average and standard deviations, and a set of smoothing equations derived from the experimental data endorsed by the evaluator;
- (iii) a graphical plot of recommended data.

The Compilation part consists of data sheets of the best experimental data in the primary literature. Generally speaking, such independent data sheets are given only to the best and endorsed data covering the known range of experimental parameters. Data sheets based on primary sources where the data are of a lower precision are given only when no better data are available. Experimental data with a precision poorer than considered acceptable are reproduced in the form of data sheets when they are the only known data for a particular system. Such data are considered to be still suitable for some applications, and their presence in the compilation should alert researchers to areas that need more work.

The typical data sheet carries the following information:

- (i) components - definition of the system - their names, formulas and Chemical Abstracts registry numbers;
- (ii) reference to the primary source where the numerical information is reported. In cases when the primary source is a less common periodical or a report document, published though of limited availability, abstract references are also given;
- (iii) experimental variables;
- (iv) identification of the compiler;
- (v) experimental values as they appear in the primary source. Whenever available, the data may be given both in tabular and graphical form. If auxiliary information is available, the experimental data are converted also to SI units by the compiler.

Under the general heading of Auxiliary Information, the essential experimental details are summarized:

- (vi) experimental method used for the generation of data;
- (vii) type of apparatus and procedure employed;
- (viii) source and purity of materials;
- (ix) estimated error;
- (x) references relevant to the generation of experimental data as cited in the primary source.

This new approach to numerical data presentation, formulated at the initiation of the project and perfected as experience has accumulated, has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

Finally, the role of education is more than corollary to the efforts we are seeking. The scientific standards advocated here are necessary to strengthen science and technology, and should be regarded as a major effort in the training and formation of the next generation of scientists and engineers. Specifically, we believe that there is going to be an impact of our project on scientific-communication practices. The quality of consolidation adopted by this program offers down-to-earth guidelines, concrete examples which are bound to make primary publication services more responsive than ever before to the needs of users. The self-regulatory message to scientists of the early 1970s to refrain from unnecessary publication has not achieved much. A good fraction of the literature is still cluttered with poor-quality articles. The Weinberg report (in 'Reader in Science Information', ed. J. Sherrod and A. Hodina, Microcard Editions Books, Indian Head, Inc., 1973, p. 292) states that 'admonition to authors to restrain themselves from premature, unnecessary publication can have little effect unless the climate of the entire technical and scholarly community encourages restraint...' We think that projects of this kind translate the climate into operational terms by exerting pressure on authors to avoid submitting low-grade material. The type of our output, we hope, will encourage attention to quality as authors will increasingly realize that their work will not be suited for permanent retrievability unless it meets the standards adopted in this project. It should help to dispel confusion in the minds of many authors of what represents a permanently useful bit of information of an archival value, and what does not.

If we succeed in that aim, even partially, we have then done our share in protecting the scientific community from unwanted and irrelevant, wrong numerical information.

A. S. Kertes

## PREFACE

This volume presents and evaluates solubility data for the orthophosphates of lithium, sodium, potassium, rubidium and cesium. There are two exceptions to this: (a) data are presented for the solubility of sodium metaphosphate in water (1) on page 46 in chapter 3; and (b) solubility values for the  $\text{NH}_3\text{-K}_2\text{O}\text{-H}_3\text{PO}_4\text{-H}_4\text{P}_2\text{O}_7\text{-H}_2\text{O}$  system (2) are given on pp. 269-270 in chapter 8. Neither of these systems is evaluated because no other comparable data are given in this volume, nor, especially in the latter case, have any similar data been reported.

The orthophosphates have been known and used for many years, but interest in these substances has varied according to their use as, e.g., for fertilizers, corrosion inhibitors and piezoelectricity.

So far as we are aware, all the relevant articles dealing with the alkali metal orthophosphates as a solid phase and published up to 1984 have been reviewed.

*Chemical Abstracts* was used to search for relevant articles published in the years 1920-84. The following three sources were used to locate articles published prior to 1920.

1. The 1928 edition of Gmelin's *Handbuch der Anorganischen Chemie*.
2. References cited in the articles that have been reviewed.
3. The review article of Wendrow and Kobe (3).

The various systems are treated in the order in which the alkali metals are listed in Group I of the Periodic Table. Most of the available solubility data are for the orthophosphates of sodium and potassium, and for these two systems an introductory chapter on the  $\text{MOH-H}_3\text{PO}_4\text{-H}_2\text{O}$  ( $\text{M} = \text{Na or K}$ ) system is given. Each of these chapters (chapters 2 and 7) also refers to compounds to be considered in later chapters. Following each of these introductory chapters there are chapters dealing with the solubility data for individual orthophosphates having different M/P ratios, and the ternary and multicomponent systems in which these orthophosphates are components. Only one chapter is devoted to each of the orthophosphates of lithium, rubidium and cesium.

A considerable amount of help was given to us in the preparation of this volume, and we wish to acknowledge this help and express our thanks to those who provided it. Dr. Mark Salomon kindly coordinated the work of the editors. Dr. Kurt Loening of Chemical Abstracts Service gave indispensable help by providing copies of articles that were difficult for us to locate, and supplying also the CAS Registry Numbers for many of the substances mentioned in this volume. Drs. G. Bohnsack, J.W. Lorimer, and H. Miyamoto provided us with copies of some of the articles reviewed in this volume. Sue Sweetman, in her patient and efficient way, typed the entire manuscript.

We also wish to thank the institutions with which we are affiliated for assistance in many ways during the work of this project. And one of us (J.E.) wishes to express special thanks to IUPAC Commission V.8 and to USSR Minister of Education Academician Prof. G.A. Yagodin for their help in making arrangements for her to spend some time in Moscow in 1984 to search the literature there for many of the articles that have been compiled in this volume. She also wishes to thank Prof. Dr. M. Ebert, Head of the Department of Inorganic Chemistry at Charles University of Prague for making her participation in this project possible and for providing good conditions in which to carry out this work.

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## INTRODUCTION TO THE SOLUBILITY OF SOLIDS IN LIQUIDS

### Nature of the Project

The Solubility Data Project (SDP) has as its aim a comprehensive search of the literature for solubilities of gases, liquids, and solids in liquids or solids. Data of suitable precision are compiled on data sheets in a uniform format. The data for each system are evaluated, and where data from different sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

### Definitions

A mixture (1, 2) describes a gaseous, liquid, or solid phase containing more than one substance, when the substances are all treated in the same way.

A solution (1, 2) describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the solvent, and may itself be a mixture, is treated differently than the other substances, which are called solutes. If the sum of the mole fractions of the solutes is small compared to unity, the solution is called a dilute solution.

The solubility of a substance B is the relative proportion of B (or a substance related chemically to B) in a mixture which is saturated with respect to solid B at a specified temperature and pressure. Saturated implies the existence of equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the corresponding substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium that is greater.) Care must be taken to distinguish true metastability from supersaturation, where equilibrium does not exist.

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the quantities used as measures of solubility and in the reference states used for definition of activities, activity coefficients and osmotic coefficients.

The qualifying phrase "substance related chemically to B" requires comment. The composition of the saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components. Thus, the solubility of a salt hydrate in water is usually given as the relative proportion of anhydrous salt in solution, rather than the relative proportions of hydrated salt and water.

### Quantities Used as Measures of Solubility

#### 1. Mole fraction of substance B, $x_B$ :

$$x_B = n_B / \sum_{s=1}^c n_s \quad [1]$$

where  $n_s$  is the amount of substance of s, and c is the number of distinct substances present (often the number of thermodynamic components in the system). Mole per cent of B is 100  $x_B$ .

#### 2. Mass fraction of substance B, $w_B$ :

$$w_B = m_B' / \sum_{s=1}^c m_s' \quad [2]$$

where  $m_s'$  is the mass of substance s. Mass per cent is 100  $w_B$ . The equivalent terms weight fraction and weight per cent are not used.

#### 3. Solute mole (mass) fraction of solute B (3, 4):

$$x_{s,B} = m_B / \sum_{s=1}^c m_s = x_B / \sum_{s=1}^c x_s \quad [3]$$

$$w_{s,B} = m_B' / \sum_{s=1}^c m_s' = w_B / \sum_{s=1}^c w_s \quad [3a]$$

where the summation is over the solutes only. For the solvent A,  $x_{S,A} = x_A/(1 - x_A)$ ,  $w_{S,A} = w_A/(1 - w_A)$ . These quantities are called Jänecke mole (mass) fractions in many papers.

#### 4. Molality of solute B (1, 2) in a solvent A:

$$m_B = n_B/n_A M_A \quad \text{SI base units: mol kg}^{-1} \quad [4]$$

where  $M_A$  is the molar mass of the solvent.

#### 5. Concentration of solute B (1, 2) in a solution of volume V:

$$c_B = [B] = n_B/V \quad \text{SI base units: mol m}^{-3} \quad [5]$$

The symbol  $c_B$  is preferred to  $[B]$ , but both are used. The terms molarity and molar are not used.

Mole and mass fractions are appropriate to either the mixture or the solution point of view. The other quantities are appropriate to the solution point of view only. Conversions among these quantities can be carried out using the equations given in Table I-1 following this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

In addition to the quantities defined above, the following are useful in conversions between concentrations and other quantities.

#### 6. Density: $\rho = m/V$ SI base units: kg m<sup>-3</sup> [6]

7. Relative density:  $d$ ; the ratio of the density of a mixture to the density of a reference substance under conditions which must be specified for both (1). The symbol  $d'$  will be used for the density of a mixture at  $t^\circ\text{C}$ , 1 bar divided by the density of water at  $t^\circ\text{C}$ , 1 bar. (In some cases 1 atm = 101.325 kPa is used instead of 1 bar = 100 kPa.)

8. A note on nomenclature. The above definitions use the nomenclature of the IUPAC Green Book (1), in which a solute is called B and a solvent A. In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing nomenclature and theoretical equations given in this Introduction with equations and nomenclature used on the evaluation and compilation sheets.

### Thermodynamics of Solubility

The principal aims of the Solubility Data Project are the tabulation and evaluation of: (a) solubilities as defined above; (b) the nature of the saturating phase. Thermodynamic analysis of solubility phenomena has two aims: (a) to provide a rational basis for the construction of functions to represent solubility data; (b) to enable thermodynamic quantities to be extracted from solubility data. Both these are difficult to achieve in many cases because of a lack of experimental or theoretical information concerning activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve critical evaluation of a large body of data that is not directly relevant to solubility. The following is an outline of the principal thermodynamic relations encountered in discussions of solubility. For more extensive discussions and references, see books on thermodynamics, e.g., (5-12).

#### Activity Coefficients (1)

(a) Mixtures. The activity coefficient  $f_B$  of a substance B is given by

$$RT \ln (f_B x_B) = \mu_B - \mu_B^* \quad [7]$$

where  $\mu_B^*$  is the chemical potential of pure B at the same temperature and pressure. For any substance B in the mixture,

$$\lim_{x_B \rightarrow 1} f_B = 1 \quad [8]$$

#### (b) Solutions.

(i) Solute B. The molal activity coefficient  $\gamma_B$  is given by

$$RT \ln (\gamma_B m_B) = \mu_B - (\mu_B^* - RT \ln m_B)^\infty \quad [9]$$

where the superscript  $^\infty$  indicates an infinitely dilute solution. For any solute B,

$$\gamma_B^\infty = 1 \quad [10]$$

Activity coefficients  $\gamma_B$  connected with concentrations  $c_B$ , and  $f_{x,B}$  (called the rational activity coefficient) connected with mole fractions  $x_B$  are defined in analogous ways. The relations among them are (1, 9), where  $\rho^*$  is the density of the pure solvent:

$$f_B = (1 + M_A \sum_s m_s) \gamma_B = [\rho + \sum_s (M_A - M_s) c_s] \gamma_B / \rho^* \quad [11]$$

$$\gamma_B = (1 - \sum_s x_s) f_{x,B} = (\rho - \sum_s M_s c_s) \gamma_B / \rho^* \quad [12]$$

$$\gamma_B = \rho^* f_{x,B} [1 + \sum_s (M_s/M_A - 1) x_s] / \rho = \rho^* (1 + \sum_s M_s m_s) \gamma_B / \rho \quad [13]$$

For an electrolyte solute  $B = C_v A_v$ , the activity on the molality scale is replaced by (9)

$$\gamma_B m_B = \gamma_{\pm} v m_B v Q v \quad [14]$$

where  $v = v_+ + v_-$ ,  $Q = (v_+ v_+ v_- v_-)^{1/v}$ , and  $\gamma_{\pm}$  is the mean ionic activity coefficient on the molality scale. A similar relation holds for the concentration activity,  $\gamma_B c_B$ . For the mole fractional activity,

$$f_{x,B} x_B = Q v f_{\pm} v x_{\pm} v \quad [15]$$

where  $x_{\pm} = (x_+ x_-)^{1/v}$ . The quantities  $x_+$  and  $x_-$  are the ionic mole fractions (9), which are

$$x_+ = v_+ x_B / [1 + \sum_s (v_s - 1) x_s]; \quad x_- = v_- x_B / [1 + \sum_s (v_s - 1) x_s] \quad [16]$$

where  $v_s$  is the sum of the stoichiometric coefficients for the ions in a salt with mole fraction  $x_s$ . Note that the mole fraction of solvent is now

$$x_A' = (1 - \sum_s v_s x_s) / [1 + \sum_s (v_s - 1) x_s] \quad [17]$$

so that

$$x_A' + \sum_s v_s x_s = 1 \quad [18]$$

The relations among the various mean ionic activity coefficients are:

$$\gamma_{\pm} = (1 + M_A \sum_s v_s m_s) \gamma_{\pm} = [\rho + \sum_s (v_s M_A - M_s) c_s] \gamma_{\pm} / \rho^* \quad [19]$$

$$\gamma_{\pm} = \frac{(1 - \sum_s x_s) f_{\pm}}{1 + \sum_s (v_s - 1) x_s} = (\rho - \sum_s M_s c_s) \gamma_{\pm} / \rho^* \quad [20]$$

$$\gamma_{\pm} = \frac{\rho^* [1 + \sum_s (M_s/M_A - 1) x_s] f_{\pm}}{\rho [1 + \sum_s (v_s - 1) x_s]} = \rho^* (1 + \sum_s M_s m_s) \gamma_{\pm} / \rho \quad [21]$$

### (11) Solvent, A:

The osmotic coefficient,  $\phi$ , of a solvent A is defined as (1):

$$\phi = (\mu_A^* - \mu_A) / RT M_A \sum_s m_s \quad [22]$$

where  $\mu_A^*$  is the chemical potential of the pure solvent.

The rational osmotic coefficient,  $\phi_x$ , is defined as (1):

$$\phi_x = (\mu_A - \mu_A^*) / RT \ln x_A = \phi M_A \sum_s m_s / \ln (1 + M_A \sum_s m_s) \quad [23]$$

The activity,  $a_A$ , or the activity coefficient,  $f_A$ , is sometimes used for the solvent rather than the osmotic coefficient. The activity coefficient is defined relative to pure A, just as for a mixture.

For a mixed solvent, the molar mass in the above equations is replaced by the average molar mass; i.e., for a two-component solvent with components J, K,  $M_A$  becomes

$$M_A = M_J + (M_K - M_J) x_{V,K} \quad [24]$$

where  $x_{V,K}$  is the solvent mole fraction of component K.

The osmotic coefficient is related directly to the vapor pressure,  $p$ , of a solution in equilibrium with vapor containing A only by (12, p.306):

$$\phi M_A \sum_s v_s m_s = - \ln(p/p_A^*) + (V_m^*, A - B_{AA})(p - p_A^*) / RT \quad [25]$$

where  $p_A^*$ ,  $V_m^*, A$  are the vapor pressure and molar volume of pure solvent A, and  $B_{AA}$  is the second virial coefficient of the vapor.

**The Liquid Phase**

A general thermodynamic differential equation which gives solubility as a function of temperature, pressure and composition can be derived. The approach is similar to that of Kirkwood and Oppenheim (7); see also (11, 12). Consider a solid mixture containing  $c$  thermodynamic components i. The Gibbs-Duhem equation for this mixture is:

$$\sum_{i=1}^c x_i'(S_i'dT - V_i'dp + d\mu_i') = 0 \quad [26]$$

A liquid mixture in equilibrium with this solid phase contains  $c'$  thermodynamic components i, where  $c' > c$ . The Gibbs-Duhem equation for the liquid mixture is:

$$\sum_{i=1}^c x_i(S_i'dT - V_i'dp + d\mu_i') + \sum_{i=c+1}^{c'} x_i(S_i'dT - V_i'dp + d\mu_i) = 0 \quad [27]$$

Subtract [26] from [27] and use the equation

$$d\mu_i = (d\mu_i)_{T,p} - S_i'dT + V_i'dp \quad [28]$$

and the Gibbs-Duhem equation at constant temperature and pressure:

$$\sum_{i=1}^c x_i(d\mu_i)_{T,p} + \sum_{i=c+1}^{c'} x_i(d\mu_i)_{T,p} = 0 \quad [29]$$

The resulting equation is:

$$RT \sum_{i=1}^c x_i'(d\ln a_i)_{T,p} = \sum_{i=1}^c x_i'(H_i - H_i')dT/T - \sum_{i=1}^c x_i'(V_i - V_i')dp \quad [30]$$

where

$$H_i - H_i' = T(S_i - S_i') \quad [31]$$

is the enthalpy of transfer of component i from the solid to the liquid phase at a given temperature, pressure and composition, with  $H_i$  and  $S_i$  the partial molar enthalpy and entropy of component i.

Use of the equations

$$H_i - H_i^0 = -RT^2(\partial \ln a_i / \partial T)_{x,p} \quad [32]$$

and

$$V_i - V_i^0 = RT(\partial \ln a_i / \partial p)_{x,T} \quad [33]$$

where superscript 0 indicates an arbitrary reference state gives:

$$RT \sum_{i=1}^c x_i' d\ln a_i = \sum_{i=1}^c x_i'(H_i^0 - H_i')dT/T - \sum_{i=1}^c x_i'(V_i^0 - V_i')dp \quad [34]$$

where

$$d\ln a_i = (d\ln a_i)_{T,p} + (\partial \ln a_i / \partial T)_{x,p} + (\partial \ln a_i / \partial p)_{x,T} \quad [35]$$

The terms involving enthalpies and volumes in the solid phase can be written as:

$$\sum_{i=1}^c x_i' H_i' = H_s^* \quad \sum_{i=1}^c x_i' V_i' = V_s^* \quad [36]$$

With eqn [36], the final general solubility equation may then be written:

$$RT \sum_{i=1}^c x_i' d\ln a_i = (H_s^* - \sum_{i=1}^c x_i' H_i^0)d(1/T) - (V_s^* - \sum_{i=1}^c x_i' V_i^0)dp/T \quad [37]$$

Note that those components which are not present in both phases do not appear in the solubility equation. However, they do affect the solubility through their effect on the activities of the solutes.

Several applications of eqn [37] (all with pressure held constant) will be discussed below. Other cases will be discussed in individual evaluations.

(a) Solubility as a function of temperature.

Consider a binary solid compound  $A_nB$  in a single solvent A. There is

no fundamental thermodynamic distinction between a binary compound of A and B which dissociates completely or partially on melting and a solid mixture of A and B; the binary compound can be regarded as a solid mixture of constant composition. Thus, with  $c = 2$ ,  $x_A = n/(n + 1)$ ,  $x_B = 1/(n + 1)$ , eqn [37] becomes:

$$d\ln(a_A^n a_B) = -\Delta H_{AB}^0 d(1/RT) \quad [38]$$

where

$$\Delta H_{AB}^0 = nH_A + H_B - (n + 1)H_S^* \quad [39]$$

is the molar enthalpy of melting and dissociation of pure solid  $A_nB$  to form A and B in their reference states. Integration between  $T$  and  $T_0$ , the melting point of the pure binary compound  $A_nB$ , gives:

$$\ln(a_A^n a_B) = \ln(a_A^n a_B)_{T=T_0} - \int_{T_0}^T \Delta H_{AB}^0 d(1/RT) \quad [40]$$

### (i) Non-electrolytes

In eqn [32], introduce the pure liquids as reference states. Then, using a simple first-order dependence of  $\Delta H_{AB}^*$  on temperature, and assuming that the activity coefficients conform to those for a simple mixture (6):

$$RT \ln f_A = w x_B^2 \quad RT \ln f_B = w x_A^2 \quad [41]$$

then, if  $w$  is independent of temperature, eqn [32] and [33] give:

$$\ln(x_B(1-x_B)^n) + \ln\left\{\frac{n^n}{(1+n)^{n+1}}\right\} = G(T) \quad [42]$$

where

$$G(T) = -\left[\frac{\Delta H_{AB}^* - T^* \Delta C_p^*}{R}\right]\left\{\frac{1}{T} - \frac{1}{T^*}\right\} + \frac{\Delta C_p^*}{R} \ln(T/T^*) - \frac{w}{R} \left[ \frac{x_A^2 + nx_B^2}{T} - \frac{n}{(n+1)T^*} \right] \quad [43]$$

where  $\Delta C_p^*$  is the change in molar heat capacity accompanying fusion plus decomposition of the pure compound to pure liquid A and B at temperature  $T^*$ , (assumed here to be independent of temperature and composition), and  $\Delta H_{AB}^*$  is the corresponding change in enthalpy at  $T = T^*$ . Equation [42] has the general form:

$$\ln(x_B(1-x_B)^n) = A_1 + A_2/(T/K) + A_3 \ln(T/K) + A_4(x_A^2 + nx_B^2)/(T/K) \quad [44]$$

If the solid contains only component B, then  $n = 0$  in eqn [42] to [44].

If the infinite dilution reference state is used, then:

$$RT \ln f_{x,B} = w(x_A^2 - 1) \quad [45]$$

and [39] becomes

$$\Delta H_{AB}^\infty = nH_A^* + H_B^\infty - (n + 1)H_S^* \quad [46]$$

where  $\Delta H_{AB}^\infty$  is the enthalpy of melting and dissociation of solid compound  $A_nB$  to the infinitely dilute reference state of solute B in solvent A;  $H_A^*$  and  $H_B^\infty$  are the partial molar enthalpies of the solute and solvent at infinite dilution. Clearly, the integral of eqn [32] will have the same form as eqn [35], with  $\Delta H_{AB}^\infty$  replacing  $\Delta H_{AB}^*$ ,  $\Delta C_p^\infty$  replacing  $\Delta C_p^*$ , and  $x_A^2 - 1$  replacing  $x_A^2$  in the last term.

See (5) and (11) for applications of these equations to experimental data.

### (ii) Electrolytes

#### (a) Mole fraction scale

If the liquid phase is an aqueous electrolyte solution, and the solid is a salt hydrate, the above treatment needs slight modification. Using rational mean activity coefficients, eqn [34] becomes:

$$\ln \left\{ \frac{x_B^v(1-x_B)^n}{[1+(v-1)x_B]^{n+v}} \right\} = \ln \left\{ \frac{n^n}{(n+v)^{n+v}} \right\} + \ln \left\{ \left[ \frac{f_B}{f_B^*} \right]^v \left[ \frac{f_A}{f_A^*} \right]^n \right\} - \left\{ \frac{\Delta H_{AB}^* - T^* \Delta C_p^*}{R} \right\} \left\{ \frac{1}{T} - \frac{1}{T^*} \right\} + \frac{\Delta C_p^*}{R} \ln(T/T^*) \quad [47]$$

where superscript \* indicates the pure salt hydrate. If it is assumed that the activity coefficients follow the same temperature dependence as the right-hand side of eqn [47] (13-16), the thermochemical quantities on the right-hand side of eqn [47] are not rigorous thermodynamic enthalpies and heat capacities, but are apparent quantities only. Data on activity coefficients (9) in concentrated solutions indicate that the terms involving these quantities are not negligible, and their dependence on temperature and composition along the solubility-temperature curve is a subject of current research.

A similar equation (with  $v = 2$  and without the heat capacity terms or activity coefficients) has been used to fit solubility data for some MOH-H<sub>2</sub>O systems, where M is an alkali metal (13); enthalpy values obtained agreed well with known values. The full equation has been deduced by another method in (14) and applied to MCl<sub>2</sub>-H<sub>2</sub>O systems in (14) and (15). For a summary of the use of equation [47] and similar equations, see (14).

### (2) Molality scale

Substitution of the mean activities on the molality scale in eqn [40] gives:

$$v \ln \left\{ \frac{\gamma_{\pm} m_B}{\gamma_{\pm}^* m_B^*} \right\} = v(m_B/m_B^* - 1) = v(m_B(\phi - 1)/m_B^* - \phi^* + 1) = G(T) \quad [48]$$

where  $G(T)$  is the same as in eqn [47],  $m_B^* = 1/nM_A$  is the molality of the anhydrous salt in the pure salt hydrate and  $\gamma_{\pm}$  and  $\phi$  are the mean activity coefficient and the osmotic coefficient, respectively. Use of the osmotic coefficient for the activity of the solvent leads, therefore, to an equation that has a different appearance to [47]; the content is identical. However, while eqn [47] can be used over the whole range of composition ( $0 < x_B < 1$ ), the molality in eqn [48] becomes infinite at  $x_B = 1$ ; use of eqn [48] is therefore confined to solutions sufficiently dilute that the molality is a useful measure of composition. The essentials of eqn [48] were deduced by Williamson (17); however, the form used here appears first in the Solubility Data Series. For typical applications (where activity and osmotic coefficients are not considered explicitly, so that the enthalpies and heat capacities are apparent values, as explained above), see (18).

The above analysis shows clearly that a rational thermodynamic basis exists for functional representation of solubility-temperature curves in two-component systems, but may be difficult to apply because of lack of experimental or theoretical knowledge of activity coefficients and partial molar enthalpies. Other phenomena which are related ultimately to the stoichiometric activity coefficients and which complicate interpretation include ion pairing, formation of complex ions, and hydrolysis. Similar considerations hold for the variation of solubility with pressure, except that the effects are relatively smaller at the pressures used in many investigations of solubility (5).

### (b) Solubility as a function of composition.

At constant temperature and pressure, the chemical potential of a saturating solid phase is constant:

$$\begin{aligned} \mu_{A_nB}^* &= \mu_{A_nB}(\text{sln}) = n\mu_A + \mu_B \\ &= (n\mu_A^* + v_+\mu_+^\infty + v_-\mu_-^\infty) + nRT \ln f_A x_A \\ &\quad + vRT \ln(\gamma_{\pm} m_{\pm} Q) \end{aligned} \quad [49]$$

for a salt hydrate  $A_nB$  which dissociates to water (A), and a salt (B), one mole of which ionizes to give  $v_+$  cations and  $v_-$  anions in a solution in which other substances (ionized or not) may be present. If the saturated solution is sufficiently dilute,  $f_A = x_A = 1$ , and the quantity  $K_s$  in

$$\begin{aligned} \Delta G^\infty &= (v_+\mu_+^\infty + v_-\mu_-^\infty + n\mu_A^* - \mu_{AB}^*) \\ &= -RT \ln K_s \end{aligned}$$

$$= -\nu RT \ln(Q\gamma_{\pm}m_B) \quad [50]$$

is called the solubility product of the salt. (It should be noted that it is not customary to extend this definition to hydrated salts, but there is no reason why they should be excluded.) Values of the solubility product are often given on mole fraction or concentration scales. In dilute solutions, the theoretical behaviour of the activity coefficients as a function of ionic strength is often sufficiently well known that reliable extrapolations to infinite dilution can be made, and values of  $K_s$  can be determined. In more concentrated solutions, the same problems with activity coefficients that were outlined in the section on variation of solubility with temperature still occur. If these complications do not arise, the solubility of a hydrate salt  $C_xA_y \cdot nH_2O$  in the presence of other solutes is given by eqn [50] as

$$\nu \ln(m_B/m_B(0)) = -\nu \ln(\gamma_{\pm}/\gamma_{\pm}(0)) - n \ln(a_A/a_A(0)) \quad [51]$$

where  $a_A$  is the activity of water in the saturated solution,  $m_B$  is the molality of the salt in the saturated solution, and (0) indicates absence of other solutes. Similar considerations hold for non-electrolytes.

Consideration of complex mixed ligand equilibria in the solution phase are also frequently of importance in the interpretation of solubility equilibria. For nomenclature connected with these equilibria (and solubility equilibria as well), see (19, 20).

#### The Solid Phase

The definition of solubility permits the occurrence of a single solid phase which may be a pure anhydrous compound, a salt hydrate, a non-stoichiometric compound, or a solid mixture (or solid solution, or "mixed crystals"), and may be stable or metastable. As well, any number of solid phases consistent with the requirements of the phase rule may be present. Metastable solid phases are of widespread occurrence, and may appear as polymorphic (or allotropic) forms or crystal solvates whose rate of transition to more stable forms is very slow. Surface heterogeneity may also give rise to metastability, either when one solid precipitates on the surface of another, or if the size of the solid particles is sufficiently small that surface effects become important. In either case, the solid is not in stable equilibrium with the solution. See (21) for the modern formulation of the effect of particle size on solubility. The stability of a solid may also be affected by the atmosphere in which the system is equilibrated.

Many of these phenomena require very careful, and often prolonged, equilibration for their investigation and elimination. A very general analytical method, the "wet residues" method of Schreinemakers (22), is often used to investigate the composition of solid phases in equilibrium with salt solutions. This method has been reviewed in (23), where [see also (24)] least-squares methods for evaluating the composition of the solid phase from wet residue data (or initial composition data) and solubilities are described. In principle, the same method can be used with systems of other types. Many other techniques for examination of solids, in particular X-ray, optical, and thermal analysis methods, are used in conjunction with chemical analyses (including the wet residues method).

#### COMPILATIONS AND EVALUATIONS

The formats for the compilations and critical evaluations have been standardized for all volumes. A brief description of the data sheets has been given in the FOREWORD; additional explanation is given below.

##### Guide to the Compilations

The format used for the compilations is, for the most part, self-explanatory. The details presented below are those which are not found in the FOREWORD or which are not self-evident.

**Components.** Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The formula is given either in terms of the IUPAC or Hill (25) system and the choice of formula is governed by what is usual for most current users: i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered according to:

- (a) saturating components;
- (b) non-saturating components in alphanumerical order;
- (c) solvents in alphanumerical order.

The saturating components are arranged in order according to a 18-column periodic table with two additional rows:  
Columns 1 and 2: H, alkali elements, ammonium, alkaline earth elements  
3 to 12: transition elements  
13 to 17: boron, carbon, nitrogen groups; chalcogenides, halogens  
18: noble gases  
Row 1: Ce to Lu  
Row 2: Th to the end of the known elements, in order of atomic number.

Salt hydrates are generally not considered to be saturating components since most solubilities are expressed in terms of the anhydrous salt. The existence of hydrates or solvates is carefully noted in the text, and CA Registry Numbers are given where available, usually in the critical evaluation. Mineralogical names are also quoted, along with their CA Registry Numbers, again usually in the critical evaluation.

**Original Measurements.** References are abbreviated in the forms given by Chemical Abstracts Service Source Index (CASSI). Names originally in other than Roman alphabets are given as transliterated by Chemical Abstracts.

**Experimental Values.** Data are reported in the units used in the original publication, with the exception that modern names for units and quantities are used; e.g., mass per cent for weight per cent; mol dm<sup>-3</sup> for molar; etc. Both mass and molar values are given. Usually, only one type of value (e.g., mass per cent) is found in the original paper, and the compiler has added the other type of value (e.g., mole per cent) from computer calculations based on 1983 atomic weights (26).

Errors in calculations and fitting equations in original papers have been noted and corrected, by computer calculations where necessary.

**Method. Source and Purity of Materials.** Abbreviations used in Chemical Abstracts are often used here to save space.

**Estimated Error.** If these data were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on the papers by Ku and Eisenhart (27).

**Comments and/or Additional Data.** Many compilations include this section which provides short comments relevant to the general nature of the work or additional experimental and thermodynamic data which are judged by the compiler to be of value to the reader.

**References.** See the above description for Original Measurements.

#### Guide to the Evaluations

The evaluator's task is to check whether the compiled data are correct, to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend "best" values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. A brief description of the evaluation sheets is given below.

**Components.** See the description for the Compilations.

**Evaluator.** Name and date up to which the literature was checked.

#### Critical Evaluation

(a) **Critical text.** The evaluator produces text evaluating all the published data for each given system. Thus, in this section the evaluator reviews the merits or shortcomings of the various data. Only published data are considered; even published data can be considered only if the experimental data permit an assessment of reliability.

(b) **Fitting equations.** If the use of a smoothing equation is justified the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets.

(c) **Graphical summary.** In addition to (b) above, graphical summaries are often given.

(d) **Recommended values.** Data are recommended if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are considered as tentative if only one set of measurements is

available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor errors. Data are considered as doubtful if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value in those instances where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are rejected. However references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here. References to those data which, by virtue of their poor precision, have been rejected and not compiled are also listed in this section.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in S.I. units (1, 28) when the data can be accurately converted.

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Table I-1

Quantities Used as Measures of Solubility of Solute B  
 Conversion Table for Multicomponent Systems  
 Containing Solvent A and Solutes s

	mole fraction $x_B =$	mass fraction $w_B =$	molality $m_B =$	concentration $c_B =$
$x_B$	$x_B$	$\frac{M_B x_B}{M_A + \sum_s (M_s - M_A) x_s}$	$\frac{x_B}{M_A (1 - \sum_s x_s)}$	$\frac{\rho x_B}{M_A + \sum_s (M_s - M_A) x_s}$
$w_B$	$\frac{w_B / M_B}{1/M_A + \sum_s (1/M_s - 1/M_A) w_s}$	$w_B$	$\frac{w_B}{M_B (1 - \sum_s w_s)}$	$\rho w_B / M_B$
$m_B$	$\frac{M_A m_B}{1 + M_A \sum_s m_s}$	$\frac{M_B m_B}{1 + \sum_s m_s M_s}$	$m_B$	$\frac{\rho m_B}{1 + \sum_s M_s m_s}$
$c_B$	$\frac{M_A c_B}{\rho + \sum_s (M_A - M_s) c_s}$	$M_B c_B / \rho$	$\frac{c_B}{\rho - \sum_s M_s c_s}$	$c_B$

$\rho$  = density of solution

$M_A, M_B, M_s$  = molar masses of solvent, solute B, other solutes s  
 Formulas are given in forms suitable for rapid computation; all calculations should be made using SI base units.

COMPONENTS:

- (1) Lithium phosphate;  $\text{Li}_3\text{PO}_4$ ; [10377-52-3]
- (2) Ammonia;  $\text{NH}_3$ ; [7664-41-7]
- (3) Lithium hydroxide;  $\text{LiOH}$ ; [1310-65-2]
- (4) Phosphoric acid;  $\text{H}_3\text{PO}_4$ ; [7664-38-2]
- (5) Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

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## CRITICAL EVALUATION:

There have been relatively few solubility studies on  $\text{Li}_3\text{PO}_4$ -aqueous systems (1-5). Four of the studies (1-4) report solubilities based on direct analysis of the binary system, and three studies (2, 3, 5) report the solubility of  $\text{Li}_3\text{PO}_4$  in ternary systems.

THE BINARY SYSTEM

1. Solubilities at 273 K to 298 K. The direct determination of the solubility of  $\text{Li}_3\text{PO}_4$  in pure water has proved difficult due to the formation of a fine colloid which cannot be removed by filtration (1,4). Thus Rammelsberg's value (1) of  $0.0104 \text{ mol kg}^{-1}$  at 288 K is undoubtedly much too high, and this work has therefore not been compiled. Although Mayer's average value of  $0.00340 \text{ mol kg}^{-1}$  ( $0.394 \text{ g kg}^{-1}$ ) appears slightly high, he certainly was aware of this problem (2,3): in a footnote on page 201 of reference (2), Mayer states that turbidity in saturated solutions does not occur if the solution is heated. Although not stated, the evaluators assume that Mayer prepared his saturated solutions by first heating the solutions (i.e. from supersaturation). Since Mayer's value is slightly high, the evaluators were considering rejecting these data but decided against this as his data constitute one of two direct measurements on the binary system [the other being from ref (4)], and his results are the most widely quoted ones in various important handbooks (e.g. see references 6-8). Mayer's value of  $0.0394 \text{ g per } 100 \text{ g H}_2\text{O}$  is usually quoted for 291 K when his solutions were equilibrated over the temperature range of 288 - 291 K.

Rollet and Lauffenburger (5) obtained solubility values for the binary system at 273 K and 293 K by extrapolation of the isotherms in the  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  ternary systems. Their results for the solubility of  $\text{Li}_3\text{PO}_4$  in pure water are:  $m_{\text{satd}} = 0.0019 \text{ mol kg}^{-1}$  at 273 K, and  $m_{\text{satd}} = 0.0026 \text{ mol kg}^{-1}$  at 293 K. These data suggest that the solubility of  $\text{Li}_3\text{PO}_4$  in pure water increases with temperature and therefore casts some doubt on the accuracy of Mayer's value of  $0.00340 \text{ mol kg}^{-1}$  at 288-291 K. Adding to the uncertainty in the solubility of this salt is the value of  $0.00227 \text{ mol dm}^{-3}$  at 298 K calculated by the evaluators (see below) using the conductivity data of Rosenheim and Reglin (4). If we assume the solubility follows a  $\log m_{\text{satd}}$  vs  $1/(T/K)$  relation, then using Rollet and Laufenburger's extrapolated solubility values for 273 K and 293 K, the evaluators calculate  $m_{\text{satd}} = 0.0028 \pm 0.0002 \text{ mol kg}^{-1}$  at 298 K (this corresponds to  $c_{\text{satd}} = 0.00279 \text{ mol dm}^{-3}$  (evaluators)).

Rosenheim and Reglin (4) measured the electrolytic conductivity of saturated  $\text{Li}_3\text{PO}_4$  slns. Their calculation of  $\kappa_{\text{salt}}$  (corrected for the electrolytic conductivity of water) is in error, and the correct average determined by the compilers is  $9.30 \times 10^{-4} \text{ S cm}^{-1}$ . In computing the solubility from  $\kappa_{\text{salt}}$ , one cannot neglect, as did Rosenheim and Reglin, the hydrolysis of the phosphate ion according to



The thermodynamic equilibrium constant for this hydrolysis reaction is obtained from

$$K_h^{\circ} = K_w^{\circ} / K_{a3}^{\circ} \quad [2]$$

## Lithium Phosphate

<b>COMPONENTS:</b> (1) Lithium phosphate; $\text{Li}_3\text{PO}_4$ ; [10377-52-3] (2) Ammonia; $\text{NH}_3$ ; [7664-41-7] (3) Lithium hydroxide; $\text{LiOH}$ ; [1310-65-2] (4) Phosphoric acid; $\text{H}_3\text{PO}_4$ [7664-38-2] (5) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	<b>EVALUATOR:</b> J. Eyseltová Charles University Prague, Czechoslovakia and M. Salomon U.S. Army Research Laboratories Ft. Monmouth, NJ 07703 U.S.A. <i>December 1981</i>
<b>CRITICAL EVALUATION:</b>	
<p>In eq [2] <math>K_w^{\circ} = 1.005 \times 10^{-14}</math> (9), and the third acid dissociation constant of <math>\text{H}_3\text{PO}_4</math> is <math>K_{\text{a}3}^{\circ} = 4.217 \times 10^{-13}</math> (10): thus <math>K_h^{\circ} = 0.02383</math> at 298 K, and the major ions in solution are <math>\text{Li}^+</math>, <math>\text{HPO}_4^{2-}</math>, <math>\text{OH}^-</math> and a small but significant amount of <math>\text{PO}_4^{3-}</math>. It is reasonable to assume that further hydrolysis to <math>\text{H}_2\text{PO}_4^-</math> is negligible (11), that ion association of <math>\text{Li}^+</math> and <math>\text{OH}^-</math> is negligible (12-14), and that ion association of <math>\text{Li}^+</math> and <math>\text{HPO}_4^{2-}</math> is negligible (15).</p>	
<p>For saturated solutions, we have</p> $K_h^{\circ} \{y_{\pm}(\text{PO}_4^{3-})/[y_{\pm}(\text{OH}^-)y_{\pm}(\text{HPO}_4^{2-})]\} = [\text{OH}^-][\text{HPO}_4^{2-}]/[\text{PO}_4^{3-}] = \alpha^2 c_{\text{satd}}/(1 - \alpha) \quad [3]$ <p>where <math>\alpha</math> is the degree of hydrolysis and <math>y_{\pm}</math> is the mean molar activity coefficient of the indicated species. The solubility of <math>\text{Li}_3\text{PO}_4</math> in pure water can be calculated from Rosenheim and Reglin's average <math>\kappa_{\text{salt}}</math> value from</p> $10^3 \kappa_{\text{salt}}/c_{\text{satd}} = 2\alpha\Lambda(\text{Li}_2\text{HPO}_4) + \alpha\Lambda(\text{LiOH}) + 3(1 - \alpha)\Lambda(\text{Li}_3\text{PO}_4) \quad [4]$ <p>where the molar conductivities, <math>\Lambda</math>, can be calculated for a given concentration, <math>c_1</math>, of the various species using Robinson and Stokes' equation (9)</p> $\Lambda = \Lambda^{\infty} - \{0.77816 z_1 z_2 q\Lambda^{\infty}/(1 + q^2) + 30.16( z_1  +  z_2 )\}c_1 \quad [5]$ <p>The reader is referred to reference (9) for definition of <math>q</math> and the origins of the numerical terms. Limiting molar conductivities are separated into individual ionic contributions, e.g. for <math>\text{Li}_2\text{HPO}_4</math>, we have <math>\Lambda^{\infty} = \lambda^{\infty}(\text{Li}^+) + \lambda^{\infty}(\text{HPO}_4^{2-})</math> and <math>c_1 = \alpha c_{\text{satd}}</math>. We first assume a value for <math>c_{\text{satd}}</math> and compute <math>\alpha</math> iteratively from eq [3]. In solving for <math>\alpha</math> from eq [3], the Davies eq</p> $\log y_{\pm} = -0.5115z^2\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.31\} \quad [6]$ <p>was used (16). The ionic strength <math>I</math> was calculated from</p> $I = 2c_{\text{satd}}(3 - \alpha) \quad [7]$ <p>For the assumed <math>c_{\text{satd}}</math> and the corresponding <math>\alpha</math>, eq [4] is solved for <math>\kappa_{\text{salt}}</math> and the calcs repeated until the experimental value <math>\kappa_{\text{salt}} = 9.30 \times 10^{-4} \text{ S cm}^{-1}</math> is obtained. Although the solution of eq [4] employing eqs [3], [5]-[7] is fairly straight forward, there is at least a 5% uncertainty in the refined <math>c_{\text{satd}}</math> due to the uncertainties in the molar conductivities at infinite dilution for <math>\text{HPO}_4^{2-}</math> and <math>\text{PO}_4^{3-}</math>. <math>\lambda^{\infty}(\text{HPO}_4^{2-})</math> values of <math>53.4 \text{ S cm}^2 \text{ mol}^{-1}</math> (17) and <math>57 \text{ S cm}^2 \text{ mol}^{-1}</math> (18) have been reported, and the uncertainty is probably higher than indicated by the closeness of these two values. For the present calculations, the evaluators have taken <math>\lambda^{\infty}(\text{HPO}_4^{2-}) = 53.4 \text{ S cm}^2 \text{ mol}^{-1}</math>. Greater uncertainty is associated with the value for <math>\lambda^{\infty}(\text{PO}_4^{3-})</math> as reported values range from <math>69.0 \text{ S cm}^2 \text{ mol}^{-1}</math> (17) to <math>82.3 \text{ S cm}^2 \text{ mol}^{-1}</math> (19) and <math>92.8 \text{ S cm}^2 \text{ mol}^{-1}</math> (20). Milazzo's value (20) appears much too high, and for consistency in the calculations, we have used Prideaux's value (17) of <math>\lambda^{\infty}(\text{PO}_4^{3-})</math> and <math>67 \text{ S cm}^2 \text{ mol}^{-1}</math>. For the remaining molar conductivities, we have used <math>\lambda^{\infty}(\text{Li}^+) = 38.71 \text{ S cm}^2 \text{ mol}^{-1}</math> (13) and <math>\lambda^{\infty}(\text{OH}^-) = 199.18 \text{ S cm}^2 \text{ mol}^{-1}</math> (21). Our final results are: <math>c_{\text{satd}} = 0.00227 \text{ mol dm}^{-3}</math> and <math>\alpha = 0.8875</math>. Thus the extent of hydrolysis of <math>\text{PO}_4^{3-}</math> in the saturated solution is about 89%, and the fact that Rosenheim and Reglin obtain a <math>c_{\text{satd}}</math> close to <math>0.00227 \text{ mol dm}^{-3}</math> neglecting hydrolysis is attributed to their use of inaccurate <math>\lambda^{\infty}</math> values.</p>	

(continued next page)

<b>COMPONENTS:</b>
(1) Lithium phosphate; $\text{Li}_3\text{PO}_4$ ; [10377-52-3]
(2) Ammonia; $\text{NH}_3$ ; [7664-41-7]
(3) Lithium hydroxide; $\text{LiOH}$ ; [1310-65-2]
(4) Phosphoric acid; $\text{H}_3\text{PO}_4$ ; [7664-38-2]
(5) Water; $\text{H}_2\text{O}$ ; [7732-18-5]

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 December 1981

**CRITICAL EVALUATION:**

We now review the status of the solubility of  $\text{Li}_3\text{PO}_4$  in pure water. Mayer's oft quoted value of  $0.0034 \text{ mol kg}^{-1}$  at 288-293 K is probably too high by at least 15%. Using the conductivity data of Rosenheim and Reglin, the evaluators have calculated a solubility value of  $0.0023 \pm 0.0001 \text{ mol dm}^{-3}$  at 298 K. This value is not in very good agreement with the extrapolated value of  $0.0028 \pm 0.0002 \text{ mol kg}^{-1}$  estimated by the evaluators from Rollet and Lauffenburger's extrapolated values of  $0.0019 \text{ mol kg}^{-1}$  at 273 K and  $0.0026 \text{ mol kg}^{-1}$  at 293K.

2. The Solubility Product Constant. For the reaction

the thermodynamic solubility product constant is defined by

$$K_{s0}^\circ = \{\text{Li}^+\}^3 \{\text{PO}_4^{3-}\} = 27(1 - \alpha)c_{\text{satd}}^4 y_\pm^3 (\text{Li}^+) y_\pm (\text{PO}_4^{3-}) \quad [9]$$

Based on the solubility of  $0.00227 \text{ mol dm}^{-3}$  calculated by the evaluators from the conductivity data, it is found that  $K_{s0}^\circ = 2.370 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$ , or  $pK_{s0}^\circ = 10.625$ . In the latest revision of Lange's Handbook, Dean (8) reports  $pK_{s0}^\circ = 8.5$ . It is not stated whether this is a pK or a  $pK^\circ$  value, what the temperature is, and the origin of this value. It appears (see below) that this  $pK_{s0}^\circ$  was incorrectly calculated from Mayer's  $m_{\text{satd}}$ , and since earlier versions of Lange's Handbook (e.g. see ref. 7) do not report a  $K_{s0}^\circ$  for  $\text{Li}_3\text{PO}_4$ , the value  $pK_{s0}^\circ = 8.5$  is probably one of Dean's contributions to the revised Handbook. If we incorrectly neglect hydrolysis and activity coefficients,  $K_{s0}^\circ$  would be given by

$$K_{s0}^\circ = [\text{Li}^+]^3 [\text{PO}_4^{3-}] = 27 c_{\text{satd}}^4 \quad [10]$$

Using Mayer's value of  $m_{\text{satd}} = 0.00340 \text{ mol kg}^{-1}$  at 288-291 K, eq [10] give  $K_{s0}^\circ = 3.61 \times 10^{-9} \text{ mol}^2 \text{ kg}^{-2}$ , or  $pK_{s0}^\circ = 8.44$  which is practically identical to Dean's value of 8.5.

Two additional sources (22,23) quote a value of  $pK_{s0}^\circ = 12.5$  but fail to state whether this is a pK or  $pK^\circ$  value, and fail to cite the original publication. The evaluators could not find the source of this  $pK_{s0}^\circ$  in spite of an exhaustive literature search. Fitting eq [3] to this  $pK_{s0}^\circ$  requires  $c_{\text{satd}} = 0.000875 \text{ mol dm}^{-3}$ , and we therefore conclude that the  $pK_{s0}^\circ$  value of 12.5 is in serious error and must be rejected.

MULTICOMPONENT SYSTEMS

Of the few solubility studies on multicomponent systems (1-3, 5, 24) only ternary systems have been investigated and only references 2,3 and 5 report quantitative data. Qualitative studies state that  $\text{Li}_3\text{PO}_4$  is soluble in strong acids (1-3, 24), is difficult to dissolve in acetic acid (2,3) and that addition of  $\text{NH}_4\text{Cl}$  tends to increase the solubility (2,3). The quantitative studies are discussed below.

1. The  $\text{Li}_3\text{PO}_4-\text{NH}_3-\text{H}_2\text{O}$  system. Mayer (2,3) reported only one data point for this system at 288-291 K. In approximately  $1.6 \text{ mol kg}^{-1}$   $\text{NH}_3$  solution, the average value of the solv as calculated by the compilers is  $0.0015 \text{ mol kg}^{-1}$  ( $\sigma = 0.0001$ ).

2. The  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  System. This is the most complete phase study available for  $\text{Li}_3\text{PO}_4$  systems. Rollet and Laueffenburger (5) reported the compositions of saturated solutions at 273 K and 293 K in mass% of  $\text{Li}_2\text{O}$  and  $\text{P}_2\text{O}_5$ . The compiler separated appropriate data (continued next page)

## Lithium Phosphate

<b>COMPONENTS:</b> (1) Lithium phosphate; $\text{Li}_3\text{PO}_4$ ; [10377-52-3] (2) Ammonia; $\text{NH}_3$ ; [7664-41-7] (3) Lithium hydroxide; $\text{LiOH}$ ; [1310-65-2] (4) Phosphoric acid; $\text{H}_3\text{PO}_4$ ; [7664-38-2] (5) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	<b>EVALUATOR:</b> J. Eysseletová Charles University Prague, Czechoslovakia and M. Salomon U.S. Army Research Laboratories Ft. Monmouth, NJ 07703 U.S.A. <i>December 1981</i>
<b>CRITICAL EVALUATION:</b>	
<p>into two compilations corresponding to the ternary systems <math>\text{Li}_3\text{PO}_4\text{-LiOH-H}_2\text{O}</math> and <math>\text{Li}_3\text{PO}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}</math>. The original phase diagrams are reproduced in Figures 1 and 2. Note that Figure 2 is an expanded detail of the initial portion of Figure 1. Numerical data corresponding to the points A-E are given in the compilations as well as the compiler's conversions from mass% to mol% and mol kg<sup>-1</sup>. At 273 K, <math>\text{LiOH}\cdot\text{H}_2\text{O}</math> is the initial solid phase up to invariant point A where <math>\text{Li}_3\text{PO}_4</math> is also in equilibrium with the solution. The solubility then decreases rapidly and then increases slowly to invariant point B at which point both <math>\text{Li}_3\text{PO}_4</math> and <math>\text{LiH}_2\text{PO}_4</math> solid phases are in equilibrium with the solution. Between B and C, <math>\text{LiH}_2\text{PO}_4</math> precipitates. The 293 K isotherm is similar to the 273 K isotherm. The invariant points are D and E. Note that point E is on the acid side of the line for <math>\text{P}_2\text{O}_5/\text{Li}_2\text{O} = 1.00</math> which means that <math>\text{LiH}_2\text{PO}_4</math> will dissolve incongruently to form <math>\text{Li}_3\text{PO}_4</math> and <math>\text{H}_3\text{PO}_4</math> until the composition of point E is reached.</p>	
<b>SOLID PHASES</b>	
<p>A number of solid phases have been reported or suggested to be in equilibrium with saturated <math>\text{Li}_3\text{PO}_4</math> solutions. They are</p> <ul style="list-style-type: none"> <li style="margin-bottom: 0.5em;">lithium hydroxide hydrate; <math>\text{LiOH}\cdot\text{H}_2\text{O}</math>; [1310-66-3]</li> <li style="margin-bottom: 0.5em;">lithium phosphate; <math>\text{Li}_3\text{PO}_4</math>; [10377-52-3]</li> <li style="margin-bottom: 0.5em;">lithium phosphate dihydrate; <math>\text{Li}_3\text{PO}_4\cdot 2\text{H}_2\text{O}</math>; [74893-09-7]</li> <li style="margin-bottom: 0.5em;">lithium phosphate hemihydrate; <math>\text{Li}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}</math>; [10102-26-8]</li> <li style="margin-bottom: 0.5em;">lithium dihydrogen phosphate; <math>\text{LiH}_2\text{PO}_4</math>; [13453-80-0]</li> </ul>	
<p>Rollet and Lauffenburger's detailed phase study (5) reports the absence of any phosphate hydrates as well as the absence of <math>\text{Li}_2\text{HPO}_4</math> for their experimental conditions. On the other hand, Rosenheim and Reglin (4) state that their solid phase is the dihydrate which forms by precipitation from aqueous <math>\text{H}_3\text{PO}_3</math> with excess <math>\text{LiOH}</math>. These conflicting results are difficult to assess since neither study describes sufficient details of the analyses of the solid phases. Presumably Rollet and Lauffenburger used a wet residue method such as Schreinemakers' method, and Rosenheim and Reglin simply air dried their solid at 289 K so that it is quite possible that the water they found in the solid was not water of hydration. Upon drying at 333 K for several days, Rosenheim and Reglin state that they obtain the hemihydrate. It may indeed be possible that the hemihydrate is stable under the conditions reported by Rosenheim and Reglin since Sanfourche (25) reported that the neutralization method of preparation of <math>\text{Li}_3\text{PO}_4</math> actually yields the hemihydrate, and that the water of hydration can be removed only at red heat. These results combined with Rollet and Lauffenburger's findings that no hydrate is formed at ambient temperatures casts some doubt on the nature of the solid phases present in all of the reported solubility studies. Because of this situation, and of the uncertainties in the reported solubility data, the evaluators feel that new studies are required before recommended data can be specified.</p>	
<i>(continued next page)</i>	

## COMPONENTS:

- (1) Lithium phosphate;  $\text{Li}_3\text{PO}_4$ ; [10377-52-3]
- (2) Ammonia;  $\text{NH}_3$ ; [7664-41-7]
- (3) Lithium hydroxide;  $\text{LiOH}$ ; [1310-65-2]
- (4) Phosphoric acid;  $\text{H}_3\text{PO}_4$ ; [7664-38-2]
- (5) Water;  $\text{H}_2\text{O}$ , [7732-18-5]

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 December 1981

## CRITICAL EVALUATION:

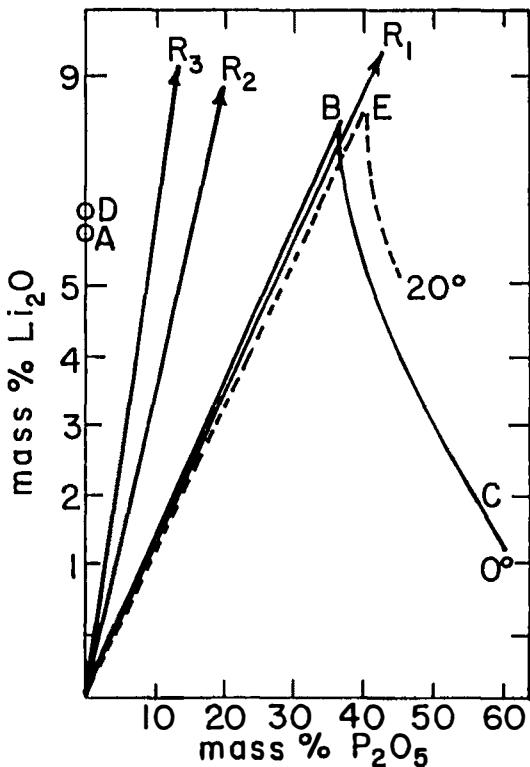


Figure 1. Isotherms for the  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  system.

$$R_1 = \text{Li}_2\text{O}/\text{P}_2\text{O}_5 = 1$$

$$R_2 = \text{Li}_2\text{O}/\text{P}_2\text{O}_5 = 2$$

$$R_3 = \text{Li}_2\text{O}/\text{P}_2\text{O}_5 = 3$$

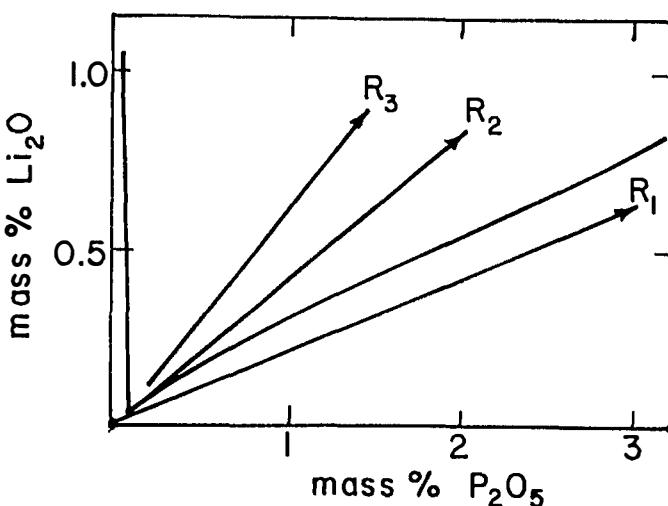


Figure 2. Detail of the 0° isotherm on Figure 1.

(continued next page)

## Lithium Phosphate

<b>COMPONENTS:</b> (1) Lithium phosphate; Li <sub>3</sub> PO <sub>4</sub> ; [10377-52-3] (2) Ammonia; NH <sub>3</sub> ; [7664-41-7] (3) Lithium hydroxide; LiOH; [1310-65-2] (4) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2] (5) Water; H <sub>2</sub> O; [7732-18-5]	<b>EVALUATOR:</b> J. Eysseltová Charles University Prague, Czechoslovakia and M. Salomon U.S. Army Research Laboratories Ft. Monmouth, NJ 07703 U.S.A. December 1981
<b>CRITICAL EVALUATION:</b>	
<u>REFERENCES</u> 1. Rammelsberg, F.C. <i>Wied. Ann.</i> <u>1882</u> , <u>16</u> , 707. 2. Mayer, W. <i>Ann. Chen. u. Pharm.</i> <u>1856</u> , <u>98</u> , 193. 3. Mayer, W. <i>Ann. Chim.</i> <u>1856</u> , <u>47</u> , 288. 4. Rosenheim, A.; Reglin, W. Z. <i>Anorg. Chem.</i> <u>1921</u> , <u>120</u> , 103. 5. Rollet, A.P.; Lauffenburger, R. <i>Bull. Soc. Chim. France</i> <u>1934</u> , 146. 6. Latimer, W.M.; Hildebrand, J.H. <i>Reference Book of Inorganic Chemistry</i> . 3rd Edit. Macmillan, N.Y. <u>1951</u> . 7. Lange, N.A.; Forker, G.M. <i>Handbook of Chemistry</i> . 10th Edit. McGraw-Hill. N.Y. <u>1961</u> . 8. Dean, J.A. <i>Lange's Handbook of Chemistry</i> . 11th Edit. McGraw-Hill. N.Y. <u>1973</u> . 9. Robinson, R.A.; Stokes, R.H. <i>Electrolyte Solutions</i> . Butterworths. London. <u>1955</u> . 10. Vanderzee, C.E.; Quist, A.S. <i>J. Phys. Chem.</i> <u>1961</u> , <u>65</u> , 118. 11. Butler, J.N. <i>Ionic Equilibrium: A Mathematical Approach</i> . Addison Wesley. Reading, Mass. <u>1964</u> . 12. Gimblett, F.G.R.; Monk, C.B. <i>Trans. Faraday Soc.</i> <u>1954</u> , <u>50</u> , 965. 13. Corti, H.; Crovetto, R.; Fernandez-Prini, R. <i>J. Solution Chem.</i> <u>1979</u> , <u>8</u> , 897. 14. Note that for the LiOH association constant, ref. 12 gives K <sub>A</sub> = 1.504 and ref. 13 gives K <sub>A</sub> = 0.97 mol <sup>-1</sup> dm <sup>3</sup> at 298 K. 15. Smith, R.M.; Alberty, R.A. <i>J. Phys. Chem.</i> <u>1956</u> , <u>60</u> , 150. These authors report K <sub>A</sub> (LiHPO <sub>4</sub> ) = 5.2 mol <sup>-1</sup> dm <sup>3</sup> at 298 K. 16. Davies, C.W. <i>Ion Association</i> . Butterworths. London. <u>1962</u> . 17. Prideaux, E.B.R. <i>J. Chem. Soc.</i> <u>1944</u> , 606. 18. Landolt-Bornstein. <i>Zahlenwerte und Funktionen</i> . 3rd Erg. Band III. <u>1936</u> . 19. Bottger, W. Z. <i>Phys. Chem.</i> <u>1903</u> , <u>46</u> , 596. 20. Milazzo, C. <i>Electrochemistry</i> . Elsevier. Amsterdam. <u>1963</u> . 21. Marsh, K.N.; Stokes, R.H. <i>Austr. J. Chem.</i> <u>1964</u> , <u>17</u> , 740. 22. Moeller, T. <i>Qualitative Analysis</i> . McGraw-Hill, N.Y. <u>1958</u> . 23. Jaulmes, P.; Brun, S. <i>Trav. Soc. Pharm. Montpellier</i> <u>1965</u> , <u>25</u> , 98. 24. de Schulten, M.A. <i>Bull. Soc. Chim.</i> <u>1889</u> , <u>1</u> , 479. 25. Sanfourche, A.A. <i>Bull. Soc. Chim.</i> <u>1938</u> , <u>5</u> , 1669.	

COMPONENTS: (1) Lithium phosphate; $\text{Li}_3\text{PO}_4$ ; [10377-52-3] (2) Water; $\text{H}_2\text{O}$ ; [7732-18-5]		ORIGINAL MEASUREMENTS: Rosenheim, A.; Reglin, W. <i>Z. Anorg. Chem.</i> <u>1921</u> , 120, 103-19.																				
VARIABLES: One temperature: 25°C		PREPARED BY: J. Eysseltová and M. Salomon																				
EXPERIMENTAL VALUES:																						
<p>The electrolytic conductances of satd <math>\text{Li}_3\text{PO}_4</math> slns at 25°C were reported</p> <table> <thead> <tr> <th>experiment No.</th> <th><math>10^4 \kappa_{\text{sln}} / \text{S cm}^{-1}</math></th> <th>experiment No.</th> <th><math>10^4 \kappa_{\text{sln}} / \text{S cm}^{-1}</math></th> </tr> </thead> <tbody> <tr> <td>1</td> <td>20.1</td> <td>5</td> <td>9.43</td> </tr> <tr> <td>2</td> <td>11.5</td> <td>6</td> <td>9.24</td> </tr> <tr> <td>3</td> <td>10.8</td> <td>7</td> <td>9.24</td> </tr> <tr> <td>4</td> <td>9.51</td> <td>8</td> <td>9.25</td> </tr> </tbody> </table>			experiment No.	$10^4 \kappa_{\text{sln}} / \text{S cm}^{-1}$	experiment No.	$10^4 \kappa_{\text{sln}} / \text{S cm}^{-1}$	1	20.1	5	9.43	2	11.5	6	9.24	3	10.8	7	9.24	4	9.51	8	9.25
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<p>The high <math>\kappa_{\text{sln}}</math> values for expts 1-3 were attributed to impurities and neglected. Based on the data from expts 4-8, the authors reported an ave <math>\kappa_{\text{sln}} = 9.40 \times 10^{-4} \text{ S cm}^{-1}</math> and <math>\kappa_{\text{salt}} = \kappa_{\text{sln}} - \kappa_{\text{H}_2\text{O}} = 9.37 \times 10^{-4} \text{ S cm}^{-1}</math>. The soly of <math>\text{Li}_3\text{PO}_4</math> was calcd from</p> $\text{soly} = \frac{1000 \kappa_{\text{salt}}}{3(\lambda_{\text{Li}}^\infty + \lambda_{\text{PO}_4^\infty})} = (7.688/3) \times 10^{-3} \text{ mol dm}^{-3} = 2.563 \times 10^{-3} \text{ mol dm}^{-3}$ <p><math>\lambda^\infty(\text{Li}^+) = 39.7 \text{ S cm}^2 \text{ mol}^{-1}</math> and was taken from Kohlraush and Holborn (1). <math>\lambda^\infty(\text{PO}_4^{3-}) = 82.3 \text{ S cm}^2 \text{ mol}^{-1}</math> was estimated by Böttger (2): both values correspond to 25°C. In the original calculation, the authors neglected to multiply <math>\kappa_{\text{salt}}</math> by 1000, and hence report a solubility too low by this factor. The author's calcns are also subject to rounding off errors amounting to an error of around +1% in the final value for the soly. Additional errors involve the uncertainties in the <math>\lambda^\infty</math> values. Although these errors are significant, they are relatively minor to the error involved in neglecting the hydrolysis of the <math>\text{PO}_4^{3-}</math> ion. The effect of hydrolysis on the calcn of the soly from conductivity data is discussed in detail in the critical evaluation.</p>																						
AUXILIARY INFORMATION																						
METHOD/APPARATUS/PROCEDURE:	<p><math>\text{Li}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}</math> was pptd from aq <math>\text{H}_3\text{PO}_4</math> with excess <math>\text{LiOH}</math>. The dihydrate was washed, air dried at about 16°C and analysed with the following results: Li 13.50, 13.66 mass% found (16.67% calcd); <math>\text{PO}_4</math> 62.53, 62.46 mass% found (62.58% calcd); <math>\text{H}_2\text{O}</math> 23.90, 23.78% found (23.72% calcd). Drying at 60°C for several days gave the hemihydrate which analysed as <math>\text{Li}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}</math>. Presumably conductivity water was used for prep of slns and washing of ppts. The compilers assume that <math>\text{Li}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}</math> was used as the starting material for all experiments.</p> <p>ESTIMATED ERROR: Nothing specified. The compilers assume the experimental precision to be around <math>\pm 1 \times 10^{-6} \text{ S cm}^{-1}</math>. The std dev in <math>\kappa_{\text{salt}}</math> is <math>4.2 \times 10^{-6} \text{ S cm}^{-1}</math>.</p> <p>REFERENCES:</p> <ol style="list-style-type: none"> <li>Kohlrausch, F.; Holborn, O. <i>Das Leitvermögen der Elektrolyte</i>. II Auflage, <u>1916</u>, Tab. 8a.</li> <li>Böttger, W. <i>Z. Phys. Chem.</i> <u>1903</u>, 46, 596.</li> </ol>																					

$$\kappa_{\text{salt}} = \kappa_{\text{sln}} - \kappa_{\text{H}_2\text{O}} = 9.30 \times 10^{-4} \text{ S cm}^{-1}$$

## Lithium Phosphate

COMPONENTS:		ORIGINAL MEASUREMENTS:																	
(1) Lithium phosphate; $\text{Li}_3\text{PO}_4$ ; [10377-52-3]		Mayer, W.																	
(2) Ammonia; $\text{NH}_3$ ; [7664-41-7]		<i>*Ann. Chem. u. Pharm.</i> <u>1856</u> , 98, 192-212;																	
(3) Water; $\text{H}_2\text{O}$ ; [7732-18-5]		<i>Ann. Chim.</i> <u>1856</u> , 288- .																	
VARIABLES:		PREPARED BY:																	
Room temperature: 15 - 18°C		J. Eyseltová and M. Salomon																	
EXPERIMENTAL VALUES: Composition of saturated solutions:																			
<table border="1"> <thead> <tr> <th>solvent composition</th> <th>sln mass/g</th> <th><math>\text{Li}_3\text{PO}_4</math> mass/g</th> <th><math>\text{g Li}_3\text{PO}_4/100 \text{ g H}_2\text{O}</math></th> <th><math>b \text{ m(Li}_3\text{PO}_4)/\text{mol kg}^{-1}</math></th> </tr> </thead> <tbody> <tr> <td>pure <math>\text{H}_2\text{O}</math></td> <td>45 45 75</td> <td>0.0176 0.0178 0.0296</td> <td>0.0391 0.0396 0.0395</td> <td>0.00338 0.00342 0.00341</td> </tr> <tr> <td>2 vol <math>\text{H}_2\text{O} + a</math> 1 vol <math>\text{NH}_4\text{OH}</math></td> <td>74.12 74.12 44.47 44.47</td> <td>0.0174 0.0190 0.0124 0.0117</td> <td>0.023 0.026 0.028 0.026</td> <td>0.0014 0.0015 0.0016 0.0015</td> </tr> </tbody> </table>					solvent composition	sln mass/g	$\text{Li}_3\text{PO}_4$ mass/g	$\text{g Li}_3\text{PO}_4/100 \text{ g H}_2\text{O}$	$b \text{ m(Li}_3\text{PO}_4)/\text{mol kg}^{-1}$	pure $\text{H}_2\text{O}$	45 45 75	0.0176 0.0178 0.0296	0.0391 0.0396 0.0395	0.00338 0.00342 0.00341	2 vol $\text{H}_2\text{O} + a$ 1 vol $\text{NH}_4\text{OH}$	74.12 74.12 44.47 44.47	0.0174 0.0190 0.0124 0.0117	0.023 0.026 0.028 0.026	0.0014 0.0015 0.0016 0.0015
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<p><i>a</i> For this <math>\text{NH}_3</math> sln, the specific gravity = 0.965 (author), but temp not specified.  Assuming temp = 20°C, the <math>\text{NH}_3</math> concn in the final sln is about 1.6 mol <math>\text{kg}^{-1}</math> (compilers).</p>																			
<p><i>b</i> Compilers' calculations. Average values and their standard deviations are given below.</p>																			
<p>In pure water. solubility = 0.0394 g/100 g <math>\text{H}_2\text{O}</math> (<math>\sigma = 0.002</math>)  = 0.00340 mol <math>\text{kg}^{-1}</math> (<math>\sigma = 0.00002</math>)</p>																			
<p>In ~ 1.6 mol <math>\text{kg}^{-1}</math> <math>\text{NH}_3</math> sln.  solubility = 0.025 g/100 g <math>\text{H}_2\text{O}</math> (<math>\sigma = 0.002</math>)  = 0.0015 mol <math>\text{kg}^{-1}</math> (<math>\sigma = 0.0001</math>)</p>																			
<p>Note: in converting to mol <math>\text{kg}^{-1}</math> in 1.6 mol <math>\text{kg}^{-1}</math> <math>\text{NH}_3</math> slns, the compilers calculated the mass of water from <math>\text{g}(\text{H}_2\text{O}) = \text{g}(\text{sln}) - \text{g}(\text{NH}_3) - \text{g}(\text{Li}_3\text{PO}_4)</math>.</p>																			
AUXILIARY INFORMATION																			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:																		
Each determination consisted of equilibrating solid + liquid for 10-14 days at 15-18°C with frequent shaking. Analysis not described, but probably was either evaporation of a satd sln followed by weighing, or by pptn of $\text{Ba}_3(\text{PO}_4)_2$ by addn of $\text{Ba}(\text{OH})_2$ followed by weighing as described elsewhere in the paper for the stoichiometric analysis of the ppt. Although not stated, it is possible that the approach to equilibrium was from supersaturation (see discussion in the critical evaluation).	Li <sub>3</sub> PO <sub>4</sub> pptd from a mixture of Na <sub>2</sub> HPO <sub>4</sub> , Li <sub>2</sub> SO <sub>4</sub> , and NH <sub>4</sub> OH. The ppt was washed with boiled water until the wash water was free of SO <sub>4</sub> <sup>2-</sup> (tested with BaCl <sub>2</sub> sln).																		
ESTIMATED ERROR:																			
Nothing specified. The reproducibility appears satisfactory, but the overall accuracy of the solubility is probably no better than 15%.																			
REFERENCES:																			

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Lithium phosphate; $\text{Li}_3\text{PO}_4$ ; [10377-52-3]	Rollet, A.P.; Lauffenburger, R.
(2) Phosphoric acid; $\text{H}_3\text{PO}_4$ ; [7664-38-2]	<i>Bull. Soc. Chim. France</i> 1934, 146-52.
(3) Lithium oxide; $\text{Li}_2\text{O}$ ; [12057-24-8]	
(4) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	
VARIABLES:	PREPARED BY:
Temperature and Composition	J. Eyseltová

## EXPERIMENTAL VALUES:

Composition of saturated solutions of  $\text{Li}_3\text{PO}_4$  at 20°C.

$\text{Li}_2\text{O}$ mass %	$\text{P}_2\text{O}_5$ mass %	$\text{H}_3\text{PO}_4^a$ mass %	mol/kg $\text{H}_2\text{O}$	$\text{Li}_3\text{PO}_4^a$ mass %	mol/kg $\text{H}_2\text{O}$	Solid phase <sup>b</sup>
7.05	0.017	----	----	0.0277	0.0026 (D)	A + B
0.077	0.016	----	----	0.0261	0.0023	B
0.0134	0.021	----	----	0.0343	0.0030	"
0.0165	0.0272	0.00152	0.00015	0.0426	0.0037	"
0.0197	0.0345	0.00456	0.00047	0.0509	0.0044	"
0.0203	0.0360	0.00538	0.00054	0.0524	0.0045	"
0.050	0.116	0.0508	0.00521	0.129	0.0111	"
0.096	0.242	0.123	0.0126	0.249	0.0216	"
0.118	0.305	0.163	0.0167	0.305	0.0264	"
0.150	0.409	0.236	0.0243	0.388	0.0337	"
0.205	0.620	0.407	0.0420	0.530	0.0461	"
0.262	0.875	0.635	0.0657	0.677	0.0593	"
5.73	27.5	25.4	4.34	14.8	2.14	"
7.63	37.1	34.5	7.70	19.7	3.72	"
7.95	38.8	36.2	8.53	20.5	4.10	"
8.45	41.6	38.9	10.14	21.8	4.81 (E)	B + C
7.73	41.7	40.7	10.55	20.0	4.38	C
6.62	43.5	45.5	12.4	17.1	3.96	"

<sup>a</sup> All these values were calculated by the compiler.<sup>b</sup> The solid phases are: A =  $\text{LiOH} \cdot \text{H}_2\text{O}$ ; B =  $\text{Li}_3\text{PO}_4$ ; C =  $\text{LiH}_2\text{PO}_4$ .

(continued next page)

## AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Phosphoric acid, lithia and water were placed in glass tubes and sealed with a Hg stirrer. The tubes, equipped with Pt electrodes for conductivity measurements, were placed in a thermostat and stirred for at least 8 h. The attainment of equil was ascertained by the constancy in the conductivity. $\text{P}_2\text{O}_5$ was detd in a few cases by titrn with NaOH soln; usually $\text{P}_2\text{O}_5$ was detd gravimetrically by pptng as $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_4$ , re-pptd as $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ , calcined and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$ . Additional gravimetric analyses were performed when the $\text{P}_2\text{O}_5/\text{Li}_2\text{O}$ ratio corresponded to the formulas $\text{Li}_3\text{PO}_4$ and $\text{LiH}_2\text{PO}_4$ . In this case the soln was evaporated and the residue calcined. The total weight of the calcined residue is the sum of $\text{P}_2\text{O}_5$ and $\text{Li}_2\text{O}$ . No other details given.	Nothing specified.
	ESTIMATED ERROR: Temp control at best is $\pm 0.1$ K Solv: exptl error not specified. For binary system $\text{Li}_3\text{PO}_4\text{-H}_2\text{O}$ extrapolations give errors of $\pm 4.5\%$ at 0° and $\pm 6.7\%$ at 20°C (authors)
	REFERENCES:

## Lithium Phosphate

COMPONENTS:				ORIGINAL MEASUREMENTS:					
(1) Lithium phosphate; $\text{Li}_3\text{PO}_4$ ; [10377-52-3]				Rollet, A.P.; Lauffenburger, R.					
(2) Phosphoric acid; $\text{H}_3\text{PO}_4$ ; [7664-38-2]				<i>Bull. Soc. Chim. France</i> 1934, 146-52.					
(3) Lithium oxide; $\text{Li}_2\text{O}$ , [12057-24-8]									
(4) Water, $\text{H}_2\text{O}$ ; [7732-18-5]									
EXPERIMENTAL VALUES, cont'd:									
Composition of saturated solutions of $\text{Li}_3\text{PO}_4$ at 0°C.									
$\text{Li}_2\text{O}$ mass %	$\text{P}_2\text{O}_5$ mass %	$\text{H}_3\text{PO}_4$ <sup>a</sup> mass %	$\text{mol/kg H}_2\text{O}$	$\text{Li}_3\text{PO}_4$ <sup>a</sup> mass %	$\text{mol/kg H}_2\text{O}$	Solid phase <sup>b</sup>			
6.70	0.00	----	----	0.00	0.00	A			
6.72	0.015	----	----	0.024	0.0023 (A)	A + B			
5.88	0.020	----	----	0.033	0.0030	B			
2.40	0.016	----	----	0.026	0.0023	"			
0.49	0.020	----	----	0.033	0.0028	"			
0.0088	0.0148	0.0012	0.0001	0.0227	0.0020	"			
0.0098	0.0163	0.0011	0.0001	0.0253	0.0021	"			
0.0185	0.0375	0.0113	0.0012	0.0478	0.0041	"			
0.025	0.058	0.0248	0.0026	0.0646	0.0056	"			
0.149	0.388	0.210	0.0216	0.385	0.0334	"			
0.167	0.414	0.207	0.0212	0.432	0.0375	"			
0.174	0.452	0.240	0.0250	0.450	0.0399	"			
0.2285	0.635	0.377	0.0389	0.590	0.0515	"			
0.266	0.785	0.502	0.0519	0.687	0.0601	"			
0.270	0.80	0.513	0.0531	0.698	0.0610	"			
0.330	0.96	0.603	0.0626	0.863	0.0747	"			
0.403	1.355	0.989	0.1031	1.04	0.0928	"			
0.520	1.88	1.46	0.153	1.34	0.119	"			
0.740	2.74	2.17	0.230	1.91	0.172	"			
2.55	11.03	9.65	1.18	6.59	0.679	"			
3.90	17.2	15.3	2.08	10.1	1.165	"			
4.58	20.26	18.0	2.61	11.8	1.46	"			
4.97	22.16	19.7	2.99	12.8	1.64	"			
5.42	24.30	21.7	3.44	14.0	1.88	"			
6.88	31.13	28.0	5.26	17.7	2.82	"			
7.55	34.43	31.0	6.40	19.5	3.41	"			
8.30 <sup>c</sup>	38.0 <sup>c</sup>	34.2	7.92	21.4	4.19 (B)	B + C			
8.19	37.95	34.5	7.94	21.2	4.12	C			
8.08	38.10	34.9	8.07	20.9	4.08	"			
7.68	38.20	35.9	8.30	19.8	3.88	"			
7.54	38.45	36.6	8.50	19.5	3.83	"			
7.18	38.85	37.9	8.90	18.6	3.68	"			
4.62	47.5	55.5	17.6	11.9	2.86	"			
3.21	53.05	66.2	26.5	8.30	2.81	"			
2.74	55.65	70.4	32.8	7.60	2.80	"			
2.22	58.8	76.3	43.4	5.74	2.76 (C)	"			

<sup>a</sup> All these values were calculated by the compiler.

<sup>b</sup> The solid phases are: A =  $\text{LiOH} \cdot \text{H}_2\text{O}$ ; B =  $\text{Li}_3\text{PO}_4$ ; C =  $\text{LiH}_2\text{PO}_4$ .

<sup>c</sup> Read from the intersection of branch lines. For discussion of points A, B, C, D, E see the discussion of the phase diagram in the Critical Evaluation.

By interpolation of the isotherms, the authors report the solubilities of  $\text{Li}_3\text{PO}_4$  at 0° and 20° in the binary system to be  $0.022 \pm 0.001$  mass % and  $0.030 \pm 0.002$  mass %, respectively. The compiler has calculated these solubility values to be  $0.0019 \text{ mol kg}^{-1}$  at 0°C and  $0.0026 \text{ mol kg}^{-1}$  at 20°C.

From the data in the region rich in  $\text{H}_3\text{PO}_4$ , the solubility of  $\text{LiH}_2\text{PO}_4$  [13453-80-0] was determined to be  $55.8 \pm 0.1$  mass % or  $12.15 \pm 0.02 \text{ mol kg}^{-1}$  (compiler's calculation) at 0°C.

COMPONENTS:	EVALUATOR:
(1) Trisodium Phosphate; Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9] (2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H <sub>2</sub> O; [7732-18-5]	J. Eyseltová Charles University Prague, Czechoslovakia July, 1986

## CRITICAL EVALUATION:

Solubility data for the Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system have been reported in 13 different publications (1-13). Some of these (1-7) report the solubility in systems in which there is a range of Na/P ratios. Others (8-13) are limited to one Na/P ratio, i.e., the solubility of a given sodium phosphate in water is reported.

Many solid phases have been reported or suggested as being in equilibrium with saturated solutions in the Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system. These are:

NaOH; [1310-73-2]	Na <sub>2</sub> HPO <sub>4</sub> ·2H <sub>2</sub> O; [10028-24-7]
Na <sub>3</sub> PO <sub>4</sub> ·1/4NaOH·12H <sub>2</sub> O; [12362-10-6]	Na <sub>2</sub> HPO <sub>4</sub> ; [7558-79-4]
Na <sub>3</sub> PO <sub>4</sub> ·1/7NaOH·12H <sub>2</sub> O; [101056-44-4]	Na <sub>2</sub> HPO <sub>4</sub> ·NaH <sub>2</sub> PO <sub>4</sub> ; [65185-91-3]
Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O; [10101-89-0]	Na <sub>2</sub> HPO <sub>4</sub> ·2NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O; [66905-89-3]
Na <sub>3</sub> PO <sub>4</sub> ·10H <sub>2</sub> O; [10361-89-4]	NaH <sub>2</sub> PO <sub>4</sub> ·4H <sub>2</sub> O; [101056-45-5]
Na <sub>3</sub> PO <sub>4</sub> ·8H <sub>2</sub> O; [60593-59-1]	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O; [13472-35-0]
Na <sub>3</sub> PO <sub>4</sub> ·6H <sub>2</sub> O; [15819-50-8]	NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O; [10049-21-5]
Na <sub>3</sub> PO <sub>4</sub> ·0.5H <sub>2</sub> O; [60593-58-0]	NaH <sub>2</sub> PO <sub>4</sub> ; [7558-80-7]
Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9]	Na <sub>3</sub> H <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·7.5H <sub>2</sub> O; [101056-46-6]
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O; [10039-32-4]	Na <sub>3</sub> H <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·1.5H <sub>2</sub> O; [101917-67-3]
Na <sub>2</sub> HPO <sub>4</sub> ·8H <sub>2</sub> O; [67417-37-2]	NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>3</sub> PO <sub>4</sub> ; [14887-48-0]
Na <sub>2</sub> HPO <sub>4</sub> ·7H <sub>2</sub> O; [7782-85-6]	H <sub>3</sub> PO <sub>4</sub> ·0.5H <sub>2</sub> O; [16271-20-8]

The conditions under which these phosphates exist is discussed in the Critical Evaluation of the respective binary systems.

Na<sub>3</sub>PO<sub>4</sub>-NaOH-H<sub>2</sub>O system. Menzel and von Sahr (1) studied this system at 298 K. They found that as the mole ratio Na<sub>2</sub>O/P<sub>2</sub>O<sub>5</sub> in the saturated solutions varied from 2.69 to 3.68, the same ratio in the solid phase increased from 3.11 to 3.22. Thereafter as the Na/P ratio in the solution increased to about 145, the same ratio in the solid phase changed only from 3.22 to 3.24. They concluded that the equilibrium solid phases were solid solutions although X-ray diffraction diagrams of four such solid phases showed little difference among them.

Kobe and Leipper (2) suggested that the commercial trisodium phosphate has the formula Na<sub>3</sub>PO<sub>4</sub>·1/7NaOH·12H<sub>2</sub>O. Later Kobe returned to this problem and studied systems of high Na<sub>2</sub>O/P<sub>2</sub>O<sub>5</sub> ratios (3). He and his co-worker found the system to be a complex one. The anhydrous form of Na<sub>3</sub>PO<sub>4</sub> as well as the hemihydrate, the hexahydrate and the octahydrate were identified as equilibrium solid phases. An alkaline complex salt was also observed. The complex was studied further and, in agreement with Bell (14), they suggested that at 273-333 K two different complexes are present: Na<sub>3</sub>PO<sub>4</sub>·1/7NaOH·12H<sub>2</sub>O and Na<sub>3</sub>PO<sub>4</sub>·1/4NaOH·12H<sub>2</sub>O but they included only the latter in their Tables. At 353-373 K they found only the hydrates of Na<sub>3</sub>PO<sub>4</sub> in the highly alkaline solutions. This agrees with the opinion of others (4) who mention no complex formation in this system at 423, 523 and 623 K.

The transition of the different hydrates and the identification of these hydrates at increasing NaOH concentrations cannot be evaluated because of lack of corroborating work by others. However, Ravich and Shcherbakova (23) did present X-ray evidence for the formation of solid solutions in Na<sub>3</sub>PO<sub>4</sub>·n Na<sub>2</sub>HPO<sub>4</sub>. These solid solutions are reported to coexist with saturated solutions having Na/P ratios even greater than 3 at 523, 573 and 638 K. This is in agreement with the observations of Broadbent, et al. (18) who found equilibrium solid phases in which the Na/P ratio varied from 2.64 to 2.82 at 524 and 573 K.

As noted above, this system has been studied at temperatures of 293 K (1), 298 K (2, 3, 5) and at elevated temperatures 423, 523 and 623 K (4) and 523, 573 and 638 K (23). The lower temperature results are shown on Figure 1. The data agree fairly well with each other except for one data point (5) which is obviously incorrect. Except for this one data point these results can be accepted tentatively. A similar comparison cannot

COMPONENTS:

- (1) Trisodium phosphate; Na<sub>3</sub>PO<sub>4</sub>; [7601-54-9]
- (2) Phosphoric acid; H<sub>3</sub>PO<sub>4</sub>; [7664-38-2]
- (3) Sodium hydroxide; NaOH; [1310-73-2]
- (4) Water; H<sub>2</sub>O; [7732-18-5]

## EVALUATOR:

J. Eysseletová  
Charles University  
Prague, Czechoslovakia

July, 1986

## CRITICAL EVALUATION:

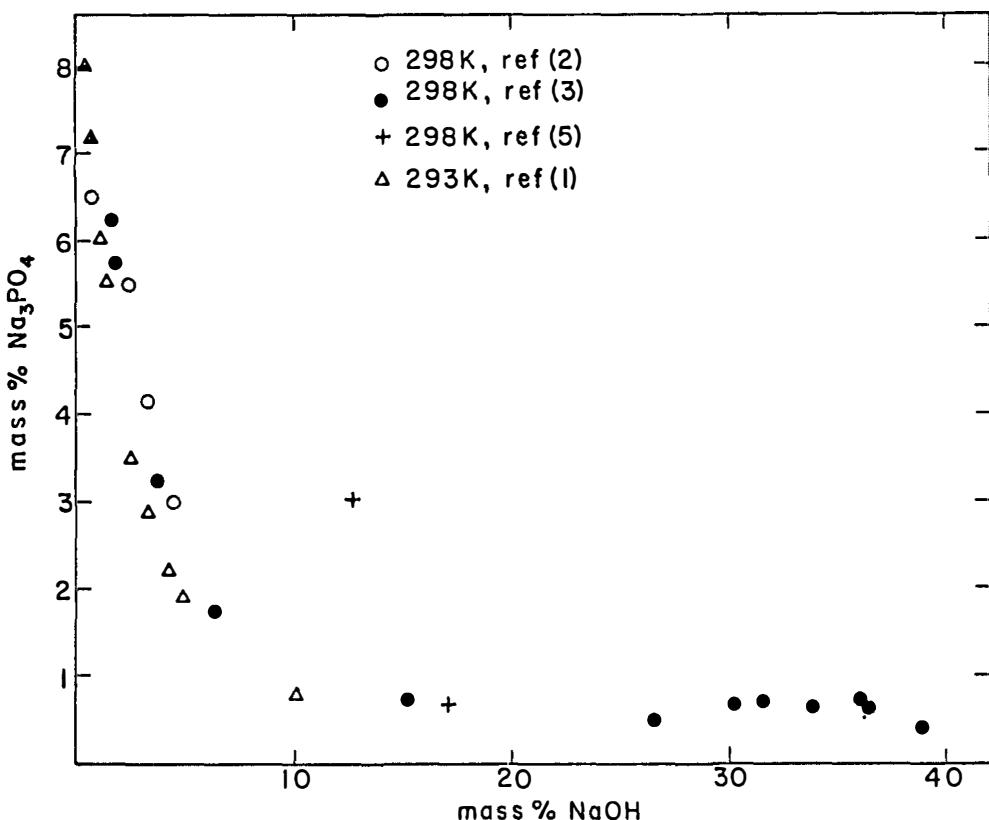
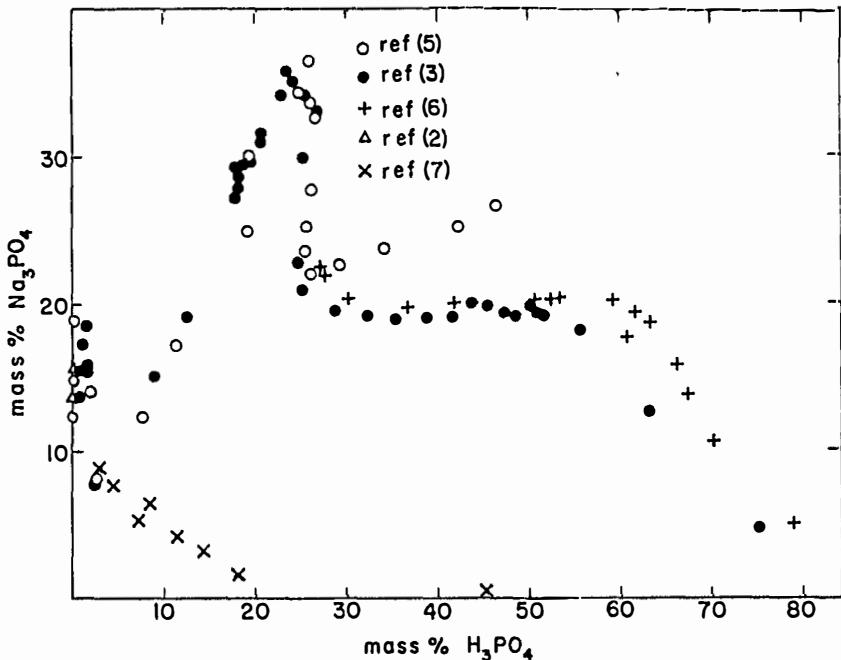
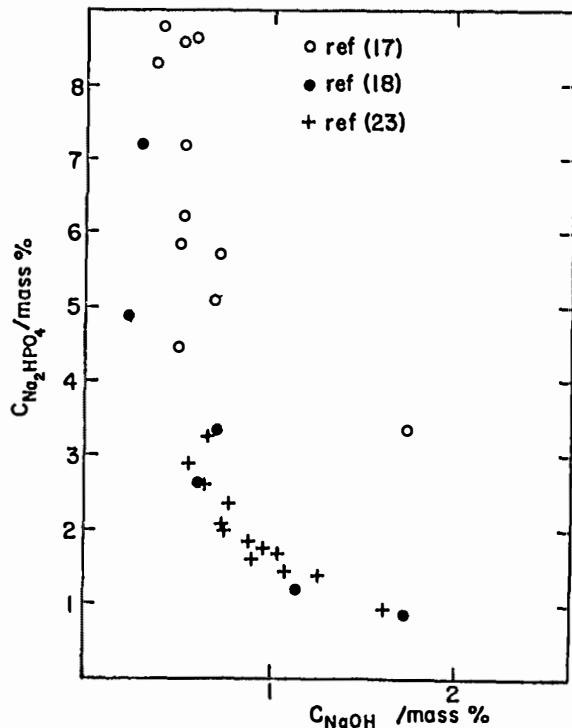


Figure 1. Solubility of Na<sub>3</sub>PO<sub>4</sub> in aqueous NaOH.

COMPONENTS:	EVALUATOR:
(1) Trisodium phosphate; Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9] (2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H <sub>2</sub> O; [7732-18-5]	J. Eyseltová Charles University Prague, Czechoslovakia July, 1986

## CRITICAL EVALUATION:

Figure 2. Solubility of Na<sub>3</sub>PO<sub>4</sub> in aqueous H<sub>3</sub>PO<sub>4</sub> at 298 K.Figure 3. Solubility of Na<sub>2</sub>HPO<sub>4</sub> in aqueous NaOH at 573 K.

<b>COMPONENTS:</b> (1) Trisodium Phosphate; Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9] (2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H <sub>2</sub> O; [7732-18-5]	<b>EVALUATOR:</b> J. Eyseltova Charles University Prague, Czechoslovakia  July, 1986
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**CRITICAL EVALUATION: (cont'd)**

be made for the results obtained at elevated temperatures. The data points of Ravich and Shcherbakova (23) are concentrated in a narrow range of Na/P ratios and can be compared with only one data point of Broadbent, et al. (18) and of Panson, et al. (17).

Na<sub>3</sub>PO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O system. Solubility studies have been made at 298 K in systems which have a wide range of Na/P ratios (3, 5). Studies at 298 K in a more limited range have also been made: the Na<sub>3</sub>PO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub>-H<sub>2</sub>O system (2); the NaH<sub>2</sub>PO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O system (6); and the Na<sub>2</sub>HPO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O system (7). The Na<sub>3</sub>PO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub>-H<sub>2</sub>O system has also been studied at 293 K (1).

Figure 2 shows the solubility results obtained at 298 K. It is apparent that the work of Beremzhanov, et al. (7) ignores the existence of NaH<sub>2</sub>PO<sub>4</sub> and the results are clearly incorrect. The data in the region where P/Na>1 (5) probably are for super-saturated solutions. For this region the results of Wendrow and Kobe (3) and Lillich, et al. (6) are tentatively accepted. Between Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> the solubility data of Wendrow and Kobe (3) and D'Ans and Schreiner (5) are very close to each other and are tentatively accepted as describing the solubility in this region. With respect to the identity of the solid phases in equilibrium with these saturated solutions, more work is needed before a decision can be made.

Phosphates in which the Na/P ratio is other than 3, 2 or 1, e.g., Na<sub>2</sub>HPO<sub>4</sub>·NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>·2NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, have been reported as existing in a very narrow concentration range (3). Their existence has not been confirmed by others, and more work is needed before a judgment about the existence of such phosphates can be made.

The hydrates Na<sub>3</sub>H<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·7.5H<sub>2</sub>O and Na<sub>3</sub>H<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·1.5H<sub>2</sub>O have been reported to exist in equilibrium with very concentrated solutions having a pH = 7 (15). There is no other report on the existence of these phosphates. They probably are metastable (5).

The existence of NaH<sub>2</sub>PO<sub>4</sub>·H<sub>3</sub>PO<sub>4</sub> in strongly acid solutions has been reported by several investigators (3,6,8). The solubility of this substance has been measured over a range of temperatures. As a result of such a study Paravano and Mieli (8) state that the system is glass-forming in the temperature range 235 to 307 K. By extrapolating their values it appears that the composition of the system at 323 K is 45 mass% NaH<sub>2</sub>PO<sub>4</sub> and 37.4 mass% H<sub>3</sub>PO<sub>4</sub>. This is in good agreement with the value reported by Lillich, et al. (6), especially if their value of 28.7 mass% H<sub>3</sub>PO<sub>4</sub> at 323 K is a typographical error and the correct value should be 38.7 mass%. Their reported value for NaH<sub>2</sub>PO<sub>4</sub> is 46 mass%. Paravano and Mieli (8) state that at temperatures below about 373 K, NaH<sub>2</sub>PO<sub>4</sub>·H<sub>3</sub>PO<sub>4</sub> has an incongruent solubility. This is consistent with work reported by others (3,6). However, there are significant differences in the 298 K solubility isotherms reported for this substance (3,6) and further work is necessary before this matter can be resolved.

Solubility measurements have also been made at elevated temperatures (17-19, 23). Some of the data are shown on Figure 3. At 573 K the solubility results of Ravich, et al. (23) and of Panson, et al. (17) agree fairly well with each other while the values reported by Broadbent, et al. (18) have a significant amount of scatter and generally report a larger NaOH content. Therefore, the data of Braodbent, et al. (18) should probably be rejected because of an apparent systematic error. There is another report of solubility data under these conditions (20) but the data are presented only in graphical form. The author states that tetrasodium diphosphate and sodium triphosphate are equilibrium solid phases, but this seems unlikely in view of the conditions for the preparation of pyro- and tri-phosphates (21). In still another report (22), Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> was the only solid phase found at 573 K and its existence was estimated to be limited to the 563-573 K temperature interval.

Marshall (19) reviewed all this work and considered that the reported compositions of the saturated solutions were in fairly good agreement.

Liquid-liquid immiscibility is the phenomenon that characterizes this system at high temperatures.

COMPONENTS:	EVALUATOR:
(1) Trisodium Phosphate; Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9] (2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H <sub>2</sub> O; [7732-18-5]	J. Eysseletová Charles University Prague, Czechoslovakia  July, 1986

## CRITICAL EVALUATION: (cont'd)

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium dihydrogenphosphate; NaH <sub>2</sub> PO <sub>4</sub> ; [7558-80-7] (2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2] (3) Water; H <sub>2</sub> O; [7732-18-5]	Paravano, N.; Mieli, A. Gazz. Chim. Ital. 1908, 38, 535-44.
VARIABLES:	PREPARED BY:
Composition and temperature. One ratio NaH <sub>2</sub> PO <sub>4</sub> /H <sub>3</sub> PO <sub>4</sub> = 1.	J. Eysseltova

## EXPERIMENTAL VALUES:

Saturation temperatures of solutions of NaH<sub>2</sub>PO<sub>4</sub>·H<sub>3</sub>PO<sub>4</sub> in water.

t/°C.	NaH <sub>2</sub> PO <sub>4</sub> · H <sub>3</sub> PO <sub>4</sub>		NaH <sub>2</sub> PO <sub>4</sub> <sup>a</sup>		H <sub>3</sub> PO <sub>4</sub> <sup>a</sup>		solid phase <sup>b</sup>
	mass%	mol%	mass%	mol/kg	mass%	mol/kg	
0	0	0	0	0	0	0	ice
-5.7	20.77	1.81	11.43	1.20	9.34	1.20	"
-7.9	26.92	2.95	14.82	1.69	12.10	1.69	"
-11.4	34.15	4.11	18.80	2.38	15.35	2.38	"
-38 <sup>c</sup>	56.66	9.75	31.19	6.00	25.47	6.00	"
----	70.52	16.50	38.82	10.97	31.70	10.97	
34.0	80.46	25.39	44.29	18.89	36.17	18.89	NaH <sub>2</sub> PO <sub>4</sub>
41.0	81.82	27.11	45.04	20.64	36.78	20.64	"
51.7	83.68	29.75	46.06	23.52	37.61	23.52	"
79.7	87.48	36.62	48.16	32.05	39.32	32.05	"
85.0	88.65	39.22	48.80	35.83	39.85	35.83	"
101.7	91.47	46.98	50.35	49.18	41.12	49.18	NaH <sub>2</sub> PO <sub>4</sub> · H <sub>3</sub> PO <sub>4</sub>
104.5	92.67	51.09	51.01	57.99	41.66	57.99	"
110.0	95.79	65.28	52.73	87.15	43.06	87.15	"
110.7	95.86	65.68	52.77	106.2	43.09	106.2	"
119.0	97.99	80.12	53.94	223.6	44.05	223.6	"
126.5	100	100	55.04	----	44.96	----	"

<sup>a</sup>These values were calculated by the compiler.<sup>b</sup>The phases were not given by the authors. The compiler derived them from a graph.<sup>c</sup>The temperature was about -38°C.

## AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Saturation temperatures were determined visually as the temperature at which the last crystal disappeared.	NaH <sub>2</sub> PO <sub>4</sub> · H <sub>3</sub> PO <sub>4</sub> was prepared from an equimolar mixture of concentrated solutions of NaH <sub>2</sub> PO <sub>4</sub> and H <sub>3</sub> PO <sub>4</sub> by slow crystallization. The analysis was:
	found                   calculated
	P <sub>2</sub> O <sub>5</sub> 65.37%         65.12%
	Na <sub>2</sub> O                 14.41            14.23
ESTIMATED ERROR:	
	Nothing is stated.
REFERENCES:	





COMPONENTS				ORIGINAL MEASUREMENTS				
(1) Disodium hydrogenphosphate; Na <sub>2</sub> HPO <sub>4</sub> ; [7558-79-4]				Ravich, M.I.; Shcherbakova, L.G. <i>Izv. Sektora Fiz. Khim. Analiza, Inst. Obsch. Neorg. Khim. Akad. Nauk SSSR</i> 1955, 26, 248-58.				
(2) Sodium hydroxide; NaOH; [1310-73-2]								
(3) Water; H <sub>2</sub> O; [7732-18-5]								

## EXPERIMENTAL VALUES cont'd.

g ion/100	g soln	g ion/100	ion	mass% <sup>a</sup>	mol/kg <sup>a</sup>			
Po <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	Po <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	Na <sub>2</sub> HPO <sub>4</sub>	NaOH	H <sub>2</sub> O	Na <sub>2</sub> HPO <sub>4</sub>	NaOH
temp = 523 K								
0.0463	0.1666	21.8	78.2	6.58	2.96	90.46	0.51	0.82

<sup>a</sup>These values were calculated by the compiler.<sup>b</sup>This equilibrium was established by starting with a supersaturated solution.

## Part 2. Composition of saturated solutions for systems in which the beginning P/Na ratio is 1/3.

g ion/100	g soln	g ion/100	g ion	mass% <sup>a</sup>	mol/kg <sup>a</sup>			
Po <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	Po <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	Na <sub>2</sub> HPO <sub>4</sub>	NaOH	H <sub>2</sub> O	Na <sub>2</sub> HPO <sub>4</sub>	NaOH
temp = 638 K								
0.0014	0.0073	16.2	83.8	0.20	0.18	99.62	0.01	0.04
0.0010	0.0079	11.8	88.2	0.14	0.14	99.62	0.01	0.06
0.0010	0.0082	11.4	88.6	0.14	0.25	99.61	0.01	0.06
0.0008	0.0086	8.3	91.7	0.11	0.28	99.61	0.01	0.07
temp = 573 K								
0.0147	0.0475	23.6	76.4	2.09	0.72	97.19	0.15	0.19
0.0146	0.0473	23.6	76.4	2.07	0.72	97.20	0.15	0.19
0.0132	0.0485	21.4	78.6	1.88	0.88	97.24	0.14	0.23
0.0123	0.0483	20.3	79.7 <sup>b</sup>	1.75	0.95	97.30	0.13	0.24
0.0112	0.0446	20.1	79.9 <sup>b</sup>	1.59	0.89	97.52	0.11	0.26
0.0118	0.0491	19.4	80.6	1.68	1.02	97.30	0.12	0.26
0.0098	0.0507	16.2	83.8	1.39	1.24	97.36	0.10	0.32
temp = 523 K								
0.0542	0.1641	24.8	75.2	7.70	2.23	90.07	0.60	0.62
0.0484	0.1527	24.0	76.0	6.88	2.24	90.88	0.53	0.61
0.0480	0.2547	23.7	76.3	6.82	2.35	90.83	0.53	0.65

<sup>a</sup>These values were calculated by the compiler.<sup>b</sup>Equilibrium was established by starting with a supersaturated solution.

<b>COMPONENTS:</b> (1) Sodium dihydrogenphosphate; NaH <sub>2</sub> PO <sub>4</sub> ; [7558-80-7] (2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2] (3) Water; H <sub>2</sub> O, [7732-18-5]		<b>ORIGINAL MEASUREMENTS:</b> Lilich, L.S.; Vanjusheva, L.N.; Chernykh, L.V. <i>Zh. Neorg. Khim.</i> 1971, 16, 2782-9.			
<b>VARIABLES:</b> Composition and temperature.		<b>PREPARED BY:</b> J. Eyseltová			
<b>EXPERIMENTAL VALUES:</b> Solubility in the NaH <sub>2</sub> PO <sub>4</sub> -H <sub>3</sub> PO <sub>4</sub> -H <sub>2</sub> O system.					
NaH <sub>2</sub> PO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> O			
mass%	mol/kg	mass%	mol/kg	mass% <sup>a</sup>	solid phase
temp. = 0°C.					
38.7	5.26	----	----	62.3	NaH <sub>2</sub> PO <sub>4</sub> · 2H <sub>2</sub> O
37.00	5.30	5.00	0.90	58.0	"
33.20	5.3	14.50	2.8	52.3	"
33.0	5.8	19.6	4.2	47.4	"
33.6	6.9	25.7	6.5	40.7	"
34.5	7.8	28.8	8.0	36.7	"
36.9	10.5	33.9	11.9	29.2	"
39.2	13.6	36.9	15.7	23.9	"
37.9	13.6	38.8	17.0	23.3	NaH <sub>2</sub> PO <sub>4</sub> · H <sub>3</sub> PO <sub>4</sub>
29.7	10.1	45.8	19.0	24.5	"
20.4	7.2	55.9	24.1	23.7	"
17.8	6.8	60.4	28.3	21.8	"
8.1	3.7	73.9	41.9	18.0	"
5.4	2.8	78.6	49.9	16.0	"
3.9	2.2	81.2	55.6	14.9	"
(continued next page)					
<b>AUXILIARY INFORMATION</b>					
<b>METHOD/APPARATUS/PROCEDURE:</b> The isothermal method was used with equilibrium being reached in 10-12 hours. Phosphoric acid was determined alkalimetrically, the sum of H <sub>3</sub> PO <sub>4</sub> and NaH <sub>2</sub> PO <sub>4</sub> was determined alkalimetrically after ion exchange. The composition of the solid phases was determined by Schreinemakers' method. In the starting materials, H <sub>3</sub> PO <sub>4</sub> was determined gravimetrically and alkalimetrically using bromcresolgreen as indicator. NaH <sub>2</sub> PO <sub>4</sub> was determined alkalimetrically after ion exchange using ionex KU-2.	<b>SOURCE AND PURITY OF MATERIALS:</b> Chemically pure 90% H <sub>3</sub> PO <sub>4</sub> was used. The NaH <sub>2</sub> PO <sub>4</sub> was dried at 80-100°C.				
		<b>ESTIMATED ERROR:</b> The analyses had a precision of ±0.8% relatively. The temperature control was: 0 ± 0.1°C; 25 ± 0.05°C; 50 ± 0.1°C.			
<b>REFERENCES:</b>					

COMPONENTS:		ORIGINAL MEASUREMENTS:		
(1) Sodium dihydrogenphosphate; NaH <sub>2</sub> PO <sub>4</sub> ;	[7558-80-7]	Lilich, L.S.; Vanjusheva, L.N.;		
(2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2]		Chernykh, L.V.		
(3) Water; H <sub>2</sub> O; [7732-18-5]		Zh. Neorg. Khim. 1971, 16, 2782-9.		

## EXPERIMENTAL VALUES cont'd:

Solubility in the NaH<sub>2</sub>PO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O system.

NaH <sub>2</sub> PO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> O		
mass%	mol/kg	mass%	mol/kg	mass% <sup>a</sup>
temp. = 25°C.				
49.4	8.13	----	----	50.6
48.8	8.1	1.1	0.2	50.1
45.5	7.8	5.7	1.2	48.8
43.8	8.5	13.3	3.2	42.9
44.4	9.8	18.0	4.9	37.6
44.5	10.6	20.5	6.0	30.5
45.7	13.4	25.8	9.3	29.5
45.5	14.6	28.6	11.2	25.9
44.8	16.2	32.1	14.2	23.1
44.6	18.2	34.9	17.4	20.5
43.2	18.9	37.8	20.2	19.0
40.1	18.6	39.0	21.1	20.9
41.5	19.3	40.6	23.2	17.9
35.1	15.9	46.5	25.8	18.4
31.7	14.3	49.8	27.4	18.5
23.2	10.3	57.9	31.4	18.9
11.7	6.3	73.0	46.5	15.3
temp. = 50°C.				
62.6	13.95	----	----	37.4
60.5	13.9	3.3	0.9	36.2
54.3	14.5	14.6	4.8	31.1
52.0	14.7	18.5	6.4	29.5
49.3	15.5	24.2	9.3	26.5
45.2	19.0	35.0	18.0	19.8
46.9	16.0	28.7	12.0	24.4
43.8	20.2	38.1	21.5	18.1
43.7	21.7	39.6	24.0	19.7
41.5	23.4	43.7	29.0	14.8
40.5	22.5	44.5	29.1	15.0
37.2	20.4	47.4	32.0	15.4
30.2	17.3	55.3	38.8	14.5
22.6	14.8	64.7	52.0	12.7
16.6	11.9	71.7	62.5	11.7
13.6	10.4	75.4	70.4	11.0

<sup>a</sup>These values were calculated by the compiler.



<b>COMPONENTS:</b>		<b>ORIGINAL MEASUREMENTS:</b>																																																																																													
(1) Disodium hydrogenphosphate; Na <sub>2</sub> HPO <sub>4</sub> ; [7558-79-4]		Beremzhanov, B.A.; Savich, R.F.; Kunanbaeva, G.S. Prikl. Teor. Khim. 1978, 8-14.																																																																																													
(2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2]																																																																																															
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<b>VARIABLES:</b>																																																																																															
Composition at 25°C.		<b>PREPARED BY:</b>																																																																																													
J. Eyseltová																																																																																															
<b>EXPERIMENTAL VALUES:</b>																																																																																															
Solubility in the Na <sub>2</sub> HPO <sub>4</sub> -H <sub>3</sub> PO <sub>4</sub> -H <sub>2</sub> O system at 25°C.																																																																																															
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th colspan="3">Na<sub>2</sub>HPO<sub>4</sub></th> <th colspan="3">H<sub>3</sub>PO<sub>4</sub></th> <th rowspan="2">pH</th> <th rowspan="2">refr. index</th> <th rowspan="2">solid phase</th> </tr> <tr> <th>mass%</th> <th>mol%</th> <th>mol/kg<sup>a</sup></th> <th>mass%</th> <th>mol%</th> <th>mol/kg<sup>a</sup></th> </tr> </thead> <tbody> <tr> <td>0.66</td> <td>0.13</td> <td>0.08</td> <td>44.22</td> <td>12.82</td> <td>8.19</td> <td>----</td> <td>1.438</td> <td>Na<sub>2</sub>HPO<sub>4</sub></td> </tr> <tr> <td>2.26</td> <td>0.34</td> <td>0.20</td> <td>17.71</td> <td>3.89</td> <td>2.26</td> <td>1.00</td> <td>1.452</td> <td>"</td> </tr> <tr> <td>4.19</td> <td>0.63</td> <td>0.36</td> <td>13.60</td> <td>2.98</td> <td>1.72</td> <td>1.14</td> <td>1.460</td> <td>"</td> </tr> <tr> <td>5.42</td> <td>0.79</td> <td>0.45</td> <td>10.48</td> <td>2.22</td> <td>1.27</td> <td>1.47</td> <td>1.469</td> <td>"</td> </tr> <tr> <td>6.96</td> <td>0.99</td> <td>0.56</td> <td>5.74</td> <td>1.18</td> <td>0.67</td> <td>2.64</td> <td>1.484</td> <td>"</td> </tr> <tr> <td>8.61</td> <td>1.26</td> <td>0.71</td> <td>6.57</td> <td>1.39</td> <td>0.79</td> <td>2.23</td> <td>1.478</td> <td>"</td> </tr> <tr> <td>10.27</td> <td>1.46</td> <td>0.82</td> <td>2.00</td> <td>0.41</td> <td>0.23</td> <td>5.12</td> <td>1.508</td> <td>"</td> </tr> <tr> <td>12.00</td> <td>1.70</td> <td>0.96</td> <td>----</td> <td>----</td> <td>----</td> <td>9.93</td> <td>1.520</td> <td>"</td> </tr> </tbody> </table>									Na <sub>2</sub> HPO <sub>4</sub>			H <sub>3</sub> PO <sub>4</sub>			pH	refr. index	solid phase	mass%	mol%	mol/kg <sup>a</sup>	mass%	mol%	mol/kg <sup>a</sup>	0.66	0.13	0.08	44.22	12.82	8.19	----	1.438	Na <sub>2</sub> HPO <sub>4</sub>	2.26	0.34	0.20	17.71	3.89	2.26	1.00	1.452	"	4.19	0.63	0.36	13.60	2.98	1.72	1.14	1.460	"	5.42	0.79	0.45	10.48	2.22	1.27	1.47	1.469	"	6.96	0.99	0.56	5.74	1.18	0.67	2.64	1.484	"	8.61	1.26	0.71	6.57	1.39	0.79	2.23	1.478	"	10.27	1.46	0.82	2.00	0.41	0.23	5.12	1.508	"	12.00	1.70	0.96	----	----	----	9.93	1.520	"
Na <sub>2</sub> HPO <sub>4</sub>			H <sub>3</sub> PO <sub>4</sub>			pH	refr. index	solid phase																																																																																							
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<b>AUXILIARY INFORMATION</b>																																																																																															
<b>METHOD/APPARATUS/PROCEDURE:</b>				<b>SOURCE AND PURITY OF MATERIALS:</b>																																																																																											
Solutions of phosphoric were saturated with Na <sub>2</sub> HPO <sub>4</sub> . Equilibrium was established in three days. Sodium was determined using flame photometry, phosphorus was determined gravimetrically. No further details are given.				No information is given.																																																																																											
				<b>ESTIMATED ERROR:</b>																																																																																											
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COMPONENTS:			ORIGINAL MEASUREMENTS:							
(1) Sodium dihydrogenphosphate; $\text{NaH}_2\text{PO}_4$ ; [7558-80-7]			Marshall, W.L.							
(2) Sodium hydroxide; NaOH; [1310-73-2]			<i>J. Chem. Eng. Data</i> 1982, 27, 175-80.							
(3) Water; $\text{H}_2\text{O}$ ; [7732-18-5]										
VARIABLES:			PREPARED BY:							
Five Na/P ratios.			J. Eysseltová							
EXPERIMENTAL VALUES:										
Immiscibility and liquid-vapor critical phenomena for aqueous sodium phosphate solutions.										
solute stoichiometry			immiscibility boundary		critical phenomenon					
Na/PO <sub>4</sub> ratio	mass%	mol/kg <sup>a</sup>	t <sup>b</sup> /°C	phase <sup>c</sup>	t/°C	mass% <sup>d</sup>				
1	4.96	0.43	376.6 ± 0.2	L <sub>2</sub>	383.4 ± 0.4	2.5				
1	9.98	0.92	375.0 ± 0.5	L <sub>2</sub>	383.7 ± 0.2	2.5				
1	20.0	2.08	374.0 ± 0.2	L <sub>2</sub>	383.5 ± 0.2	2.5				
1	30.1	3.59	376.5 ± 0.3	L <sup>x</sup>	384 <sup>d</sup>	2.5				
1	34 <sup>d</sup>	4.29	384 <sup>d</sup>	L <sub>1</sub>	e	e				
1	40.0	4.29	e	L <sub>1</sub>	e	e				
1	50.0	8.33	e	e	e	e				
1	60.1	12.55	e	e	e	e				
1.20	4.55 <sup>b</sup>	0.38	350 <sup>b</sup>	L <sub>2</sub>		2				
1.20	5.13	0.43	347.7 ± 0.5	L <sub>2</sub>	378.4 ± 0.5	2				
1.20	10.0	0.89	340.3 ± 0.4	L <sub>2</sub>	380.9 ± 0.5	2				
1.20	20.1	2.01	340.7 ± 0.3	L <sub>2</sub>	382.9 ± 0.5	2				
1.20	30.3	3.47	345.7 ± 0.1	L <sub>2</sub>	383.5 ± 0.6	2				
1.20	39.8	5.27	353.5 ± 0.1	L <sup>x</sup>	380 ± 2	2				
1.20	40.6 <sup>b</sup>	5.45	350 <sup>b</sup>	L <sub>1</sub>		2				
1.20	50.3	8.07	369.0 ± 0.5	L <sub>1</sub>	380 <sup>d</sup> ± 2	2				
1.20	55 <sup>d</sup>	9.75	382 <sup>d</sup>	L <sub>1</sub>	382	2				
1.20	60.1	12.01	e	L <sub>1</sub>	e	e				

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium dihydrogenphosphate; NaH <sub>2</sub> PO <sub>4</sub> ; [7558-80-7]	Marshall, W.L.
(2) Sodium hydroxide; NaOH; [1310-73-2]	J. Chem. Eng. Data <u>1982</u> , 27, 175-80.
(3) Water; H <sub>2</sub> O; [7732-18-5]	

## EXPERIMENTAL VALUES cont'd:

Immiscibility and liquid-vapor critical phenomena for aqueous sodium phosphate solutions.

Na/PO <sub>4</sub> ratio	solute stoichiometry	mass%	mol/kg <sup>a</sup>	immiscibility boundary		critical phenomenon	mass% <sup>d</sup>
				t <sup>b</sup> /°C	phase <sup>c</sup>		
1.50	2.05 <sup>f</sup>	0.16	350 <sup>b</sup>	L <sub>2</sub>			1
1.50	4.99	0.40	329.9 ± 0.1	L <sub>2</sub>		378.4 ± 0.1	1
1.50	9.59	0.80	319.0 ± 0.1	L <sub>2</sub>		378.8 ± 0.1	1
1.50	20.0	1.89	310.3 ± 0.1	L <sub>2</sub>		379.3 ± 0.2	1
1.50	30.3	3.29	310.1 ± 0.1	L <sub>2</sub>		378.8 ± 0.1	1
1.50	40.1	5.07	313.1 ± 0.1	L <sub>x</sub>		379.3 ± 0.1	1
1.50	50.2	7.64	319.9 ± 0.1	L <sub>1</sub>		379.3 ± 0.1	1
1.50	60.2	11.46	343.2 ± 0.3	L <sub>1</sub>			1
1.50	63.1 <sup>f</sup>	12.96	350 <sup>b</sup>	L <sub>1</sub>			1
1.50	67 <sup>d</sup>	15.4	379 <sup>d</sup>	L <sub>1</sub>		379 <sup>d</sup>	1
2.00	0.8 <sup>g</sup>	0.06	365 <sup>g</sup>	L <sub>2</sub>			0.5
2.00	1.14 <sup>f</sup>	0.08	350 <sup>b</sup>	L <sub>2</sub>			0.5
2.00	3.0 <sup>h</sup>	0.2	324 <sup>h</sup>	L <sub>2</sub>			0.5
2.00	5.0 <sup>i</sup>	0.37	321.3 ± 0.4	L <sub>2</sub>		374.7 ± 0.5	0.5
2.00	10.0 <sup>i</sup>	0.78	300 <sup>i</sup>	L <sub>2</sub>			0.5
2.00	10.3 <sup>h</sup>	0.81	305.2 ± 0.1	L <sub>2</sub>		374.7 ± 0.5	0.5
2.00	12.4 <sup>h</sup>	1.00	300 <sup>h</sup>	L <sub>2</sub>			0.5
2.00	20.0	1.76	293.6 ± 0.2	L <sub>2</sub>		375.4 ± 0.5	0.5
2.00	30.0	3.01	290.6 ± 0.2	L <sub>2</sub>		375.1 ± 0.3	0.5
2.00	40.0 <sup>i</sup>	4.69	290.6 ± 0.4	L <sub>2</sub>		374.7 ± 0.5	0.5
2.00	57.3 <sup>j</sup>	9.44	300 <sup>i</sup>	L <sub>x</sub>			0.5
2.00	72 <sup>b</sup>	18.09	350 <sup>b</sup>	L <sub>1</sub>			0.5
2.00	74 <sup>d</sup>	20.02	375 <sup>d</sup>	L <sub>1</sub>		375 <sup>d</sup>	0.5
2.16	4.85	0.35	301 ± 1	L <sub>2</sub>			
2.16	10.0	0.76	291 ± 1	L <sub>2</sub>			
2.16	20.0	1.71	282 ± 1	L <sub>2</sub>			
2.16	28.9	2.77	281 ± 1	L <sub>2</sub>			
2.16	37.5	4.10	279 ± 1	L <sub>2</sub>			

<sup>a</sup>The mol/kg H<sub>2</sub>O values were calculated by the compiler.

<sup>b</sup>Lower boundary of observation (appearance of second liquid phase with rising temperature).

<sup>c</sup>L<sub>1</sub> = dilute liquid phase; L<sub>2</sub> = concentrated liquid phase; L<sub>x</sub> = liquid phase near the consolute solution composition (where composition L<sub>1</sub> = composition L<sub>2</sub>).

<sup>d</sup>Values at the upper temperature limit of immiscibility, determined graphically.

<sup>e</sup>No second liquid or critical phenomenon is observed at temperatures up to 410°C.

<sup>f</sup>From the plots of ref. (2).

<sup>g</sup>From the plots in ref. (3).

<sup>h</sup>From the plots in ref. (4).

<sup>i</sup>From the plots in ref. (5).

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The Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O System

COMPONENTS:								ORIGINAL MEASUREMENTS:																																																																																																																																																																																																													
(1) Trisodium phosphate; Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9]								D'Ans, J.; Schreiner, O.																																																																																																																																																																																																													
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<table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center;"><math>\text{Na}_3\text{PO}_4^b</math></th> <th style="text-align: center;"><math>\text{NaOH}^b</math></th> <th style="text-align: center;"><math>\text{H}_3\text{PO}_4^b</math></th> <th style="text-align: center;">solid<sub>c</sub></th> </tr> <tr> <th><math>\text{C}_{\text{Na}^+}^a</math></th> <th><math>\text{C}_{\text{PO}_4^{3-}}^a</math></th> <th>mass%</th> <th>mol/kg</th> <th>mass%</th> <th>mol/kg</th> <th>mass%</th> <th>mol/kg</th> <th>phase</th> </tr> </thead> <tbody> <tr><td>4.28</td><td>0.040</td><td>0.66</td><td>0.05</td><td>17.07</td><td>5.18</td><td>----</td><td>----</td><td>A</td></tr> <tr><td>3.24</td><td>0.183</td><td>3.00</td><td>0.22</td><td>12.72</td><td>3.77</td><td>----</td><td>0.05</td><td>"</td></tr> <tr><td>2.24</td><td>0.752</td><td>12.26</td><td>0.85</td><td>----</td><td>----</td><td>0.05</td><td>0.01</td><td>"</td></tr> <tr><td>2.73</td><td>1.08</td><td>14.94</td><td>1.09</td><td>----</td><td>----</td><td>1.67</td><td>0.20</td><td>"</td></tr> <tr><td>3.48</td><td>1.33</td><td>19.04</td><td>1.46</td><td>----</td><td>----</td><td>1.67</td><td>0.21</td><td>A + B</td></tr> <tr><td>2.62</td><td>1.09</td><td>14.33</td><td>1.04</td><td>----</td><td>----</td><td>2.12</td><td>0.26</td><td>B</td></tr> <tr><td>1.56</td><td>0.78</td><td>8.54</td><td>0.58</td><td>----</td><td>----</td><td>2.55</td><td>0.29</td><td>"</td></tr> <tr><td>2.38</td><td>1.60</td><td>13.02</td><td>1.00</td><td>----</td><td>----</td><td>7.90</td><td>1.02</td><td>"</td></tr> <tr><td>3.18</td><td>2.24</td><td>17.40</td><td>1.49</td><td>----</td><td>----</td><td>11.56</td><td>1.66</td><td>"</td></tr> <tr><td>4.65</td><td>3.55</td><td>25.44</td><td>2.82</td><td>----</td><td>----</td><td>19.60</td><td>3.64</td><td>"</td></tr> <tr><td>5.63</td><td>3.87</td><td>30.80</td><td>3.77</td><td>----</td><td>----</td><td>19.53</td><td>4.01</td><td>"</td></tr> <tr><td>6.31</td><td>4.63</td><td>34.52</td><td>5.16</td><td>----</td><td>----</td><td>24.76</td><td>6.20</td><td>C</td></tr> <tr><td>6.76</td><td>4.88</td><td>36.99</td><td>6.04</td><td>----</td><td>----</td><td>25.74</td><td>7.05</td><td>"</td></tr> <tr><td>7.31</td><td>5.55</td><td>40.00</td><td>8.25</td><td>----</td><td>----</td><td>30.51</td><td>10.56</td><td>metastable soln</td></tr> <tr><td>6.76</td><td>4.88</td><td>36.99</td><td>6.04</td><td>----</td><td>----</td><td>25.74</td><td>7.05</td><td>C + D<sup>e</sup></td></tr> <tr><td>6.19</td><td>4.68</td><td>33.87</td><td>5.09</td><td>----</td><td>----</td><td>25.64</td><td>6.46</td><td>E<sup>d</sup></td></tr> <tr><td>6.01</td><td>4.67</td><td>32.88</td><td>4.88</td><td>----</td><td>----</td><td>26.13</td><td>6.51</td><td>"</td></tr> <tr><td>5.12</td><td>4.36</td><td>28.01</td><td>3.70</td><td>----</td><td>----</td><td>26.00</td><td>5.77</td><td>"</td></tr> <tr><td>4.81</td><td>4.22</td><td>26.32</td><td>3.33</td><td>----</td><td>----</td><td>25.64</td><td>5.45</td><td>"</td></tr> <tr><td>4.36</td><td>4.08</td><td>23.86</td><td>2.88</td><td>----</td><td>----</td><td>25.74</td><td>5.21</td><td>"</td></tr> <tr><td>4.06</td><td>4.03</td><td>22.21</td><td>2.62</td><td>----</td><td>----</td><td>26.23</td><td>5.19</td><td>"</td></tr> </tbody> </table>												$\text{Na}_3\text{PO}_4^b$	$\text{NaOH}^b$	$\text{H}_3\text{PO}_4^b$	solid <sub>c</sub>	$\text{C}_{\text{Na}^+}^a$	$\text{C}_{\text{PO}_4^{3-}}^a$	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	phase	4.28	0.040	0.66	0.05	17.07	5.18	----	----	A	3.24	0.183	3.00	0.22	12.72	3.77	----	0.05	"	2.24	0.752	12.26	0.85	----	----	0.05	0.01	"	2.73	1.08	14.94	1.09	----	----	1.67	0.20	"	3.48	1.33	19.04	1.46	----	----	1.67	0.21	A + B	2.62	1.09	14.33	1.04	----	----	2.12	0.26	B	1.56	0.78	8.54	0.58	----	----	2.55	0.29	"	2.38	1.60	13.02	1.00	----	----	7.90	1.02	"	3.18	2.24	17.40	1.49	----	----	11.56	1.66	"	4.65	3.55	25.44	2.82	----	----	19.60	3.64	"	5.63	3.87	30.80	3.77	----	----	19.53	4.01	"	6.31	4.63	34.52	5.16	----	----	24.76	6.20	C	6.76	4.88	36.99	6.04	----	----	25.74	7.05	"	7.31	5.55	40.00	8.25	----	----	30.51	10.56	metastable soln	6.76	4.88	36.99	6.04	----	----	25.74	7.05	C + D <sup>e</sup>	6.19	4.68	33.87	5.09	----	----	25.64	6.46	E <sup>d</sup>	6.01	4.67	32.88	4.88	----	----	26.13	6.51	"	5.12	4.36	28.01	3.70	----	----	26.00	5.77	"	4.81	4.22	26.32	3.33	----	----	25.64	5.45	"	4.36	4.08	23.86	2.88	----	----	25.74	5.21	"	4.06	4.03	22.21	2.62	----	----	26.23	5.19	"
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Analytical methods: H <sub>3</sub> PO <sub>4</sub> was precipitated as NH <sub>4</sub> MgPO <sub>4</sub> . 6H <sub>2</sub> O and weighed as Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . Na <sup>+</sup> was determined as Na <sub>2</sub> SO <sub>4</sub> after removing of H <sub>3</sub> PO <sub>4</sub> with the aid of lead method.																																																																																																																																																																																																																					
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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Trisodium phosphate, Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9]	D'Ans, J.; Schreiner, O.
(2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2]	Z. Anorg. Chem. 1911, 75, 95-102.
(3) Sodium hydroxide; NaOH; [1310-73-2]	
(4) Water; H <sub>2</sub> O, [7732-18-5]	

## EXPERIMENTAL VALUES cont'd:

Solubility in the system: Na<sub>3</sub>PO<sub>4</sub>-NaOH-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O at 25°C.

C <sub>Na</sub> <sup>+</sup> <sup>a</sup>	C <sub>PO<sub>4</sub><sup>3-</sup></sub> <sup>a</sup>	Na <sub>3</sub> PO <sub>4</sub> <sup>b</sup>	NaOH <sup>b</sup>	H <sub>3</sub> PO <sub>4</sub> <sup>b</sup>	solid <sup>c</sup> phase
4.19	4.38	22.92	2.91	----	29.24    6.24    E
4.32	4.96	23.64	3.43	----	34.50    8.41    "
4.65	5.89	25.44	4.83	----	42.53    13.55    "
4.88	6.40	26.70	6.12	----	46.78    18.00    "d

<sup>a</sup> These concentrations are expressed as mol/kg of solution.<sup>b</sup> All these values were calculated by the compiler.<sup>c</sup> The solid phases are: A = Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O; B = Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O; C = Na<sub>2</sub>HPO<sub>4</sub>·7H<sub>2</sub>O;  
D = Na<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O; E = NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O.<sup>d</sup> These solid phases were analyzed.<sup>e</sup> The compiler considers this to be an obvious error. It should be C + E.

<b>COMPONENTS:</b> (1) Trisodium phosphate; Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9] (2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H <sub>2</sub> O; [7732-18-5]	<b>ORIGINAL MEASUREMENTS:</b> Menzel, H.; v. Sahr, E. <i>Z. Elektrochem.</i> <u>1937</u> , 2, 104-19.
<b>VARIABLES:</b> One temperature: 20°C Composition	<b>PREPARED BY:</b> J. Eysselová

## **EXPERIMENTAL VALUES:**

### Composition of saturated solutions of the $\text{Na}_2\text{O}\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ system at 20°C.

	$\text{Na}_2\text{O}$	$\text{P}_2\text{O}_5$		$\text{Na}_3\text{PO}_4$	<sup>b</sup>		$\text{NaOH}$	<sup>b</sup>		$\text{H}_3\text{PO}_4$	<sup>b</sup>		solid phase
$\text{N}_o$	mass%	mass%	$\text{N}_1$	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	$\text{Na}_2\text{O}:\text{P}_2\text{O}_5:\text{H}_2\text{O}$			
2.00	3.06	3.51	2.00	5.41	0.35	----	----	1.62	0.18	2.00	1	25.0	
2.12	3.79	3.97	2.19	6.70	0.44	----	----	1.49	0.16	2.00	1	25.09	
2.30	6.01	5.51	2.50	10.63	0.74	----	----	1.27	0.15	2.01	1	24.64	
2.40	7.24	6.38	2.60	12.80	0.90	----	----	1.18	0.14	2.02	1	25.85	
2.50	8.44	7.25	2.67	14.92	1.08	----	----	1.11	0.14	2.12	1	24.48	
2.60	8.43	7.25	2.67	14.91	1.08	----	----	1.12	0.14	2.33	1	21.52	
2.70	8.45	7.27	2.67	14.94	1.08	----	----	1.13	0.14	3.09	1	23.67	
2.80	8.32	7.09	2.69	14.71	1.06	----	----	1.02	0.12	3.11	1	25.27	
2.85	7.35	6.06	2.78	13.00	0.92	----	----	0.62	0.07	3.13	1	23.73	
2.90	7.45	6.11	2.79	13.17	0.93	----	----	0.58	0.07	3.14	1	25.41	
3.00	6.61	5.22	2.90	11.69	0.81	----	----	0.24	0.03	3.18	1	24.82	
3.05	6.17	4.79	2.95	10.91	0.74	----	----	0.11	0.01	3.19	1	25.28	
3.10	5.34	4.03	3.03	9.33	0.63	0.08	0.02	----	----	3.19	1	24.73	
3.20	4.80	3.46	3.18	8.01	0.53	0.34	0.09	----	----	3.21	1	24.32	
3.30	4.53	3.11	3.34	7.20	0.48	0.59	0.16	----	----	3.22	1	23.97	
3.50	4.26	2.65	3.68	6.14	0.40	1.02	0.27	----	----	3.22	1	23.73	

(continued next page)

## AUXILIARY INFORMATION

<p><b>METHOD/APPARATUS/PROCEDURE:</b></p> <p>The components were brought into solution at an elevated temperature. After reaching 20°C each system was equilibrated for 2 or 3 days. The liquid phase was then analyzed and reanalyzed after another 2 or 3 days. The solid phase was separated by a Schott filter and then either washed with ice water or filtered under a pressure of CO<sub>2</sub>. It was then dried on a porous plate in an empty desiccator. The samples were titrated with 0.5 mol dm<sup>-3</sup> HCl using dimethyl yellow as indicator. The indicator was then destroyed by boiling with Br<sub>2</sub> water. The samples were then titrated with 0.5 mol dm<sup>-3</sup> NaOH using thymolphthalein as indicator. Water was determined by difference.</p>	<p><b>SOURCE AND PURITY OF MATERIALS:</b></p> <p>Na<sub>2</sub>HPO<sub>4</sub> was from Sorensen-Kahlbaum, Merck. The NaOH was carbonate-free. The water was conductivity water.</p>
	<p><b>ESTIMATED ERROR:</b></p> <p>Temperature was constant to within ± 0.1 K.</p>
	<p><b>REFERENCES:</b></p>

COMPONENTS:						ORIGINAL MEASUREMENTS:					
(1) Trisodium phosphate; Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9]						Menzel, H., v. Sahr, E.					
(2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2]						Z. Elektrochem. 1937, 2, 104-19.					
(3) Sodium hydroxide; NaOH; [1310-73-2]											
(4) Water; H <sub>2</sub> O; [7732-18-5]											

## EXPERIMENTAL VALUES cont'd:

Composition of saturated solutions of the Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system at 20°C.

N <sub>o</sub> <sup>a</sup>	Na <sub>2</sub> O		P <sub>2</sub> O <sub>5</sub>		Na <sub>3</sub> PO <sub>4</sub> <sup>b</sup>		NaOH <sup>b</sup>		H <sub>3</sub> PO <sub>4</sub> <sup>b</sup>		solid phase	
	mass%	N <sub>1</sub> <sup>a</sup>	mass%	N <sub>1</sub>	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	Na <sub>2</sub> O:P <sub>2</sub> O <sub>5</sub> :H <sub>2</sub> O	
3.70	4.13	2.38	3.97	5.51	0.36	1.31	0.35	----	----	3.22	1	23.88
3.75	4.07	1.54	6.05	3.56	0.23	2.65	0.71	----	----	3.23	1	24.15
4.00	4.20	1.24	7.75	2.87	0.19	3.32	0.89	----	----	3.23	1	24.12
4.50	4.47	0.95	10.78	2.20	0.14	4.16	1.11	----	----	3.23	1	24.12
5.00	4.77	0.83	13.2	1.92	0.12	4.75	1.27	----	----	3.23	1	23.98
7.00	8.17	0.35	52.8	0.81	0.06	9.95	2.79	----	----	3.23	1	24.11
9.00	13.18	0.20	144.9	0.46	0.03	16.67	5.03	----	----	3.24	1	24.32
	17.86	0.08		0.18	0.01	22.92	7.45	----	----			
	21.73	0.09		0.21	0.02	27.90	9.70	----	----			
	25.39	0.17		0.39	0.04	32.48	12.10	----	----			
	25.85	0.22		0.51	0.05	32.99	12.40	----	----			
	27.79	0.19		0.44	0.04	35.55	13.88	----	----			
	28.15											
	28.36	0.21		0.49	0.05	36.25	14.32	----	----			
	30.23	0.21		0.49	0.05	38.66	15.88	----	----			
	31.07	0.21		0.49	0.05	39.75	16.63	----	----			
	31.18	0.20		0.46	0.05	39.91	16.73	----	----			
	31.64											
	31.97	0.15		0.35	0.04	41.01	17.48	----	----			
	32.58	0.12		0.28	0.03	41.85	18.08	----	----			

<sup>a</sup> N<sub>o</sub> is the original ratio of Na<sub>2</sub>O/P<sub>2</sub>O<sub>5</sub>; N<sub>1</sub> is ratio of Na<sub>2</sub>O/P<sub>2</sub>O<sub>5</sub> in saturated solution.<sup>b</sup> All these values were calculated by the compiler.

For the composition of the equilibrium solid phases see the Critical Evaluation.



<b>COMPONENTS:</b> (1) Trisodium phosphate; $\text{Na}_3\text{PO}_4$ ; [7601-54-9] (2) Phosphoric acid; $\text{H}_3\text{PO}_4$ ; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	<b>ORIGINAL MEASUREMENTS:</b> Wendrow, B.; Kobe, K.A. <i>Ind. Eng. Chem.</i> <u>1952</u> , <u>44</u> , 1439-48.
<b>VARIABLES:</b> Composition and temperature.	<b>PREPARED BY:</b> J. Eysseltová

## **EXPERIMENTAL VALUES:**

## Composition of saturated solutions of the $\text{Na}_2\text{O-P}_2\text{O}_5-\text{H}_2\text{O}$ system.

Na <sub>2</sub> O		P <sub>2</sub> O <sub>5</sub>		Na <sub>3</sub> PO <sub>4</sub> <sup>a</sup>		NaOH <sup>a</sup>		H <sub>3</sub> PO <sub>4</sub> <sup>a</sup>		solid phase <sup>b</sup>
mass%	mol%	mass%	mol%	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	
temp. = 0°C.										
2.23	0.67	1.75	0.23	3.93	0.25	----	----	0.06	0.00	A
2.10	0.62	0.61	0.08	1.41	0.08	1.67	0.43	----	----	A
3.03	0.92	2.25	0.30	5.20	0.33	0.10	0.02	----	----	A
0.754	0.22	0.855	0.11	1.33	0.08	----	----	0.38	0.04	B12
0.746	0.22	0.840	0.11	1.31	0.08	----	----	0.37	0.03	B12
9.28	3.58	21.26	3.58	16.39	1.55	----	----	19.58	3.12	C2
9.36	3.66	21.43	3.66	16.53	1.58	----	----	19.73	3.15	C2
temp. = 25°C.										
30.35	11.23	0.16	0.025	0.37	0.03	38.90	16.01	----	----	D0.5
28.61	10.44	0.28	0.045	0.64	0.06	36.45	14.48	----	----	D0.5
28.30	10.21	0.31	0.050	0.71	0.06	36.00	14.22	----	----	D0.5 + D6
26.48	9.49	0.28	0.042	0.64	0.06	33.70	12.83	----	----	D6
24.77	8.75	0.30	0.046	0.69	0.06	31.46	11.59	----	----	D6
23.73	8.32	0.29	0.043	0.67	0.05	30.13	10.88	----	----	D6 + A
20.82	7.10	0.22	0.033	0.50	0.04	26.50	9.07	----	----	A
12.31	3.86	0.31	0.043	0.71	0.05	15.13	4.49	----	----	A
5.75	1.75	0.75	0.099	1.73	0.11	6.15	1.67	----	----	A
4.65	1.41	1.40	0.186	3.23	0.21	3.63	0.97	----	----	A
4.61	1.41	2.50	0.335	5.78	0.38	1.72	0.46	----	----	A
4.79	1.48	2.70	0.363	6.24	0.41	1.61	0.43	----	----	A

(continued next page)

#### AUXILIARY INFORMATION

**METHOD/APPARATUS/PROCEDURE:**

A standard-type constant temperature bath fitted with automatic controls. Water with ethylene glycol at 0°C, water at 25-60°C and white mineral oil at 80 and 100°C were used as the bath. Self-constructed apparatus for agitation. Analyses: phosphorus was determined according to (1) except for highly alkaline solutions in which the content of  $P_2O_5$  was 0.8% or less where gravimetric method using magnesium ammonium phosphate was used. Sodium: nothing given, the compiler supposes Smith's method (2) was used. Schreinemakers' method of wet residue was combined with microscopic examination of solid phases.

**SOURCE AND PURITY OF MATERIALS:**

All chemicals used were C. P. reagent grade.  $H_3PO_4$ , disodium phosphate and monosodium phosphate from J. T. Baker and Co. and disodium phosphate and hemisodium phosphate from Monsanto were used. Merck's sodium hydroxide pellets were used in the preparation of both the samples and the standard NaOH solution.

**ESTIMATED ERROR:**

Nothing given; the compiler assumes the reproducibility of the analysis to be better than 1%.

## **REFERENCES:**

1. Gerber, A.B.; Miles, P.T. *Ind. Eng. Chem., Anal. Ed.* 1941, 13, 406.
  2. Smith, J.H. *J. Soc. Chem. Ind. London* 1917, 36, 420.

COMPONENTS:  
 (1) Trisodium phosphate; Na<sub>3</sub>PO<sub>4</sub>, [7601-54-9]  
 (2) Phosphoric acid; H<sub>3</sub>PO<sub>4</sub>; [7664-38-2]  
 (3) Sodium hydroxide, NaOH, [1310-73-2]  
 (4) Water, H<sub>2</sub>O, [7732-18-5]

ORIGINAL MEASUREMENTS:  
 Wendrow, B.; Kobe, K.A.  
*Ind. Eng. Chem.*, 1952, 44, 1439-48.

## EXPERIMENTAL VALUES cont'd:

Composition of saturated solutions of the Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system.

Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Na <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	NaOH <sup>a</sup>	H <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	Solid b phase									
mass%	mol%	mass%	mol%	mass%	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg
7.76	2.53	6.12	0.87	13.70	0.97	----	----	----	0.27	0.03	A			
8.99	3.00	7.50	1.09	15.87	1.16	----	----	----	0.88	0.10	A			
9.91	3.36	8.53	1.26	17.50	1.31	----	----	----	1.34	0.16	A			
10.66	3.67	9.39	1.41	18.82	1.44	----	----	----	1.73	0.22	A + B12			
9.04	3.03	8.20	1.20	15.96	1.18	----	----	----	1.80	0.22	B12			
8.93	2.99	8.01	1.17	15.77	1.16	----	----	----	1.65	0.20	B12			
4.52	1.42	5.23	0.72	7.98	0.54	----	----	----	2.46	0.28	B12			
8.61	3.02	12.95	1.95	15.20	1.21	----	----	----	8.81	1.18	B12			
11.02	4.17	17.59	2.90	19.46	1.74	----	----	----	12.68	1.90	B12			
15.30	6.56	24.58	4.60	27.02	2.98	----	----	----	17.82	3.29	B12			
15.82	6.88	25.05	4.75	27.94	3.14	----	----	----	17.92	3.38	B12			
16.07	7.02	25.32	4.83	28.38	3.22	----	----	----	18.03	3.43	B12			
16.24	7.12	25.37	4.85	28.68	3.27	----	----	----	17.92	3.42	B12			
16.71	7.38	25.69	4.95	29.51	3.41	----	----	----	17.87	3.46	B12 + B8			
16.71	7.45	26.33	5.12	29.51	3.47	----	----	----	18.75	3.70	B8			
16.76	7.54	26.91	5.27	29.60	3.54	----	----	----	19.50	3.91	B8			
17.58	8.12	28.26	5.70	31.05	3.90	----	----	----	20.50	4.32	B8			
17.87	8.31	28.48	5.79	31.56	4.01	----	----	----	20.50	4.36	B8			
19.48	9.61	31.39	6.75	34.40	4.90	----	----	----	22.82	5.44	B8			
20.44	10.40	32.62	7.24	36.10	5.44	----	----	----	23.51	5.94	B8 + E			
19.88	10.04	32.60	7.20	35.11	5.24	----	----	----	24.07	6.02	E			
19.48	9.85	32.93	7.26	34.40	5.15	----	----	----	24.95	6.26	E			
19.08	9.70	33.49	7.44	33.70	5.11	----	----	----	26.14	6.64	E			
18.93	9.60	33.53	7.43	33.43	5.06	----	----	----	26.36	6.69	E + C2			
17.28	8.30	31.20	6.54	30.52	4.17	----	----	----	24.88	5.69	C2			
13.24	5.82	28.06	5.38	23.38	2.75	----	----	----	24.80	4.88	C2			
13.22	5.79	27.84	5.33	23.35	2.72	----	----	----	24.51	4.79	C2			
12.01	5.16	27.50	5.16	21.21	2.41	----	----	----	25.32	4.83	C2			
11.15	4.88	29.50	5.63	19.69	2.33	----	----	----	28.99	5.76	C2			
10.83	4.87	31.65	6.21	19.13	2.39	----	----	----	32.29	6.78	C2			
10.71	4.82	33.94	6.66	18.91	2.53	----	----	----	35.58	7.98	C2			
10.82	5.17	36.23	7.57	19.11	2.75	----	----	----	38.63	9.32	C2			
10.98	5.45	38.60	8.37	19.39	3.03	----	----	----	41.73	10.95	C2			
11.41	5.87	40.51	9.08	20.15	3.41	----	----	----	43.91	12.47	C2			
11.33	5.85	40.95	9.26	20.01	3.44	----	----	----	44.61	12.86	C1			
10.93	5.77	42.70	9.89	19.30	3.53	----	----	----	47.44	14.56	C1			
10.88	5.80	43.37	10.13	19.21	3.61	----	----	----	48.42	15.27	C1			
11.31	6.21	44.85	10.74	19.97	4.05	----	----	----	50.01	17.01	C1 + C			
11.16	6.18	45.39	11.00	19.71	4.08	----	----	----	50.92	17.69	C			
11.08	6.23	45.65	11.18	19.57	4.10	----	----	----	51.36	18.03	C			
10.30	5.92	48.26	12.10	18.19	4.26	----	----	----	55.78	21.88	C + F			
7.25	4.20	51.33	12.99	12.80	3.25	----	----	----	63.24	26.94	F			
2.88	1.73	56.77	14.88	5.08	1.58	----	----	----	75.35	39.31	F			

temp. = 40°C.

34.71	13.38	0.12	0.02	0.27	0.03	44.59	20.22	----	----	----		
29.19	10.75	0.31	0.052	0.71	0.07	37.15	14.94	----	----	----	D0.5	
28.79	10.52	0.38	0.061	0.87	0.08	36.51	14.58	----	----	----	D0.5	
28.37	10.36	0.42	0.067	0.97	0.09	35.90	14.22	----	----	----	D0.5	
27.78	10.11	0.48	0.076	1.11	0.10	35.04	13.72	----	----	----	D6	
27.54	10.00	0.47	0.074	1.08	0.10	34.02	13.11	----	----	----	D6	
26.98	9.73	0.47	0.074	1.08	0.10	34.02	13.11	----	----	----	D6	
25.43	9.06	0.53	0.082	1.22	0.11	31.92	11.94	----	----	----	D6	
24.42	8.61	0.56	0.086	1.29	0.11	30.57	11.51	----	----	----	D6	
23.80	8.36	0.61	0.093	1.41	0.12	29.68	10.77	----	----	----	D6	
23.36	8.20	0.66	0.101	1.52	0.13	29.03	10.45	----	----	----	D6 + A	
19.85	6.75	0.55	0.082	1.27	0.10	24.69	8.33	----	----	----	A	

(continued next page)

COMPONENTS:

- (1) Trisodium phosphate; Na<sub>3</sub>PO<sub>4</sub>; [7601-54-9]
- (2) Phosphoric acid; H<sub>3</sub>PO<sub>4</sub>, [7664-38-2]
- (3) Sodium hydroxide; NaOH; [1310-73-2]
- (4) Water; H<sub>2</sub>O; [7732-18-5]

## ORIGINAL MEASUREMENTS:

Wendrow, B; Kobe, K.A.

Ind. Eng. Chem. 1952, 44, 1439-48.

## EXPERIMENTAL VALUES cont'd:

Composition of saturated solutions of the Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system.

Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Na <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	NaOH <sup>a</sup>	H <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	Solid <sup>b</sup> phase
mass%	mol%	mass%	mol%	mass%	
mass%	mol%	mass%	mol/kg	mass%	mol/kg
15.64	5.13	0.55	0.079	1.27	0.09
15.32	5.02	0.59	0.084	1.36	0.10
9.30	2.93	1.17	0.16	2.70	0.18
8.59	2.70	1.54	0.21	3.56	0.24
7.63	2.41	3.18	0.44	7.35	0.50
7.54	2.40	3.73	0.52	8.62	0.59
8.97	2.96	6.30	0.91	14.56	1.05
12.21	4.28	9.60	1.47	21.56	1.68
12.38	4.26	9.81	1.48	21.86	1.71
13.88	5.02	11.31	1.79	24.51	2.00
14.16	5.16	11.76	1.87	25.01	2.06
14.33	5.26	12.13	1.94	25.31	2.11
15.00	5.57	12.73	2.06	26.49	2.25
15.59	5.90	13.94	2.30	27.53	2.40
17.15	6.78	16.52	2.84	30.29	2.84
17.72	7.10	17.31	3.03	31.30	3.00
19.27	8.05	19.18	3.50	34.03	3.46
18.78	7.78	18.93	3.42	33.17	3.34
16.05	6.36	17.52	3.03	28.35	2.68
15.10	5.92	17.33	2.96	26.67	2.48
14.71	5.73	17.09	2.91	25.98	2.40
15.34	6.10	18.32	3.18	27.09	2.58
16.14	6.63	20.24	3.65	28.50	2.86
17.87	7.83	24.05	4.60	31.56	3.55
18.36	8.25	25.58	5.02	32.41	3.82
19.18	8.80	26.43	5.30	33.87	4.14
19.39	8.96	26.72	5.39	34.25	4.23
19.33	8.96	26.99	5.46	34.14	4.25
19.54	9.13	27.41	5.59	34.51	4.36
19.55	9.19	27.82	5.71	34.53	4.41
19.90	9.68	29.94	6.36	35.15	4.81
20.44	10.20	31.23	6.80	36.10	5.20
20.63	10.44	32.00	7.07	36.44	5.40
20.74	10.56	32.34	7.19	36.63	5.50
20.82	10.65	32.53	7.27	36.77	5.56
21.34	11.20	33.79	7.75	37.69	6.02
21.12	11.22	34.73	8.06	37.30	6.14
20.68	11.12	35.79	8.40	36.52	6.21
20.32	10.98	36.26	8.53	35.89	6.17
20.44	11.16	37.01	8.83	36.10	6.40
19.46	10.31	35.90	8.31	34.37	5.72
18.95	9.94	35.71	8.18	33.47	5.48
18.76	9.79	35.52	8.10	33.13	5.37
17.56	8.90	34.60	7.66	31.01	4.76
17.09	8.60	34.50	7.58	30.18	4.57
16.92	8.48	34.39	7.53	29.88	4.50
15.77	7.73	33.78	7.23	27.85	4.03
14.66	7.07	33.62	7.08	25.89	3.65
13.96	6.84	35.31	7.56	24.65	3.63
13.61	6.78	36.71	7.99	24.04	3.69
13.07	6.61	38.05	8.40	23.08	3.68
12.37	6.56	41.70	9.66	21.85	3.96
12.53	6.72	42.27	9.90	22.13	4.12
12.25	6.59	42.73	10.04	21.63	4.08
11.77	6.54	45.10	10.95	20.79	4.31
11.44	6.60	46.38	11.68	20.20	4.42
10.92	6.38	48.72	12.44	19.28	4.71
10.66	6.51	51.35	13.69	18.82	5.33

(continued next page)

## COMPONENTS:

- (1) Trisodium phosphate; Na<sub>3</sub>PO<sub>4</sub>; [7601-54-9]  
 (2) Phosphoric acid; H<sub>3</sub>PO<sub>4</sub>; [7664-38-2]  
 (3) Sodium hydroxide; NaOH; [1310-73-2]  
 (4) Water; H<sub>2</sub>O; [7732-18-5]

## ORIGINAL MEASUREMENTS:

Wendrow, B., Kobe, K.A.  
*Ind. Eng. Chem.* 1952, 44, 1439-48.

## EXPERIMENTAL VALUES cont'd:

Composition of saturated solutions of the Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system.

Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Na <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	NaOH <sup>a</sup>	H <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	Solid <sup>b</sup> phase						
mass%	mol%	mass%	mol%	mass%	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	phase
10.33	6.36	52.07	14.00	18.24	5.36	----	----	61.01	30.02	F	
7.39	4.48	53.66	14.22	13.05	3.85	----	----	66.30	32.78	F	
5.10	3.09	55.39	14.64	9.00	2.76	----	----	71.11	36.49	F	
2.68	1.71	60.24	16.80	4.73	1.93	----	----	80.35	54.00	F	
temp. = 60°C.											
34.39	13.22	0.094	0.016	0.21	0.02	44.22	19.90	----	----	D	
30.14	11.16	0.136	0.022	0.31	0.03	38.67	15.84	----	----	D	
28.72	10.52	0.31	0.050	0.71	0.06	36.54	14.56	----	----	D	
28.29	10.34	0.52	0.082	1.20	0.11	35.63	14.10	----	----	D + DO.5	
26.25	9.46	0.90	0.14	2.08	0.19	32.36	12.34	----	----	DO.5	
25.68	9.24	1.19	0.19	2.75	0.25	31.13	11.77	----	----	DO.5	
25.01	8.97	1.37	0.21	3.16	0.28	29.96	11.20	----	----	DO.5	
23.76	8.44	1.54	0.24	3.56	0.31	28.06	10.26	----	----	DO.5	
20.60	7.17	2.16	0.33	4.99	0.42	22.93	7.95	----	----	DO.5	
19.72	6.84	2.47	0.37	5.71	0.47	21.27	7.28	----	----	A	
18.71	6.43	2.55	0.38	5.89	0.48	19.83	6.67	----	----	A	
15.79	5.30	2.59	0.38	5.98	0.46	16.00	5.12	----	----	A	
14.71	4.02	3.05	0.45	7.05	0.54	13.83	4.37	----	----	A	
13.71	4.62	4.18	0.61	9.66	0.73	10.62	3.33	----	----	A	
13.28	4.58	7.41	1.11	17.13	1.33	4.61	1.47	----	----	A	
15.91	5.84	11.02	1.76	25.48	2.13	1.90	0.65	----	----	A	
17.15	6.46	12.24	2.01	28.30	2.45	1.44	0.51	----	----	A + D8	
17.29	6.65	12.71	2.13	29.39	2.56	0.82	0.29	----	----	D8	
17.79	6.80	13.01	2.17	30.08	2.65	0.96	0.35	----	----	D8	
19.20	7.70	15.94	2.79	33.91	3.21	----	----	1.79	0.28	D8	
21.73	9.10	20.63	3.95	38.38	4.17	----	----	5.60	1.02	D8	
22.13	9.75	21.04	4.05	39.09	4.31	----	----	5.74	1.06	D8	
22.48	10.05	21.65	4.21	39.70	4.47	----	----	6.22	1.17	D8	
22.62	10.18	22.06	4.33	39.95	4.55	----	----	6.63	1.26	D8 + B2	
22.12	9.90	21.85	4.25	39.07	4.40	----	----	6.87	1.29	B2	
20.86	9.56	21.82	4.16	36.84	4.08	----	----	8.16	1.51	B2	
20.68	9.48	21.99	4.19	36.52	4.05	----	----	8.58	1.59	B2	
19.26	8.34	22.11	4.17	34.02	3.71	----	----	10.24	1.87	B2	
19.69	8.93	25.13	4.97	34.78	4.13	----	----	13.96	2.78	B2	
19.95	9.31	27.09	5.52	35.23	4.43	----	----	16.39	3.45	B2	
20.58	10.14	30.32	6.52	36.35	5.09	----	----	20.19	4.74	B2	
21.38	10.96	32.29	7.23	37.76	5.72	----	----	22.07	5.60	B2	
21.55	11.18	32.90	7.45	38.06	5.91	----	----	22.73	5.91	B2	
21.81	11.44	33.43	7.66	38.52	6.13	----	----	23.19	6.18	B2 + G	
21.79	11.45	33.53	7.70	38.48	6.14	----	----	23.35	6.24		
21.79	11.45	33.60	7.71	38.48	6.16	----	----	23.44	6.28	G	
21.66	11.39	33.69	7.74	38.26	6.12	----	----	23.70	6.36	G	
21.37	11.35	34.52	8.01	37.74	6.20	----	----	25.16	6.92	G	
21.30	11.31	34.67	8.05	37.62	6.20	----	----	25.44	7.02	G	
20.93	11.33	36.17	8.55	36.97	6.41	----	----	27.90	8.10	G	
21.02	11.53	36.78	8.81	37.12	6.61	----	----	28.64	8.54	G	
20.79	11.49	37.52	9.06	36.72	6.70	----	----	29.91	9.14	G	
20.74	11.61	38.20	9.32	36.63	6.87	----	----	30.90	9.71	G + C	
18.92	10.07	36.76	8.55	33.42	5.69	----	----	30.83	8.80	C	
17.50	9.09	36.21	8.20	30.91	5.01	----	----	31.56	8.58	C	
17.16	8.86	36.16	8.15	30.31	4.88	----	----	31.85	8.59	C	
16.83	8.65	36.13	8.09	29.72	4.75	----	----	32.16	8.61	C	
16.11	8.04	36.89	8.04	28.45	4.61	----	----	33.97	9.22	C	
15.08	7.77	37.72	8.49	26.63	4.36	----	----	36.20	9.94	C	
13.54	7.12	40.29	9.27	23.91	4.19	----	----	41.37	12.16	C	
12.41	6.72	43.02	10.18	21.92	4.20	----	----	46.33	14.89	C	

(continued next page)

COMPONENTS:							ORIGINAL MEASUREMENTS:									
(1) Trisodium phosphate, $\text{Na}_3\text{PO}_4$ ; [7601-54-9]							Wendrow, B.; Kobe, K.A.									
(2) Phosphoric acid; $\text{H}_3\text{PO}_4$ ; [7664-38-2]							<i>Ind. Eng. Chem.</i> 1952, 44, 1439-48.									
(3) Sodium hydroxide; $\text{NaOH}$ ; [1310-73-2]																
(4) Water; $\text{H}_2\text{O}$ ; [7732-18-5]																
EXPERIMENTAL VALUES cont'd:																
Composition of saturated solutions of the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ system.																
$\text{Na}_2\text{O}$		$\text{P}_2\text{O}_5$		$\text{Na}_3\text{PO}_4^a$		$\text{NaOH}^a$		$\text{H}_3\text{PO}_4^a$			Solid <sup>b</sup> phase					
mass%	mol%	mass%	mol%	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	mass%						
11.43	6.82	49.48	12.90	20.18	5.22	----	----	56.28	24.41	C						
11.39	6.89	50.32	13.29	20.11	5.47	----	----	57.48	26.19	C						
11.19	6.90	51.52	13.87	19.76	5.76	----	----	59.35	29.00	C						
10.89	7.02	54.09	15.23	19.23	6.67	----	----	63.21	36.76	C						
8.91	5.62	54.53	15.02	15.73	5.22	----	----	65.91	36.65	F						
7.59	4.77	55.46	15.23	13.40	4.53	----	----	68.58	38.86	F						
6.01	3.73	56.11	15.22	10.61	3.54	----	----	71.14	39.80	F						
3.63	2.83	59.01	16.30	6.41	2.45	----	----	77.65	49.73	F						
temp. = 80°C.																
36.39	14.30	0.140	0.024	0.32	0.03	46.73	22.06	----	----	D						
32.11	12.10	0.210	0.034	0.48	0.05	41.09	17.58	----	----	D						
30.64	11.42	0.314	0.051	0.72	0.07	39.01	16.18	----	----	D						
30.28	11.26	0.373	0.061	0.86	0.08	38.45	15.84	----	----	D						
29.85	11.06	0.514	0.083	1.18	0.11	37.65	15.39	----	----	DO.5						
28.03	10.24	0.605	0.096	1.39	0.13	35.15	13.85	----	----	DO.5						
27.72	10.07	0.617	0.098	1.42	0.13	34.73	13.60	----	----	DO.5						
25.60	9.25	1.65	0.26	3.81	0.35	30.25	11.47	----	----	DO.5						
25.24	9.12	1.79	0.28	4.13	0.38	29.55	11.14	----	----	DO.5						
24.83	9.11	2.60	0.41	6.01	0.55	27.65	10.42	----	----	DO.5						
23.87	8.75	4.29	0.69	9.92	0.90	23.55	8.85	----	----	DO.5 + D6						
21.61	8.11	8.35	1.37	19.31	1.75	13.77	5.14	----	----	D6						
21.35	8.35	12.15	2.08	28.09	2.63	7.01	2.70	----	----	D6						
23.20	9.98	18.20	3.41	40.98	4.28	----	----	0.69	0.12	D6						
24.51	11.07	20.96	4.13	43.29	4.92	----	----	3.13	0.59	D6						
22.94	10.50	23.29	4.66	40.52	4.79	----	----	8.00	1.58	B2						
20.59	9.25	23.56	4.61	36.37	4.19	----	----	10.84	2.09	B2						
temp. = 100°C.																
38.36	15.36	0.41	0.072	0.94	0.11	48.81	24.29	----	----	D						
30.05	11.17	0.80	0.13	1.85	0.18	37.43	15.41	----	----	D						
26.19	9.48	1.32	0.21	3.07	0.28	31.55	12.06	----	----	D						
23.79	8.70	4.17	0.67	9.64	0.88	23.65	8.86	----	----	D						
24.37	9.46	9.26	1.57	21.41	2.07	15.79	6.29	----	----	D						
24.26	9.45	9.53	1.62	22.03	2.13	15.20	6.05	----	----	D						
25.98	10.76	13.18	2.38	30.48	3.18	11.24	4.82	----	----	D						
25.43	10.50	13.41	2.42	31.01	3.21	10.15	4.31	----	----	DO.5						
24.97	10.42	14.00	2.66	33.76	3.50	7.54	3.21	----	----	DO.5						
25.18	10.66	15.62	2.89	36.12	3.80	6.09	2.63	----	----	DO.5						
25.76	11.18	16.93	3.20	39.15	4.24	4.62	2.05	----	----	DO.5						
26.51	11.74	17.79	3.43	41.14	4.58	4.13	1.89	----	----	DO.5						
26.75	12.03	18.87	3.70	43.63	4.94	2.62	1.22	----	----	D6						
26.90	11.86	19.29	3.71	44.61	5.10	2.10	0.98	----	----	D6						
27.89	13.22	21.77	4.51	49.26	5.99	----	----	0.68	0.14	D6						
28.31	13.69	23.01	4.86	50.00	6.34	----	----	1.95	0.41	D6						
27.48	13.30	23.46	4.95	48.54	6.16	----	----	3.45	0.73	B						
25.73	12.35	24.29	5.08	45.44	5.75	----	----	6.44	1.36	B						
24.69	11.73	24.59	5.10	43.61	5.48	----	----	7.95	1.67	B						
23.53	11.08	24.84	5.12	41.56	5.17	----	----	9.52	1.98	B						
22.13	10.35	25.56	5.22	39.09	4.86	----	----	11.98	2.50	B						
23.39	12.56	33.64	7.90	41.31	6.82	----	----	21.81	6.03	B						
24.34	13.93	36.61	9.15	42.99	8.16	----	----	24.91	7.92	B + E						
23.07	13.31	38.09	9.57	40.75	8.02	----	----	28.29	9.33	E						
22.54	13.14	39.21	10.00	39.81	8.14	----	----	30.40	10.41	E						
22.33	13.18	40.00	10.32	39.44	8.33	----	----	31.71	11.22	E						
22.40	13.31	42.73	11.64	39.56	9.63	----	----	35.41	14.44	E + C						

COMPONENTS:							ORIGINAL MEASUREMENTS:				
(1) Trisodium phosphate; Na <sub>3</sub> PO <sub>4</sub> ; [7601-54-9]							Wendrow, B., Kobe, K.A.				
(2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2]							Ind. Eng. Chem. 1952, 44, 1439-48.				
(3) Sodium hydroxide; NaOH; [1310-73-2]											
(4) Water; H <sub>2</sub> O; [7732-18-5]											

## EXPERIMENTAL VALUES cont'd:

Composition of saturated solutions of the Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system.

Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Na <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	NaOH <sup>a</sup>	H <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	solid <sup>b</sup> phase					
mass%	mol%	mass%	mol%	mass%	mol/kg	mass%	mol/kg	mass%	mol/kg	solid <sup>b</sup> phase
21.48	13.00	41.91	11.04	37.94	8.62	----	----	35.24	13.41	C
19.87	11.55	41.25	10.50	35.09	7.40	----	----	36.03	12.73	C
19.16	11.07	41.40	10.46	33.84	7.06	----	----	36.98	12.93	C
18.36	10.51	41.72	10.46	32.43	6.74	----	----	38.27	13.32	C
18.31	10.53	41.92	10.53	32.34	6.78	----	----	38.60	13.55	C
16.71	9.57	42.90	10.74	29.51	6.23	----	----	41.63	14.72	C
14.63	8.93	48.22	12.88	25.84	6.85	----	----	51.17	22.72	C
13.14	9.95	58.04	18.33	23.21	13.48	----	----	66.30	64.51	C
12.32	8.80	57.95	18.05	21.76	11.84	----	----	67.04	61.10	F
10.70	7.55	58.68	18.03	18.90	10.15	----	----	69.75	62.74	F
9.86	7.06	60.08	18.74	17.41	10.60	----	----	72.57	73.98	F
9.37	6.86	61.42	19.63	16.55	11.85	----	----	74.93	89.86	F

<sup>a</sup> All these values were calculated by the compiler.<sup>b</sup> The solid phases are: A = 4(Na<sub>3</sub>PO<sub>4</sub> · 12H<sub>2</sub>O) · NaOH;B = Na<sub>2</sub>HPO<sub>4</sub>; B2 = Na<sub>2</sub>HPO<sub>4</sub> · 2H<sub>2</sub>O; B7 = Na<sub>2</sub>HPO<sub>4</sub> · 7H<sub>2</sub>O; B8 = Na<sub>2</sub>HPO<sub>4</sub> · 8H<sub>2</sub>O;B12 = Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O;C = NaH<sub>2</sub>PO<sub>4</sub>; C1 = NaH<sub>2</sub>PO<sub>4</sub> · H<sub>2</sub>O; C2 = NaH<sub>2</sub>PO<sub>4</sub> · 2H<sub>2</sub>O;D = Na<sub>3</sub>PO<sub>4</sub>; D0.5 = Na<sub>3</sub>PO<sub>4</sub> · 0.5H<sub>2</sub>O; D6 = Na<sub>3</sub>PO<sub>4</sub> · 6H<sub>2</sub>O; D8 = Na<sub>3</sub>PO<sub>4</sub> · 8H<sub>2</sub>O;E = Na<sub>2</sub>HPO<sub>4</sub> · 2NaH<sub>2</sub>PO<sub>4</sub> · 2H<sub>2</sub>O;F = NaH<sub>2</sub>PO<sub>4</sub> · H<sub>2</sub>PO<sub>4</sub>;G = Na<sub>2</sub>HPO<sub>4</sub> · NaH<sub>2</sub>PO<sub>4</sub>.

<b>COMPONENTS:</b>		<b>ORIGINAL MEASUREMENTS:</b>							
(1) Disodium hydrogenphosphate; Na <sub>2</sub> HPO <sub>4</sub> ; [7558-79-4]		Panson, A.J.; Economy, G.; Liu, Chia-sun; Bulischeck, T.S.; Lindsay Jr., W.T.							
(2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2]		J. Electrochem. Soc. 1975, 122, 915-8.							
(3) Sodium hydroxide; NaOH; [1310-73-2]									
(4) Water; H <sub>2</sub> O; [7732-18-5]									
<b>VARIABLES:</b>		<b>PREPARED BY:</b>							
Composition at 548, 573 and 597 K.		J. Eysseletová							
<b>EXPERIMENTAL VALUES:</b>									
Solubility in the Na <sub>2</sub> HPO <sub>4</sub> -H <sub>3</sub> PO <sub>4</sub> -NaOH-H <sub>2</sub> O system.									
Na/PO <sub>4</sub> ratio		PO <sub>4</sub>		Na <sub>2</sub> HPO <sub>4</sub> <sup>a</sup>					
solution		mol/kg		mass%					
temp = 548 K									
2.0	---	>8.0							
2.10	---	>2.5							
2.15	2.13	3.79		34.88					
2.15	2.23	3.26		31.54					
2.24	2.87	1.29		15.37					
2.25	2.86	0.64		8.26					
2.32	2.73	0.74		9.41					
2.57	2.84	0.42		5.52					
2.69	2.76	0.41		5.37					
3.24	2.83	0.26		3.40					
temp = 573 K									
1.58	1.62	5.73		27.66					
1.60	1.60	5.68		28.38					
1.65	1.65	6.95		34.25					
1.75	1.84	2.94		22.62					
1.81	1.91	0.94		5.20					
1.92	1.99	1.06		12.09					
1.97	2.04	0.85		10.47					
2.00	2.22	0.51		6.76					
2.10	2.37	0.64		8.31					
2.11	2.23	0.68		8.78					
2.13	2.56	0.33		4.46					
2.13	2.63	0.44		5.86					
<i>(continued next page)</i>									
<b>AUXILIARY INFORMATION</b>									
<b>METHOD/APPARATUS/PROCEDURE:</b>			<b>SOURCE AND PURITY OF MATERIALS:</b>						
The experiments were carried out in two-liter autoclaves of stainless steel (A.I.S.I. Type 316) and Inconel Alloy 600 fitted with internal sampling tubes and filters. Three different experimental procedures were used: nonisothermal procedures, isothermal procedures with saturation approached from below, and experiments in which saturation was approached by evaporation at approximately isothermal conditions. Samples of solution were removed periodically from the autoclave and analyzed by a potentiometric acid-base titration.			No information is given.						
			<b>ESTIMATED ERROR:</b>						
			No information is given.						
			<b>REFERENCES:</b>						

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Disodium hydrogenphosphate; Na <sub>2</sub> HPO <sub>4</sub> ; [7558-79-4]	Panson, A.J.; Economy, G.; Liu, Chia-sun; Bulischeck, T.S.; Lindsay Jrs., W.T.
(2) Phosphoric acid; H <sub>3</sub> PO <sub>4</sub> ; [7664-38-2]	J. Electrochem. Soc. 1975, 122, 915-8.
(3) Sodium hydroxide; NaOH; [1310-73-2]	
(4) Water; H <sub>2</sub> O; [7732-18-5]	

## EXPERIMENTAL VALUES cont'd:

Solubility in the Na<sub>2</sub>HPO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub>-NaOH-H<sub>2</sub>O system.

Na/PO <sub>4</sub> ratio solution	PO <sub>4</sub> solid phase	Na <sub>2</sub> HPO <sub>4</sub> <sup>a</sup> mol/kg	Na <sub>2</sub> HPO <sub>4</sub> <sup>a</sup> mass%	H <sub>3</sub> PO <sub>4</sub> <sup>a</sup> mass%	NaOH <sup>a</sup> mass%
temp = 573 K cont'd.					
2.14	2.28	0.47	6.23	---	0.52
2.14	2.44	0.55	7.21	---	0.52
2.14	2.35	0.66	8.53	---	0.51
2.16	2.33	0.67	8.64	---	0.58
2.18	2.55	0.38	5.09	---	0.68
2.19	2.58	0.43	5.72	---	0.71
2.46	2.82	0.25	3.37	---	1.74
2.89	2.75	0.14	1.89	---	3.37
temp = 597 K					
1.48	1.71	2.08	11.37	8.49	---
1.55	1.79	0.70	5.04	2.84	---
1.56	1.66	3.63	19.99	10.83	---
1.63	1.70	3.86	23.27	9.42	---
1.71	1.90	0.38	3.66	1.03	---
1.89	2.03	0.28	3.41	0.29	---
1.93	2.16	0.33	4.17	0.22	---
1.97	2.01	0.34	4.47	0.10	---
1.97	2.14	0.19	2.55	0.05	---
1.98	2.27	0.26	3.49	0.05	---
2.08	2.29	0.24	3.29	----	0.31
2.13	2.37	0.26	3.55	----	0.50
2.14	2.54	0.17	2.35	----	0.54
2.15	2.44	0.20	2.75	----	0.58
2.17	2.48	0.19	2.61	----	0.66
2.32	2.42	0.07	0.97	----	1.25
2.54	2.76	0.11	1.51	----	2.08
3.04	2.74	0.08	1.08	----	3.95
3.28	2.72	0.06	0.80	----	4.83

<sup>a</sup>These values were calculated by the compiler.

COMPONENTS:	EVALUATOR:
(1) Sodium dihydrogenphosphate; $\text{NaH}_2\text{PO}_4$ ; [7558-80-7]	J. Eysseltová and J. Makovička Charles University Prague, Czechoslovakia
(2) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	May 1985

## CRITICAL EVALUATION:

## THE BINARY SYSTEM

The isothermal method has been used to determine the solubility of sodium dihydrogenphosphate in water (1, 2). The solubility has also been reported as a limiting condition in the study of several multicomponent systems (3-12). The nature of the equilibrium solid phases was studied in detail by Imadsu (2). He reported the existence of the following solid phases:  $\text{NaH}_2\text{PO}_4$  [7558-80-7];  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  [10049-21-5];  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  [13472-35-0]; and  $\text{NaH}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$  [101056-45-5]. The transition temperature of the anhydrous salt to the monohydrate was estimated to be 330.5 K while that of the monohydrate to the dihydrate was estimated to be 313.9 K. The transition between the dihydrate and the tetrahydrate was not determined but was considered to be below 273 K (2).

Evaluation Procedure. All the data were examined and evaluated by using the method described by Cohen-Adad (13). Only experimentally obtained data were evaluated. Data obtained from smoothing equations or by extrapolation were excluded from consideration. The data calculated on the basis of sodium determination (1) and the 298 K values reported by others (3, 4) are clearly incorrect and were not included. Some data (4) were reported as  $\text{mol dm}^{-3}$  and could not be used here because no density information was given and the values could not be recalculated in terms of mole fraction. All the other data are consistent with each other and were evaluated together.

The data were fitted to equation [1], suggested by Cohen-Adad (13).

$$\ln(x/x_0) = A \cdot (1/T - 1/T_0) + B \cdot \ln(T/T_0) + C \cdot (T - T_0) \quad [1]$$

A, B and C are adjustable parameters. No attempt was made to give a physical meaning to them. The system is too complex for that, as is shown by reported activity coefficient data (14, 15).  $x_0$  is a reference mole fraction at temperature  $T_0$ . Its choice is arbitrary. The evaluators used the following two criteria for making their selection.

1.  $x_0$  was chosen as the mean value of the experimental data of more than one study. Furthermore, the standard deviation did not exceed the experimental uncertainty in obtaining the data.
2.  $T_0$  was chosen near the middle of the temperature range in which the hydrate exists rather than at or near a transition point of one hydrate into another.

Each datum selected was given a weight equal to the number of independent determinations of the value. In some reports (5, 7, 10, 12) a given value appears to be reported more than once. In such cases the value was given a weight of one. Then an iterative method analogous to that described by others (16) was used. It was necessary to know the experimental uncertainty of the values before the next iteration could be made. However, such information was included in only two reports (2, 4). Therefore, the evaluators tried to estimate the experimental uncertainty on the basis of the data that were included in the report. It appears that for the isothermal studies (1-4, 6-9, 11, 12) the precision is 0.1 to 0.5% while for data derived from polythermal studies (5, 10) it is about 1%. The selection conditions that were used are given in equation [2].  $x_j$  and  $T_j$  are the coordinates of the experimental point  $j$  in terms of mole fraction and

$$\left| \frac{x_j - x(T_j)}{x(T_j)} \right| \leq 0.015 \quad [2]$$

temperature.  $x(T_j)$  is the calculated mole fraction. Data points that did not meet the conditions of equation [2] were eliminated before the next iteration.

The value of coefficients A, B and C of equation [1] were determined by using a non-linear regression with the experimental points selected as described above. For the regression, equation [1] was put in the form of equation [3]. The calculation was stopped

$$x = x_0 \cdot \exp[A(1/T - 1/T_0) + B \cdot \ln(T/T_0) + C \cdot (T - T_0)] \quad [3]$$

when steady values were obtained for A, B and C.

The solubility results are summarized in Table I. During the iteration procedure all the data in refs (6-8, 12) and most of the data in ref (1) were eliminated. Table II

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Sodium dihydrogenphosphate; $\text{NaH}_2\text{PO}_4$ ; [7558-80-7]	J. Eyseltová and J. Makovička Charles University Prague, Czechoslovakia
(2) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	May 1985

## CRITICAL EVALUATION: (cont'd)

Table I. Solubility of  $\text{NaH}_2\text{PO}_4$  in water.

T/K	mass%	ref.	init/final	T/K	mass%	ref.	init/final
$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$							
263.3	32.4	5	1/1	298.2	48.97	1	1/1
263.3	30.4	10	1/0	298.2	48.62	2	2/2
266.2	33.6	10	1/1	298.2	48.69	9	1/1
268.2	35.4	12	1/0	298.2	48.03	8	1/0
268.9	34.6	10	1/1	298.2	48.47	11	1/0
273.2	36.1	1	1/0	299.2	49.16	2	1/1
273.2	36.4	5	1/1	299.2	49.17	2	1/1
273.2	36.25	11	1/1	300.2	49.80	2	2/2
273.2	37.6	12	1/0	301.2	50.43	2	1/1
273.3	36.64	2	1/1	301.2	50.41	2	1/1
274.2	37.13	2	1/1	303.2	51.55	2	1/1
274.2	37.15	2	1/1	303.2	51.57	2	1/1
276.2	38.06	2	1/1	303.2	51.2	5	1/1
276.2	38.08	2	1/1	306.2	52.15	2	1/1
278.2	38.95	2	1/1	306.2	52.12	2	1/1
278.2	38.96	2	1/1	307.2	53.93	2	1/1
283.2	41.12	2	1/1	307.2	53.96	2	1/1
283.2	41.14	2	1/1	308.2	54.63	2	1/1
283.2	40.5	5	1/0	308.2	54.64	2	1/1
283.2	42.2	12	1/0	308.2	54.79	3	1/1
288.2	43.42	2	1/1	308.7	53.65	1	1/0
288.2	43.41	2	1/1	313.2	56.41	1	1/0
293.2	46.01	2	1/1	313.2	58.02	2	1/0
293.2	46.00	2	1/1	313.2	58.00	2	1/0
293.2	45.30	5	1/0	313.2	56.31	7	1/0
293.2	46.60	12	1/0				
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$							
314.2	58.76	2	1/1	323.2	61.16	6	1/0
314.2	58.78	2	1/1	323.2	60.58	8	1/0
315.2	58.98	2	1/1	325.2	62.11	2	1/1
315.2	58.99	2	1/1	325.2	62.09	2	1/0
317.2	57.97	1	1/0	328.2	63.85	1	1/0
318.2	59.71	2	2/2	328.2	63.09	2	1/1
323.2	61.81	1	1/1	328.2	63.07	2	1/1
323.2	61.32	2	1/1	329.2	63.41	2	1/1
323.2	61.34	2	1/1	329.2	63.39	2	1/1
$\text{NaH}_2\text{PO}_4$							
331.2	65.53	1	1/0	338.2	65.89	1	1/0
331.2	63.94	2	1/0	342.2	65.54	2	1/1
331.2	63.92	2	1/0	342.2	65.55	2	1/1
333.2	64.20	2	2/2	343.2	66.25	1	1/0
334.2	65.77	1	1/0	348.2	67.21	1	1/0
335.2	64.44	2	1/1	348.2	66.57	11	1/1
335.2	64.48	2	1/1	353.2	67.44	2	1/0
338.2	64.92	2	1/1	353.2	67.48	2	1/1
338.2	64.90	2	1/1	356.2	69.13	1	1/1

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