SYMPOSIUM ON REACTIONS AND EQUILIBRIA IN CHEMICAL SYSTEMS UNDER HIGH PRESSURE[1]

INTRODUCTION TO THE SYMPOSIUM

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It is of interest to note that the American Chemical Society has reached its one-hundredth meeting before it has held a session devoted solely to that phase of physical chemistry which is concerned with the effects of high pressure on chemical reactions. From a detached thermodynamic point of view it may seem surprising that studies of the effects of temperature and of composition variations should so far have outrun studies of the effects of pressure variations because the three variables,—pressure, temperature, and composition,—are of coördinate thermodynamic importance in determining the state of a chemical system. From the practical point of view, however, we know that chemistry does not advance systematically but that its progress follows lines along which it is pushed by economic necessity, by externally stimulated curiosity, or by a burning zeal to overcome an opponent in a polemic. Natural fluctuations of temperature produce more profound effects on chemical systems than natural fluctuations of pressure, and we know that the large changes in reacting systems that may be wrought by an inexpensive Bunsen burner can only be matched by means of a very expensive piece of pressure apparatus.

While it would be interesting from an historical and philosophical point of view to follow this theme farther, our business in this Symposium is to take cognizance of the fact that interest in the behavior of chemical systems under pressure changes has increased in the last decade, and to consider some recent advances that have been made. By way of introduction to the papers that follow, I wish to call attention to six general fields in the study of material systems under high pressure that are of interest to chemists.

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[1] This Symposium was held under the auspices of the Division of Physical and Inorganic Chemistry at the One-hundredth Meeting of the American Chemical Society, Detroit, Michigan, September 9–13, 1940.

GENERAL FIELDS IN THE STUDY OF MATERIAL SYSTEMS UNDER HIGH PRESSURE

1. The displacement of equilibria in homogeneous systems by rise of pressure

The displacement of equilibria in homogeneous systems by rise of pressure may result in larger yields of desirable products than can be obtained otherwise, if the reactions are sufficiently slow or the products readily removable. The use of this effect in gas reactions, especially the Haber process, is well known. Little work of this sort has been done with condensed systems which form the main subjects for very high pressure work. We may, however, mention the displacement of the tautomeric equilibrium of γ,δ-isoheptenoic acid to the lactone form (16) and the effect of pressure on ionic equilibria, especially acid–base equilibria in sea water (13). The paper of B. B. Owen and S. R. Brinkley in this Symposium contributes to this aspect of pressure chemistry. Although the thermodynamic principles involved in this part of the subject have been well known for a long time, there is still need for development in their application to practical systems. The papers by L. J. Gillespie and by Manson Benedict and his coworkers deal with this question.

2. The displacement of equilibria in heterogeneous systems

The displacement of equilibria in heterogeneous systems, of which the change of solubility under pressure is a simple example, has been studied to a considerable extent, although it offers possibilities which have not yet been adequately exploited. The use of pressure changes in effecting separations by crystallization, particularly when the interactions of the solvent and the solutes to be separated are markedly different, is an example of this. For instance, the solubility of anhydrous sodium bromide in water increases significantly with a rise of pressure of 1000 bars, whereas the solubility of cesium bromide decreases markedly under the same conditions (17). The principles correlating the effect of pressure on solid–liquid equilibrium in condensed systems with other thermodynamic properties have been developed and applied to specific cases by E. Cohen and his school (14) at moderate pressures, and by L. H. Adams (1, 2) at high pressures.

The use of high pressure to confine volatile components in heterogeneous systems has led to results of great technical, geological, and chemical importance. The papers by H. H. Storch, R. Wiebe, and W. B. Kay deal with interesting technical and physicochemical aspects of this topic. Of special geological interest are the studies of the solubility of water in rocks and minerals at high pressures and temperatures made by R. W. Goranson (19), who has demonstrated that a rock like granite or a mineral such as albite can readily dissolve 10 per cent of its weight of water, and that the melting point of the rock or mineral is lowered several hundred degrees by the dissolved water. L. H. Adams' paper will give a survey of high-temperature and high-pressure investigations of heterogeneous systems.

3. Acceleration or retardation of chemical reactions by pressure

During the last decade quite a number of examples of the effect of pressure on reaction velocities in condensed systems have been studied, especially by workers at the Imperial Chemical Industries Laboratory (16, 27, 33) and at Imperial College, London (26), and I regret that Professor Linstead could not be present to discuss the results of some of these investigations. In condensed systems pressure changes may produce large changes in reaction velocity, including the special case of reactions which do not go at atmospheric pressure, proceeding at finite rates under high pressures. For example, the workers at the Imperial Chemical Industries Laboratory found that the velocity constant of the addition of dimethylaniline to isopropyl iodide is increased some 500-fold by a rise of pressure of 12,500 atmospheres. This result is typical, if somewhat larger than the average, of the effect of pressure on "slow" reactions. They found that the effect of pressure on the rates of "normal" reactions, i.e., those in which the steric factor is close to unity, is much smaller and almost linear, while unimolecular decompositions were somewhat retarded by increase of pressure. The pioneering work of Bridgman and Conant on polymerization under pressure should also be mentioned. The paper by Eyring and Stearn discusses the effect of pressure on reaction velocities from a theoretical standpoint, and the paper by R. B. Dow, "The denaturation of proteins by high pressure," presents new work in a closely related field.

4. New phenomena

By extending greatly our range of observation, advances in high-pressure technique open up the possibilities of encountering new phenomena. New phases of solids existing only at high pressures, such as the five forms of ice, are now familiar from the work of Tammann (31, 32) and of Bridgman (5, 8), and, indeed, the latter's recent experiments (9, 10) up to 50,000 kg. per cm.^{2} show that most solids have at least one polymorphic inversion in this range. Bridgman's experiments on the effect of shearing stress combined with high hydrostatic pressure (6, 7), by which he showed among other things that oxides such as lead dioxide or silver oxide decompose explosively under these conditions, have opened up an extremely important field in the chemistry of solids. Under this heading we may also class the work of Poulter on the penetration of liquids into glass under high pressures (29), and the recent work of Gibson and Loeffler on the effect of hydrostatic pressure on the absorption of light by mixtures of certain organic compounds (18).

5. Knowledge of the behavior of naturally occurring substances under extreme conditions

Even at moderate depths within the earth, high pressures and elevated temperatures prevail, and in the depths of the ocean, pressures of 1000 atmospheres are reached. It is interesting to note that curiosity about geological and oceanographic phenomena, especially about the processes that have given the substance of the earth its present form, has provided the chief stimuli for piezochemical research. The best equation, in my opinion, that we have for representing the volume of a liquid as a function of the pressure was proposed by Tait in 1881, during his work on the observations of the Challenger Expedition. The work of Brander (4) on the effect of pressure on the conductivity of solutions and on acid–base equilibrium was also done under oceanographic auspices, and several articles of direct physicochemical interest are to be found in rather inaccessible journals devoted to marine studies (12). Under this general heading Dr. Berl's paper on "The rôle of carbohydrates in the formation of bituminous coals, asphalts, oils, and natural gas" is classified.

6. *New methods of attacking old problems*

Theories of matter in the gaseous state are largely based on pressure–volume–temperature observations, and studies of the effect of temperature and composition changes on condensed systems have provided much of the material employed in the theories of physical chemistry, especially those dealing with liquids and solutions. In principle, however, the results of temperature changes at constant pressure are less easy to interpret than the results of temperature changes at constant volume or volume changes at constant temperature, and, indeed, recent systematic investigations of the behavior of liquids and solutions under simultaneous changes of pressure and temperature have thrown valuable light on some outstanding problems in the physical chemistry of aqueous solutions. This aspect of pressure chemistry is still in its infancy.

INTERRELATIONS

In order to illustrate the place of the various types of high-pressure investigations in the general scheme of physical chemistry, and to answer the still frequent question "What do P–V–T measurements have to do with chemistry?", a chart showing the interrelations among the various activities has been prepared (see chart I).

APPARATUS

The development of the experimental technique of making accurate observations under high pressures is an important branch of this subject, and all investigators in this field acknowledge a deep indebtedness to Professor Bridgman, who has been in the forefront of all these developments for more than thirty years, and whose early experiments really made accurate high-pressure work possible. He has recently (11) extended these measurements up to 50,000 kg. per cm.^{2} It is impossible to list all contributions to these experimental methods (25), but mention may be made of the apparatus for observing systems under pressures up to 4000 atmospheres at 1500°C., developed by Adams (30), and the simple but effective means of installing transparent windows in pressure bombs devised by Poulter (28).

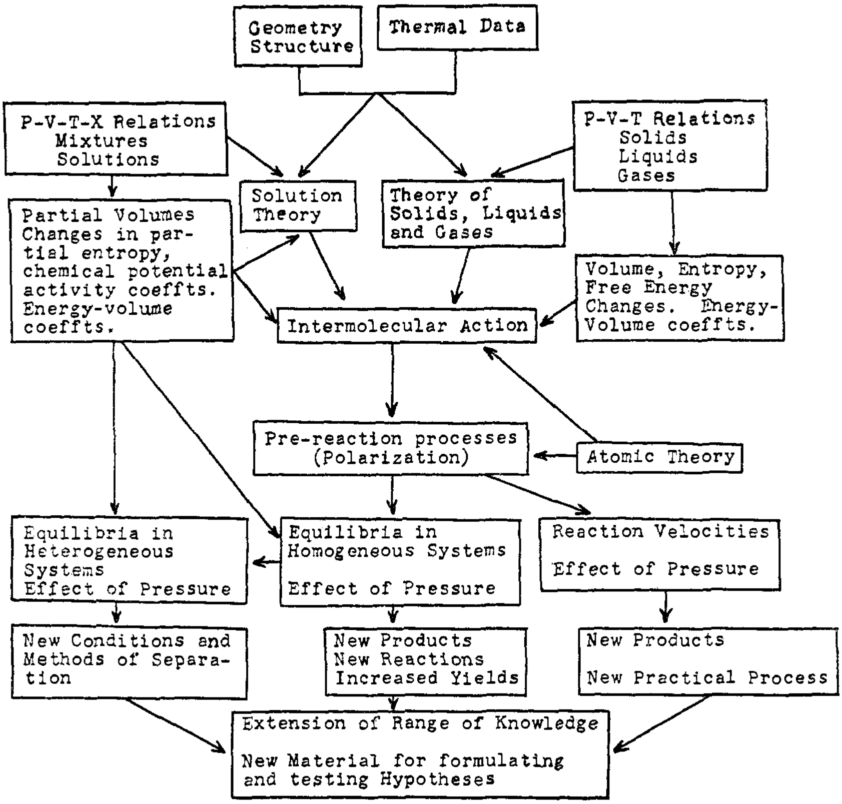

CHART 1

Recently Griggs (24), working in Bridgman's laboratory, and Goranson (22), at the Geophysical Laboratory, established on experimental and theoretical grounds the principle that the strengths of materials increase rapidly when the hydrostatic pressure around them increases. This has led to the construction by Bridgman (12) and by Goranson and Johnson (23) of apparatus in which pressures exceeding 200,000 atmospheres have been generated. Dr. Goranson develops this subject with special reference to the design of high-pressure apparatus in his paper before the Symposium.

For a variety of reasons the following papers delivered at the Symposium are not published here (the figures in parentheses give references to articles in which the authors have discussed closely related subjects): "The denaturation of proteins by high pressure," by R. B. Dow (15); "The formation of natural gas, asphalts, oils, and coals in nature and in the laboratory and the importance of high pressure," by E. Berl; "Non-uniform pressure phenomena and their relation to the design of high-pressure apparatus," by R. W. Goranson (20, 21); "An empirical equation for thermodynamic properties of mixtures of light hydrocarbons under pressure," by Manson Benedict, George B. Webb, and Louis C. Rubin (3).

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