Book Reviews

E. Berecz and M. Balla-Achs, *Gas Hydrates* (Studies in Inorganic Chemistry Vol. 4), Elsevier Science Publishers, Amsterdam, Oxford, New York, 1983, ISBN 0-444-99657-5, $75, Dfl.195.

Since the existence of natural gas hydrate deposits in regions of permafrost was officially recorded as discovery 75 by the government of the U.S.S.R. on 25 December 1969, there has been a spectacular expansion in interest in this kind of clathrate. Much work devoted to problems related to the exploitation of this significant new energy resource has been done in the Soviet Union, where extensive hydrate deposits have been identified. This work is mostly described in Russian sources, often in reports not readily accessible to the international community. It is therefore useful to have, in the first book on gas hydrates to be published in English, a compilation of information about gas hydrates which includes 200 Russian and Eastern European references among the almost 600 cited.

Professor Berecz and Dr Balla-Achs are with the Department of General and Physical Chemistry of the Technical University for Heavy Industry, Miskolc, Hungary. Their book emphasizes properties important to engineering applications of gas hydrates and indeed deals in detail almost exclusively with the temperature dependence of dissociation pressures and related quantities. It is likely to prove disappointing to those readers of this journal who are also interested in other, and more fundamental, properties of these unique clathrate systems. Unfortunately, the uncritical nature of the authors' review of a substantial part of the extensive gas hydrate literature, as well as the poor quality of the translation from the Hungarian, has managed to make an exciting subject rather dull.

The field of gas hydrates has perhaps been more subject than most to errors and misconceptions, many pre-dating the structural and thermodynamic studies of the 1950s which established their nature. Among errors perpetuated here are that the dissociation pressure of CF_4 hydrate is only about 1 atm, that Br_2 forms a type I hydrate, that CCl_4 by itself does not form a hydrate (cf. Lameris [1]), and that 'double hydrates' with H_2S are stoichiometric. The phase diagram of the methane-water system is drawn (following Makogon) without regard to the low critical temperature of methane. No indication is given that the method of Wilcox [2] for calculating dissociation pressures of hydrates formed from gas mixtures and the method of Miller and Strong [3] for determining hydrate compositions are based on concepts that are no longer valid. The nature of the 'special investigations' that 'demonstrate' that *two* nitrogen molecules can be accommodated in the larger cavities of type II hydrate is not specified.

Although some of the literature is covered up to 1980, important new developments have not been included, particularly in the areas of detection of submarine gas hydrate deposits and of speculation about the occurrence of gas hydrates elsewhere in the solar system. Some treatment of these broader aspects can be found in Cox [4].

No doubt the Berecz-Balla-Achs monograph will prove convenient as a guide to the literature and to the conditions of stability of some of the most important gas hydrates. The best all-round treatment of the chemistry and physics of gas hydrates, however, remains the Russian-language text written by Byk, Makogon and Fomina [5].

References

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2. W. L. Wilcox, D. B. Carson, and D. L. Katz, *Ind. Eng. Chem.* **33**, 662 (1941).
3. B. Miller and E. R. Strong, *Prov. Amer. Gas Assoc.* **27**, 80 (1945).
4. J. L. Cox (ed.): *Natural Gas Hydrates: Properties, Occurrence and Recovery*, Butterworth (1983).
5. S. Sh. Byk, Yu. F. Makogon, and V. I. Fomina: *Gazovye Gidraty*, Khimiya, Moscow (1980).

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John L. Cox (ed.): *Natural Gas Hydrates: Properties, Occurrence and Recovery*, Butterworth, London, 1983, 125 pp., £28.50.

This slim volume is concerned with gas (clathrate) hydrates in relation to their natural occurrence under terrestial conditions. It is a multi-author work containing eight papers. Four papers are on physicochemical properties of gas hydrates, and four on geophysical and geochemical aspects. In the first paper, D. W. Davidson provides an excellent concise summary and review of physical properties of gas hydrates, emphasising those of methane and propane to give perspective in relation to natural gas. The second paper, by Sloan and Parrish, reviews gas hydrate phase equilibria, especially methods for thermodynamic calculations. Vysniauskas and Bishnoi then discuss the kinetics of gas hydrate formation, on which very little work has so far been done. They describe a recent experiment and kinetic modelling for the formation of the methane hydrate. The final paper on physical properties, by Pandit and King, describes an experiment on the measurement of elastic wave velocities in a propane hydrate by the pulse transmission method. They also describe similar measurements on ice Ih but fail to compare these results with literature values, which is a serious omission.

In the geological sciences part of this book Kvenvolden reviews evidence for the presence of hydrates (mainly methane) in marine sediments under the expected pressure-temperature conditions. He also gives arguments for ascribing such deposits to microbiological activity, taking geological time scales into account. Dillon and Paull then review work on seismic reflection profiles which indicate the probable presence of a layer of gas hydrate, several hundred meters thick, lying just below and parallel to the sea floor in parts of the continental crust. The bottom surface of the hydrate layer appears to arise from hydrate dissociation on rising temperature along the geothermal gradient, with a methane gas phase being present at greater depths. The possible recovery of this gas phase is considered by Holder, Angert and Pereira on the basis of a thermodynamic and heat transport calculation. The basic idea is that extraction of gas will cause a drop in pressure, which in turn will cause some of the hydrate to dissociate to yield gas phase. Their formula for the rate of dissociation contains the thermal conductivity of the hydrate, and in their numerical calculation they use a value for the thermal conductivity which is about that for ice Ih. As pointed out by Davidson earlier in the volume, the actual thermal conductivity of clathrate hydrates is now know to be only about one-sixth of that of ice. It is to be regretted that the various authors could not have exchanged

manuscripts amongst themselves in order to avoid such an inconsistency. The final paper by Franklin refers to permafrost conditions and describes a practical drilling procedure in hydrate deposits whereby some gas can be recovered under safe operating conditions.

This volume attempts to cover a new and interdisciplinary area, and in such a situation a multi-author work is perhaps inevitable. As a result, there is some duplication of material, although this is not excessive. A more serious criticism is that the coverage is uneven in both scope and quality. Some of the papers provide a valuable critical review whereas others only describe a single experiment or process. On the whole, the volume should aid communication between the two main bodies of potentially interested readers, physicists and chemists on the one hand and geochemists and geophysicists on the other. The price is rather high considering the size of the book, but this is perhaps understandable since the total readership is likely to be small in such a new field at the present time.

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