

ADVANCES IN
CHEMICAL PHYSICS

Volume II

54.2
A244
2:2

ADVANCES IN
CHEMICAL PHYSICS

Edited by I. PRIGOGINE
University of Brussels, Brussels, Belgium

VOLUME II

2636-74

中國科學院
1960.12.22

INTERSCIENCE PUBLISHERS, INC., NEW YORK
INTERSCIENCE PUBLISHERS LTD., LONDON 1959

FIRST PUBLISHED, 1959

ALL RIGHTS RESERVED

LIBRARY OF CONGRESS CATALOG CARD NUMBER 58-9935

INTERSCIENCE PUBLISHERS, INC., 250 Fifth Avenue, New York 1, N. Y.

INTERSCIENCE PUBLISHERS LTD., 88/90 Chancery Lane, London W. C. 2

PRINTED IN THE NETHERLANDS

BY DIJKSTRA'S DRUKKERIJ N.V., VOORHEEN BOEKDRUKKERIJ GERR. HOUTEMA, CRONINGEN

INTRODUCTION TO THE SERIES

In the last decades, Chemical Physics has attracted an ever increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of Chemical Physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern Chemical Physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into

something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity has been attained — a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

I. PRIGOGINE

CONTRIBUTORS TO VOLUME II

JULES DUCHESNE, Institut d' Astrophysique, University of Liège, Sarte-Scllessin, Belgium

PER-OLOF LÖWDIN, Quantum Chemistry Group, University of Uppsala, Uppsala, Sweden

R. A. ORIANI, General Electric Research Laboratory, Schenectady, New York

KENNETH S. PITZER, Dean, College of Chemistry and Radiation Laboratory, University of California, Berkeley, California

J. C. PLATTEEUW, Koninklijke/Shell-Laboratorium, Amsterdam, Holland

M. J. RICHARDSON, Department of Chemistry, The University, Manchester, England

J. S. ROWLINSON, Department of Chemistry, The University, Manchester, England

M. SZWARC, State University of New York, College of Forestry, Syracuse, New York

J. H. VAN DER WAALS, Koninklijke/Shell-Laboratorium, Amsterdam, Holland

E. BRIGHT WILSON, JR., Department of Chemistry, Harvard University, Cambridge, Massachusetts

HIROYUKI YOSHIZUMI, Physics Department, University of Tokyo, Tokyo, Japan (Deceased)

CONTENTS

Clathrate Solutions. By <i>J. H. van der Waals</i> and <i>J. C. Platteeuw</i>	1
Inter- and Intramolecular Forces and Molecular Polarizability. By <i>Kenneth S. Pitzer</i>	59
The Solubility of Solids in Compressed Gases. By <i>J. S. Rowlinson</i> and <i>M. J. Richardson</i>	85
Thermodynamics of Metallic Solutions. By <i>R. A. Oriani</i>	119
Recent Advances in Polymer Chemistry. By <i>M. Szwarc</i>	147
Nuclear Quadrupole Resonance in Irradiated Crystals. By <i>Jules Duchesne</i>	187
Correlation Problem in Many-Electron Quantum Mechanics. I. Review of Different Approaches and Discussion of Some Current Ideas. By <i>Per-Olov Löwdin</i>	207
Correlation Problem in Many-Electron Quantum Mechanics. II. Bibliographical Survey of the Historical Developments with Comments. By <i>Hiroyuki Yoshizumi</i>	323
The Problem of Barriers to Internal Rotation in Molecules. By <i>E. Bright Wilson, Jr.</i>	367
Author Index	395
Subject Index	403

CLATHRATE SOLUTIONS

J. H. VAN DER WAALS and J. C. PLATTEEUW, *Koninklijke/Shell-Laboratorium, Amsterdam*

CONTENTS

I. Introduction	2
A. General Nature of Clathrates	2
B. Structural Information	6
(1) Hydroquinone Clathrates	6
(2) Hydrates	7
II. Statistical Theory	10
A. Basic Assumptions	10
B. Construction of Partition Function	12
C. Nature of the Approximation	16
D. Stability of Clathrate and the Equilibrium Q° -clathrate- A (gas)	18
(1) Hydroquinone Clathrates	20
(2) Hydrates	21
E. Evaluation of the Cell Partition Function by the Method of Lennard-Jones and Devonshire	23
F. Numerical Calculations	28
(1) Hydroquinone Clathrates	28
(2) Hydrates	31
III. Heterogeneous Equilibria	34
A. General Remarks	34
B. Hydroquinone Clathrates	35
(1) The Binary System Hydroquinone-Rare Gas	35
(2) The Binary System Hydroquinone-Methanol	39
C. Hydrates	41
(1) Binary Systems	41
(2) Ternary Systems	44
(a) Systems in which Hydrates of One Structure Occur	44
(b) Systems in which Hydrates of Both Structures Occur	46
References	55

I. INTRODUCTION

A. General Nature of Clathrates

Some ten years ago Palin²³ and Powell^{24, 31, 32} studied the peculiar "compounds" which are formed by hydroquinone with a large number of gases and volatile liquids. They showed that in these compounds the hydroquinone molecules, as a result of hydrogen bonding, form two interpenetrating three-dimensional networks which enclose roughly spherical cavities, in a ratio of 1 cavity to every 3 hydroquinone molecules. If the cavities are all empty the crystal lattice is that of the metastable β modification of hydroquinone. However, if a certain fraction of the cavities is occupied by molecules of a second component, the crystals may be thermodynamically stable in a certain region of temperature and pressure. The type of molecules which may be bound in the cavities is very diverse, as it includes O_2 , N_2 , CH_4 , C_2H_2 , CH_3OH , HCl , SO_2 and even the noble gases Ar, Kr, Xe. Apparently almost any substance may be bound, provided its molecules are neither too large (CCl_4) nor too small (He).

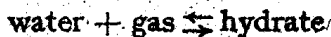
Once such a molecular complex with hydroquinone has been formed it may persist under conditions where it is no longer thermodynamically stable. Because the molecules of the second component are enclosed in the cavities they cannot escape without breaking a number of hydrogen bonds in the β -hydroquinone lattice. This corresponds to a considerable energy of activation which may prevent the attainment of thermodynamic equilibrium.

An example is the complex with argon which can be kept indefinitely in an ordinary bottle, although the equilibrium pressure of argon over the crystal amounts to several atmospheres at room temperature. Powell³¹ named these complexes "clathrate compounds," which according to him are those compounds "in which two or more components are associated without ordinary chemical union but through complete enclosure of one set of molecules in a suitable structure formed by another."

Not only hydroquinone, but also phenol and a number of related substances have been reported^{30, 31, 33, 44} to form clathrate compounds of a similar type. But this class of substances proves to be

even larger. Before any structural information was available Nikitin²⁰ already expressed the opinion that the binding mechanism operating in the so-called gas hydrates, and which remained a mystery despite a century of extensive research, should be of the same type as that in the phenol compounds just mentioned. Recently Nikitin's contention was indeed confirmed by the results of the x-ray work on gas hydrates of von Stackelberg and Müller,^{42, 43} and Pauling and Marsh.²⁴ Before we come to a discussion of the work of these authors it seems appropriate to relate a few relevant facts from the earlier investigations on the nature of the gas hydrates.*

In 1810 Davy discovered chlorine hydrate when cooling a saturated solution of chlorine in water below 9°C. Research by Villard, de Forcrand and many others subsequently showed that this type of hydrate can be formed by water with a large number of gases or volatile liquids such as Cl₂, Br₂, H₂S, CO₂, CH₄, CHCl₃ and again the inert gases A, Kr, Xe. It was further established that the process.



is a univariant equilibrium, so that at a given temperature the pressure of the gas has a unique value. (According to de Forcrand krypton hydrate, for instance, has an equilibrium pressure of 14.5 atm at 0°C, which rises to 47.5 atm at 12.5°C.) In fact, the study of gas hydrates constituted an essential step in the development of the theory of heterogeneous equilibria by Bakhuis Roozeboom.¹

The accurate composition of the gas hydrates for a long time remained a controversial subject, since direct analysis leads to ambiguous results owing to decomposition of the hydrate and/or inclusion of mother liquor in the crystals. Thus it was firmly believed that the nonstoichiometric compositions of gas hydrates found experimentally were all due to errors in the analysis. But more recent determinations of the composition by the indirect

* For a detailed account of the work on gas hydrates and references prior to 1925 the reader is referred to Schröder's historical account of this subject,⁴⁰ while later references are given in von Stackelberg's papers.⁴²⁻⁴⁴

method of Scheffer and Meyer (cf. Section III.C.(1)) in some cases also led to clearly nonstoichiometric results.

The mechanism responsible for the formation of gas hydrates became clear when von Stackelberg and his school^{42, 43} in Bonn succeeded in determining the x-ray diffraction patterns of a number of gas hydrates and Claussen⁶ helped to formulate structural arrays fitting these patterns. Almost simultaneously Pauling and Marsh²⁰ determined the crystal structure of chlorine hydrate.

According to these authors all gas hydrates crystallize in either of two cubic structures (I and II) in which the hydrated molecules are situated in cavities formed by a framework of water molecules linked together by hydrogen bonds. The numbers and sizes of the cavities differ for the two structures, but in both the water molecules are tetrahedrally coordinated as in ordinary ice. Apparently gas hydrates are clathrate compounds.

A common feature of all clathrates discussed so far is a host lattice, by itself thermodynamically unstable, which is stabilized by inclusion of the second component. The forces binding this component must be similar in nature to the intermolecular forces in liquids. It seems natural, therefore, to regard a clathrate "compound" as a *solid solution of the second component in the (metastable) host lattice*.

In the present review a description is given of the phase behavior of clathrates on the basis of a solution theory. The treatment is restricted to those cases where the empty host lattice ("solvent") is indeed unstable, although many of the present considerations also apply to the few cases known where the host lattice is stable. An example of the latter is the chroman complex first discovered by Dianin⁹ and recently examined by Baker and McOmie and Powell and Wetters.³⁴

Although it is difficult to predict exactly which solute molecules will form clathrate solutions in any given host lattice, the general principle is quite clear. All molecules which fit into the cavities will be able to stabilize the host lattice, unless they show a specific chemical interaction with the solvent molecules. HCl (or the other hydrogen halides), for instance, does not form a clathrate with water, but rather the stoichiometric compounds $\text{HCl} \cdot \text{H}_2\text{O}$,

$\text{HCl} \cdot 2\text{H}_2\text{O}$ and $\text{HCl} \cdot 3\text{H}_2\text{O}$; it readily forms a hydroquinone clathrate. Ammonia, on the other hand, does not form clathrates with either water or hydroquinone. Molecules with a very low polarizability (He , Ne , H_2) are not known to form clathrate solutions by themselves, but they do help to stabilize the clathrate of a more polarizable solute simultaneously present.⁴⁷ It is almost needless to say that in the following we shall only consider those hydrates which are in fact clathrates and which are frequently referred to as "gas hydrates," although the molecules of certain volatile liquids may also be included.

In the next section we shall give a brief account of the crystal structure of the hydroquinone clathrates and of the gas hydrates, as far as is needed for a proper understanding of the subsequent parts. The reader who is interested in the phenomenology of other clathrate compounds should consult one of the many review articles^{7,8,20} on inclusion compounds.

Part II is devoted to a rigorous analysis of the thermodynamic behavior of clathrates on the basis of statistical mechanics, using a model analogous to that commonly employed for describing ideal localized adsorption. The formulas are derived for the general case of a clathrate containing n types of cavities and M different encaged solutes. Stability conditions are formulated for clathrates relative to the gaseous solutes and the stable modification of the solvent, and the method of Lennard-Jones and Devonshire is used in a quantitative analysis of the thermodynamic properties of some hydroquinone clathrates ($n = 1$) and gas hydrates ($n = 2$).

In Part III heterogeneous equilibria involving clathrates are discussed, from the experimental point of view. In particular a method is presented for the reversible investigation of the equilibrium between clathrate and gas, circumventing the hysteresis effects. The phase diagrams of a number of binary and ternary systems are considered in some detail, since controversial statements have appeared in the literature on this subject.

B. Structural Information

(1) *Hydroquinone Clathrates*

Figure 1 illustrates the structure of β -hydroquinone as determined by Palin and Powell.^{23, 24} Some of the cavities are represented by transparent spheres containing a ball corresponding in size with an encaged argon atom. At the top and bottom of each cavity

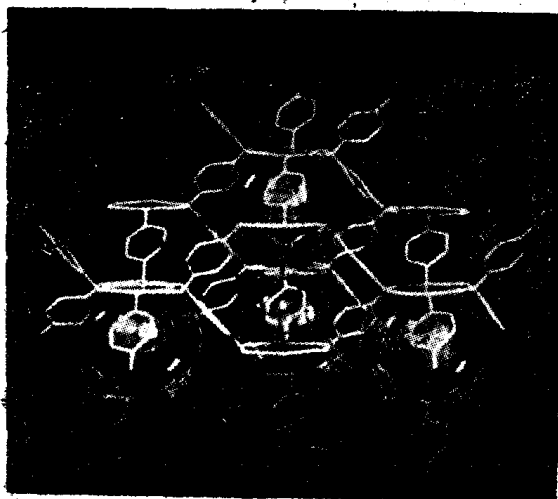


Fig. 1. The crystal structure of β -hydroquinone clathrate according to Palin and Powell.²³ The balls inside the transparent spheres represent argon atoms encaged in the cavities formed by the two interpenetrating lattices. (photograph kindly supplied by Dr. Powell).

there is a hexagon of oxygen atoms formed by six hydroquinone molecules linked to each other by hydrogen bonds, three of them pointing upwards and three downwards (this is particularly clear at the top of the upper sphere in Fig. 1).

The cavity is further bounded by two carbon atoms and an adjacent hydrogen atom of each of six of the hydroquinone molecules in the manner shown in the figure. Hence, the wall of the cavity is formed by 12 oxygen atoms, 12 carbon atoms, and 18

hydrogen atoms, about evenly distributed over a sphere with radius 3.95 Å. The field within the cavity, however, may not be expected to have complete spherical symmetry: a quadrupole placed at the center will show a preferred orientation because the oxygen atoms are all nearer the poles of the cavity and the carbon atoms nearer the equator.

The foregoing lattice is that which is found in the clathrates of hydroquinone with small molecules (C_2H_2 , HCl , etc.). Powell⁴⁴ further showed that if larger molecules are included, the hydroquinone lattice is distorted to form oblong cavities; this distortion increases in the series CH_3OH , SO_2 , CO_2 , and has become extreme for CH_3CN .

(2) Hydrates

The unit cell of Structure I is illustrated in Fig. 2, taken from the paper by von Stackelberg and Müller.⁴⁵ It contains 46 water molecules which enclose two types of cavities. The smaller cavities are

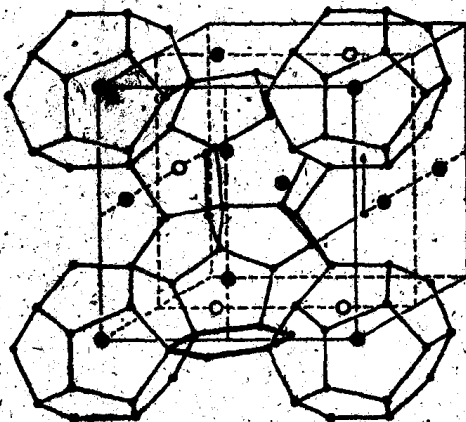


Fig. 2. Unit cell of a gas hydrate of Structure I according to von Stackelberg and Müller.⁴⁵ For the sake of clarity only the elements lying in the nearer half of the unit cell have been drawn. The smaller dots indicate the tetrahedrally surrounded water molecules, the larger dots represent the centers of the two types of cavities.

located at the vertices and the center of the unit cell; they are each formed by a pentagonal dodecahedral array of 20 water molecules. The remaining six water molecules in the unit cell form bridges

TABLE I. Thermodynamic Data and Lattice Constants of Some Hydrates

(The data in the table have been copied from the papers by von Stackelberg and Müller^a and von Stackelberg and Jahns,^b except when otherwise indicated.)

Solute (in order of increasing bp)	Dissoc. pressure at 0° C	Max. temp. at which hydrates exist, °C	Heat of formation from pure water and gas at 0° C kcal/mole solute	Lattice constant, Å
A	95.5 atm ^c	no maximum exists		
CH ₄	26.0 atm	no maximum exists	14.5	
Kr	14.5 atm	no maximum exists	13.9 ± 0.5	
Xe	1.15 atm ^d	no maximum exists	16.7 ± 0.5	12.0
C ₂ H ₄	5.44 atm ^e	no maximum exists	15.0 ^f	
C ₂ H ₆	5.2 atm	14.5	16.3 ^g	
N ₂ O	10 atm	12	14.7	12.03
C ₂ H ₂	5.7 atm	16	16	
CO ₂	12.47 atm ^h	10.20 ⁱ	14.4	12.07
H ₂ S	698 mm ^h	29.5 ^h	14.8 ^l	12.02
Cl ₂	252 mm	28.7	16.0	12.03
CH ₃ Cl	311 mm	21	18.1	12.00
SO ₂	297 mm	12.1	16.6	11.97
CH ₃ Br	187 mm	14.5	19.5	12.09
CH ₃ SH	239 mm	12	16.6	12.12
Br ₂	43.90 mm ^j	5.81 ^j	20.88 ^j	12.1
C ₂ H ₆	1.74 atm ^k	5.69 ^l	32 ^k	17.40
CHCl ₃ F	115 mm ^m	8.61 ^m	32.7 ^m	
C ₂ H ₅ Cl	201 mm	4.8	31.9	17.30
CH ₂ Cl ₂	116 mm	1.7	29	17.33
CH ₃ I	74 mm	4.3	35.4	17.14
CHCl ₃	(50 mm ⁿ)	1.6	31	17.33

^a Stackelberg, M. von, and Müller, H. R., *Z. Elektrochem.* **58**, 25 (1954), Table I.

^b Stackelberg, M. von, and Jahns, W., *Z. Elektrochem.* **58**, 162 (1954), Table II.

^c Diepen, G. A. M., private communication.

^d Schroöder, W., *Die Geschichte der Gaskydrate*, F. Enke, Stuttgart, 1925, p. 87.

^e Diepen, G. A. M., and Scheffer, F. E. C., *Ned. Versl. Akad.* **69**, 593 (1956).

^f Roberts, O. L., Brownscombe, E. R., and Burt, L. S., *Oil Gas J.* **39**, No. 30, 37 (1940).

between these dodecahedra in such a way that a second type of cavity is formed: a tetrakaidecahedron having two opposite hexagonal faces and twelve pentagonal faces. (One of these hexagons has been marked by heavier lines in the lower center of Fig. 2.)

Although the agreement between the observed x-ray intensities and those calculated from the aforementioned model is not perfect, the latter is thought to be essentially correct. The "composition" of a gas hydrate of Structure I is then characterized by

46 water molecules,

2 smaller cavities: $z_1 = 20$, $a_1 = 3.95 \text{ \AA}$

6 larger cavities: $z_2 = 24$, $a_2 = 4.30 \text{ \AA}$

The number of oxygen atoms surrounding the two types of cavities are denoted by z_1 , z_2 , and a_1 , a_2 are the average distances of these atoms to the centers of the cages. The smaller cavities are very nearly spherical and have a free diameter of approximately 5.1 \AA when assuming Pauling's value²⁸ of 1.4 \AA for the van der Waals radius of oxygen. The larger cavities are slightly oblate, since the distances from the center to the surrounding oxygen atoms vary between 4.04 \AA and 4.65 \AA . Their free diameter is approximately 5.8 \AA . (Cf. ref. 30; figures are based on a unit cell edge = 12.0 \AA .)

According to von Staackelberg and Müller,⁴³ the hydrates tabulated in the top section of Table I all crystallize in Structure I.

The molecules of the gases bound in these hydrates are relatively small and in general occupy both types of cavities. If all cavities were filled, the composition would be 1 gas $5\frac{1}{2} \text{ H}_2\text{O}$, but as we shall see, a certain fraction of the cavities must remain empty when the

²⁸ Herreillers, H. W., Thesis, Amsterdam, 1936.

²⁹ Selleck, F. T., Carmichael, L. T., and Sage, B. H., *Ind. Eng. Chem.* **44**, 2219 (1952).

³⁰ Scheffer, F. R. C., and Meyer, G., *Proc. Acad. Sci. Amsterdam* **21**, 1338 (1919).

³¹ Mulders, E. M. J., Thesis, Delft, 1937.

³² Frost, E. M., and Deaton, W. M., *Proc. Nat. Gas Dept., AGA*, 1946.

³³ Miller, B., and Strong, E. R., Jr., *AGA Monthly*, **28**, No. 2, 63 (1943).

³⁴ Banks, W. P., Heston, B. O., and Blankenship, F. F., *J. Phys. Chem.* **58**, 962 (1954).

hydrate is formed in equilibrium with an aqueous phase. The molecules of CH_3Br , CH_3SH , and Br_2 have such dimensions that while they are still crystallizing in Structure I, they cannot occupy the smaller cavities. This is supported by the high water content of the bromine hydrate ($1 \text{ Br}_2 \cdot 8.47 \text{ H}_2\text{O}$) found by Miss Mulders¹⁸ and further proved by the intensity of its x-ray diffraction pattern.⁴⁸

The unit cell of the hydrates crystallizing in Structure II is rather complicated, and for a detailed description the reader is referred to the original publications.^{6, 48} Its "composition" is characterized by:

136 water molecules,

16 smaller cavities: $z_1 = 20$, $a_1 = 3.91 \text{ \AA}$

8 larger cavities: $z_2 = 28$, $a_2 = 4.73 \text{ \AA}$

The smaller cavities are distorted pentagon dodecahedra (distance of oxygen atoms to center varies between 3.77 and 3.95 \AA); their average free diameter is only about 5.0 \AA . The larger cavities are almost spherical; the oxygen atoms lie at the vertices of hexadecahedra and their free diameter is 6.7 \AA . The distances have been calculated on the basis of a unit cell edge of 17.40 \AA as found for propane hydrate.

Hydrates of Structure II are formed only by molecules which are too large to be accommodated in Structure I. This implies that they occupy only the larger cavities. Also very common are the so-called mixed hydrates discussed by von Stackelberg and Meinhold⁴⁷ in which large molecules (e.g. CHCl_3) occupy the larger cavities of Structure II and small molecules (e.g. CO_2 , N_2 , H_2S) occupy the smaller cavities as well as some of the larger ones. In Section III. C. (2) (b) a quantitative discussion is given of the phase behavior of the system methane-propane-water in which such a mixed hydrate occurs.

II. STATISTICAL THEORY

A. Basic Assumptions

The thermodynamic properties of clathrates can be derived from a simple model which corresponds to the three-dimensional generalization of ideal localized adsorption. In ref. 52 the deriva-