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The Beginnings of Experimental Petrology

Van't Hoff's study of marine evaporites was the first systematic effort in this field.

Hans P. Eugster

Between 1896 and 1908, Jacobus Henricus Van't Hoff, one of the founders of the new science of physical chemistry, devoted his entire professional efforts to the solution of a single problem: the mineral equilibria underlying the Permian marine salt deposits of Germany (Stassfurt). Together with some 30 collaborators and students, he published 52 papers on the subject, erecting an edifice that remains little changed to the present day. For the first time, chemical experiments were applied in a systematic and methodical manner to the solution of a geological problem.

There is a mystery here. Why did this famous chemist, a founder of and acknowledged leader in theoretical chemistry, choose for his later years a "messy" environmental problem that was to involve him in a great amount of tedious experimentation and that produced no new theory? A satisfactory answer to this question may never be found, but, in looking into how this particular research topic was chosen, I have learned some surprising things about the study, about Van't Hoff, and about the intellectual climate of the period.

Background

In order to understand the reasons for Van't Hoff's choice of marine evaporites as a principal research topic, we must briefly review his background and previous contributions. Van't Hoff was born in 1852 in Rotterdam, the son of a doctor (*1*). He showed an early interest in the natural sciences and particularly in chemical experimentation. After some initial training as a practicing chemist, he decided to study mathematics at the University of Leiden and he eventually obtained a Ph.D. in physics and mathematics from the University of Utrecht (1874). In the meantime, his love for chemistry reasserted itself and he worked with Kekulé in Bonn and with Wurtz in Paris, both centers of the new science of stereochemistry. A major publication, entitled "Chemistry in Space," established his reputation (*2*). Subsequently he taught chemistry at the University of Utrecht and wrote a book on organic chemistry. He had become interested in organic reactions and particularly their temporal progress, and this led him to study chemical kinetics. In 1877 he was called to the University of Amsterdam as a lecturer, and in 1878 was appointed professor of chemistry, mineralogy, and geology. Within a short time he had acquired a large circle of students and collaborators. Their work was concerned principally with chemical kinetics, and a summary entitled *Studies in Chemical Dynamics* was published in 1884 (*3*). The book immediately became famous. In addition to defining the concept of reaction rate and measuring the effect of temperature on reaction rate, Van't Hoff was concerned with chemical equilibrium and enunciated, for the first time, his "law of the incompatibility of condensed systems." This law is a special case of the phase rule, which had been published 6 years earlier by Gibbs, but with which Van't Hoff was unfamiliar. Van't Hoff contemplated different types of equilibria and divided them into physical (melting, vaporization) and chemical (chemical reactions, phase transformations) equilibria. Among the latter he concerned himself with cases of homogeneous, heterogeneous, and condensed (no vapor phase present) equilibria, and he was struck by the difference between equilibria such as

$$2\,H_2 + O_2 \rightleftharpoons 2\,H_2O$$

and

$$\text{rhombic sulfur} \rightleftharpoons \text{monoclinic sulfur}$$

The first he called a mobile equilibrium, whose position shifts with temperature, but he noted that the latter exhibits a transition point, at which the two phases can coexist, but above or below which the two phases are incompatible. He was led to this conclusion on the basis of a consideration of published observations on ammonium nitrate, and he stated very clearly that, if monoclinic and rhombic sulfur were brought together in a vacuum, a vapor equilibrium would be established until the maximum sulfur pressure was attained. If that pressure was higher than the equilibrium vapor pressure of one of the solids, the vapor would condense on that solid and the solid with the higher vapor pressure would volatilize until it was exhausted (*3*, p. 143):

> The point of transition is the temperature at which the vapors of the two bodies have maximum and equal tensions.

The author is professor of geochemistry at Johns Hopkins University, Baltimore, Maryland. This article is an abbreviated version of a lecture that was given at the Pettijohn Sedimentology Conference, 22 and 23 January 1971, Baltimore, Maryland.

Double Salts and Salt Equilibria

During the next 2 years, Van't Hoff's attention was focused in another direction. The last section in his *Studies in Chemical Dynamics* dealt with problems of chemical affinity. In order to measure affinity, he used semipermeable membranes and he derived the Van't Hoff equation for gases and dilute solutions:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant, T is the absolute temperature, H is enthalpy, and R is the gas constant. This work was published in Sweden in 1885 (*4*) and was immediately hailed as a major contribution. Even the discrepancies remaining in the theory were extremely important, as they led Arrhenius to formulate his theory of electrolytic dissociation (*5*). International fame was now assured for Van't Hoff, and in 1887 he was called to a chair at the University of Leipzig, where Wilhelm Ostwald, the leading German physical chemist, taught. He declined the offer, as the University of Amsterdam had promised him a new institute. Nevertheless, he became cofounder and coeditor with Ostwald of the new periodical *Zeitschrift für Physikalische Chemie*, in which much of his subsequent work was published.

Meanwhile, Van't Hoff continued to concern himself with chemical equilibria. He extended his concept of transition points and phase incompatibility to hydrated salts, such as

$$\underset{\text{mirabilite}}{Na_2SO_4 \cdot 10\,H_2O} \rightleftharpoons \underset{\text{thenardite}}{Na_2SO_4 + 10\,H_2O}$$

again comparing this "chemical" transformation to "physical" melting. The next step was obvious. What about more complex salts, such as double salts? Do they also have transition points? He asked one of his students, Van Deventer, to check a double salt, and the choice of a particular salt was crucial: $Na_2Mg(SO_4)_2 \cdot 4H_2O$, known as astrakanite or bloedite from the Stassfurt deposits. The results, fully supporting his "incompatibility law" were published in the first issue of *Zeitschrift für Physikalische Chemie* (*6*). This paper is important as a model for much of the subsequent work on salt systems. It contains data for the reaction

$$\underset{\text{mirabilite}}{Na_2SO_4 \cdot 10H_2O} + \underset{\text{epsomite}}{MgSO_4 \cdot 7H_2O} \rightleftharpoons \underset{\text{bloedite}}{Na_2Mg(SO_4)_2 \cdot 4H_2O} + 13\,H_2O$$

Using the volume change of the reaction as an indicator, Van't Hoff and Van Deventer found that the transition temperature was located at 21.5°C. Simple dilatometers, topped with oil to prevent evaporation, were used, and the observations were found to be most consistent when a mixture of reactants and products was used as the starting material. Van't Hoff and Van Deventer also were interested in the relationship between solubility curves and the transition temperature. They found that (*6*, p. 178):

> . . . the solution of the stable system is more dilute, while that of the metastable system exhibits the properties of a supersaturated solution and indeed crystallizes by contact with the components of the stable system. . . . at the transition temperature itself the solubility of the two systems is equal, in other words, that temperature corresponds to the intersection of the two solubility curves.

Accurate solubility determinations are difficult to make, and hence Van't Hoff and Van Deventer decided to (*6*, p. 180):

> . . . determine the intersection of the vapor pressure curves of the saturated solutions instead of that of the solubility curves; since the vapor pressure depends only on the concentration, the two intersections must be identical.

In this manner, the transition point was again found to lie at 21.5°C.

Van't Hoff and Van Deventer went one step further and determined the effect of additional salts on the transition temperature. In the presence of halite the transition temperature is located at 5°C, and they concluded that this result (*6*, pp. 182–183)

> . . . extends the analogy between melting point and transition temperature; indeed we have here a situation which is completely analogous to the depression of the melting point of ice in the presence of salts. . . .

Origin of Phase Theory

The work of Van't Hoff and Van Deventer attracted the attention of another Dutch chemist, Bakhuis Roozeboom, who was later to become Van't Hoff's successor as professor of chemistry at the University of Amsterdam in 1896. At the time, Roozeboom was working in Ostwald's laboratory in Leipzig, and he had just published an extensive summary of his work (*7*) on chemical equilibria, in which he classified different types of equilibria according to Gibbs's phase rule. Van der Waals, then professor of physics at the University of Amsterdam, had made him aware of Gibbs's contributions in 1885, and Roozeboom first used the phase rule in 1887 (*8*) to explain heterogeneous equilibria. Roozeboom subjected the data of Van't Hoff and Van Deventer to a similar analysis and found the first quintuple point: mirabilite + epsomite + bloedite + solution + gas, located at about 22°C (*9*). Roozeboom had a clear grasp of the meaning of the phase rule and its implications, and he was primarily responsible for its introduction into European science and into chemistry (*7*, pp. 473–474):

> The complete heterogeneous equilibrium is expressed by a curve (p, t) [p, pressure; t, temperature], independent of the quantity of each phase present. If one follows such a curve in either direction, one arrives at a point where a new phase occurs and where a further change of temperature or pressure is not possible, unless one of the coexisting phases disappears. As soon as this happens, a new system of $n + 1$ phases remains, for which a curve originates in the end point of the former curve. Hence at the intersection itself $n + 2$ phases coexist. Since one can remove any phase one chooses without destroying the equilibrium, this point must be the beginning or end of all $n + 1$ curves which represent the equilibrium of each system of $n + 1$ phases contained within $n + 2$ phases.

Roozeboom's efforts culminated in his famous treatise on heterogeneous equilibria (*10*).

A teacher of Roozeboom's, J. M. Van Bemmelen, professor of chemistry at the University of Leiden, provided the next important impetus. Van Bemmelen had long been interested in weathering processes, particularly the weathering of volcanic rocks to form clay minerals and laterites. In an address as rector of the University in 1889, he pointed out that studies such as those of Van't Hoff and Van Deventer could be used to elucidate the origin of the Stassfurt evaporites, a remark Van't Hoff himself recalled (*11*, p. 2).

Van't Hoff and Van Deventer's work on bloedite (*6*) was followed by further studies on double salts. In 1888, W. Meyerhoffer became a student of Van't Hoff's after having worked with Ostwald in Leipzig. He investigated the copper-potassium chloride salts (*12*, *13*) and found two quintuple points. Meyerhoffer settled in Vienna (1891–1896). He later was to exert a decisive influence on Van't Hoff's choice of marine evaporites as a research topic and was to become his first and most permanent collaborator. During his years in Vienna he wrote the first book in any language on the phase rule and an important paper on reciprocal salt pairs (*14, 15*). He seems to have originated the term "Phasenregel," translated with a slight, but significant shift in meaning as "phase rule," and he gives clear and concrete definitions of the terms "phase" and "component" (*13*, pp. 122–123):

> The "phase rule" and its application to the preceding solubility determinations: According to T. Willard Gibbs, a heterogeneous equilibrium is completely defined when *n* substances, which come together in an equilibrium, appear in $(n + 1)$ phases. With respect to the term "phase," a concrete definition has been missing up to now. One could describe a phase as that part of a mixture of any bodies in any state of aggregation which can be isolated by mechanical means. . . . The equilibrium is completely defined when the compositions of the phases are independent of the amount of the individual constituents.
>
> Components ["Stoffe" in Meyerhoffer, "bodies" in Gibbs] are all those substances which come together in varying amounts and whose combinations or mutual transformations suffice to form all those compounds which play a role in the equilibrium.

These definitions are explicit and are essentially those used today. They preceded the full-scale introduction of the work of Gibbs by Riecke (*16*) in the next volume of the same journal.

The power of the geometric methods developed by Gibbs was pointed out 3 years later by Van Rijn van Alkemade (*17*). With this publication, the adoption of the phase rule and of phase theory on the continent was essentially completed.

The close connection between the work on double salts and the evolution of phase theory is further emphasized by the contribution of another student of Van Bemmelen's in Leiden, E. A. H. Schreinemakers (*18*), who worked on the compound $K_2PbI_4 \cdot 2\frac{1}{2}H_2O$. Schreinemakers applied Roozeboom's analysis of bloedite in his work. He was later to become best known for his work on ternary systems, completing the treatise left unfinished by Roozeboom (*19*).

Marine Evaporites

Meanwhile, Van't Hoff and his students continued their work on double salts. Van der Heide (*20*) chose the system K_2SO_4-$MgSO_4$-H_2O. Earlier, Precht and Wittgen (*21*), working at Stassfurt, had published solubility curves which exhibited unexplained kinks and inflections. Van der Heide showed that these kinks were due to the presence of the compound $K_2Mg(SO_4)_2 \cdot 4H_2O$, subsequently found at Stassfurt as the mineral leonite (*22*). The other double salt of this system, $K_2Mg(SO_4)_2 \cdot 6H_2O$, had long been known as the mineral schoenite.

Van't Hoff asked R. Löwenherz to continue the work by adding chlorides to the system K_2SO_4-$MgSO_4$-H_2O. Löwenherz (*23*) devised a projection for reciprocal salt systems, the Löwenherz projection, which was used exclusively by Van't Hoff for the subsequent work on the Stassfurt deposits. In his study, based primarily on solubility determinations, Löwenherz produced the first important diagram directly applicable to the Stassfurt deposits (Fig. 1), containing information on the minerals epsomite, hexahydrite, bischofite, carnallite, sylvite, and schoenite.

The next significant contribution was made by Meyerhoffer, who was now working in Vienna (*15*). Although concerned principally with compounds in the system Na-NH_4-NO_3-H_2O, the thrust of the investigation was now clearly spelled out (*15*, p. 854):

> The salt deposits of Stassfurt, Wieliczka, and elsewhere, as far as they are of marine origin, cannot be interpreted in detail until the solubility and equilibrium relations of the salts of the sea have been studied systematically.

Meyerhoffer went on to say that, although isothermal evaporation experiments should be used as a guide to interpretation, actual deposition may not be strictly isothermal. He also pointed out the possibility of solid solution in some compounds, the possibility of the modification of brine composition through the influx of other brines, and the possible effects of pressure.

The Move to Berlin and the Choice of a Research Topic

Van't Hoff's new Amsterdam institute was completed in 1891. His circle of students and collaborators continued to grow and with it his administrative duties, much to his chagrin. His restlessness became known in Hol-

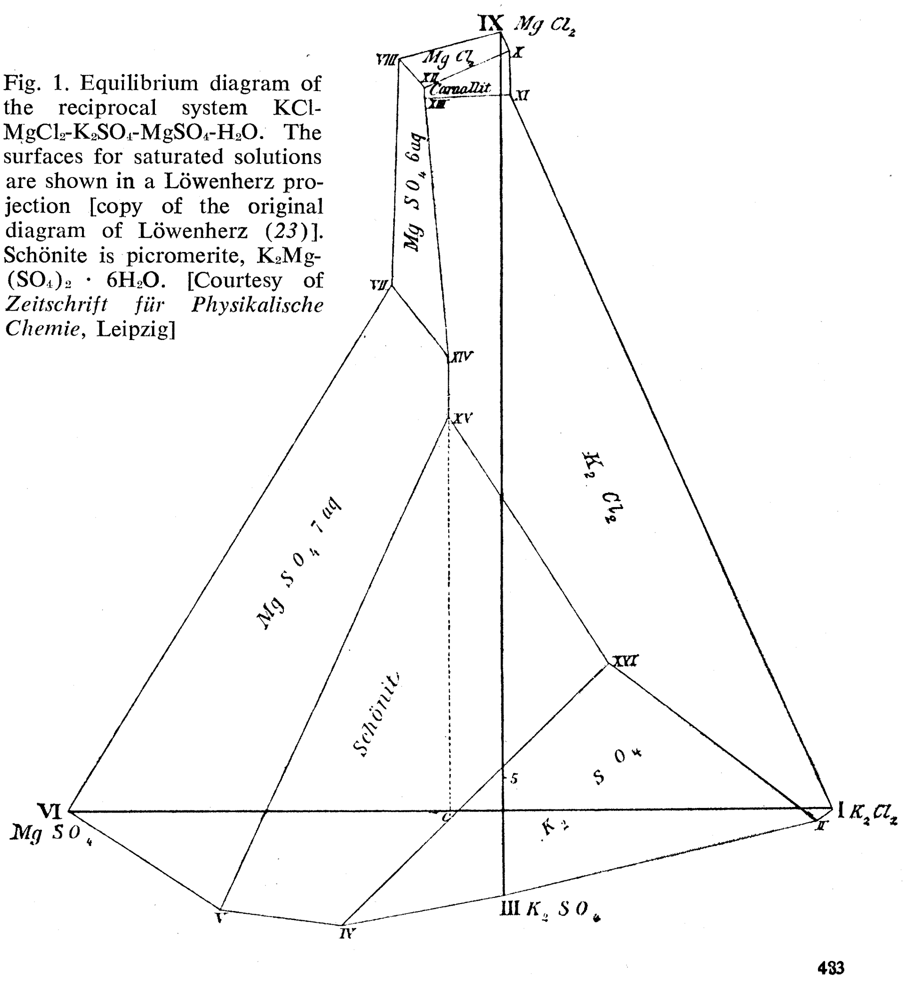

Fig. 1. Equilibrium diagram of the reciprocal system KCl-$MgCl_2$-K_2SO_4-$MgSO_4$-H_2O. The surfaces for saturated solutions are shown in a Löwenherz projection [copy of the original diagram of Löwenherz (*23*)]. Schönite is picromerite, $K_2Mg(SO_4)_2 \cdot 6H_2O$. [Courtesy of *Zeitschrift für Physikalische Chemie*, Leipzig]

land and abroad and resulted in a call to the chair of physics at the University of Berlin (1894) as successor to Helmholtz. Planck acted as negotiator. Van't Hoff was flattered but declined. He let it be known that a position free of administrative and teaching duties would suit him better. To underscore his dissatisfaction with his lack of freedom, he suddenly resigned his chair at the University of Amsterdam in 1895 and began a period of rest with his family in the Black Forest of southern Germany. As fall approached, he walked with his wife and four children across the Swiss Alps toward Lugano and the sun, using the railroad only for short stretches (*24*).

Meanwhile his friends in Berlin considered an appointment to the Berlin Academy of Sciences, which would make Van't Hoff the first foreign member in over 100 years. Negotiations continued, and in the winter of 1895–1896 they succeeded in offering him such an appointment, coupled with an honorary professorship at Berlin University. Van't Hoff accepted and moved to Berlin in the spring of 1896. It was not possible to suddenly put a large research institute at his disposal, and the necessity to begin with modest means was crucial in the choice of research topics. Van't Hoff himself recalls this (*11*, p. 1):

> When I exchanged my position in Amsterdam with that at the Berlin Academy of Sciences and the Berlin University, I gained almost unlimited time for myself and had to decide on a work plan. I wanted to continue some of my investigations of the Amsterdam period, that is, oxidation mechanisms, optical activity, and the formation of double salts.
>
> To continue with oxidation mechanisms, delicate measurements were necessary to evaluate the electrical effects, for which my Berlin laboratory was not suitable. The study of optically active substances was essentially completed, as we had pursued this phenomenon in many directions. However, the formation of double salts and its application to natural salt deposits could lead to an extensive investigation. . . .

Meyerhoffer's direct influence on the choice was acknowledged (*11*). In fact, Meyerhoffer's persuasion was offered in person. Shortly after Van't Hoff arrived in Berlin, Meyerhoffer paid him a visit and accepted an offer to join him as collaborator. Meyerhoffer rented a house for himself in the Berlin suburb of Wilmersdorf (Uhlandstrasse 39), and this is where the laboratory was first established. A chemical analyst was hired, and the investigations began with an astonishing élan. Conceived with exemplary clarity, the study is still a model of how to proceed in such a case. Van't Hoff recalls the basic choice of a laboratory topic as follows (*11*, pp. 2–3):

> As the main thrust of the work was directed toward natural evaporite deposits, a certain restriction of the task was essential. We adopted the view that, although we were confronted with a concrete problem of nature, it was desirable to maintain as broad an approach as possible. . . . The restriction was achieved by considering only the main constituents of the salt deposits. . . . In addition to sodium chloride, they were principally hydrated chlorides and sulfates of magnesium and potassium; they represent the main mass of the salt layers, the lower rock salt, and the overlying saline formations. Next we added calcium compounds, which are important in separating the lower rock salt into anhydrite and polyhalite regions. In terms of quantity, bromine would be next, but it was eliminated as being less significant for the general problem. However, borates were considered, because they represent important occurrences as well as special problems. This gave our task a certain completeness, delineated as it was by the next corresponding problem of nature: the formation of silicates.

The credo of the modern experimental petrologist is to be found in the same introduction (*11*, p. 3):

> The answer to these questions are pursued as far as their solutions are contained within the tasks formulated in the broadest sense. However, in the specific execution, contact is maintained with the natural environment in order to avoid unnecessary detailed work.

Van't Hoff practiced this conviction by keeping in close contact with the natural deposits, using W. Kubierschky and H. Precht of the Stassfurt Mining Company as geologic guides.

Van't Hoff's Contribution to Marine Evaporites

The work commenced in 1896 and was nearly completed in the spring of 1908. The approach, in general and in detail, remained consistent throughout and essentially followed the procedures established in the first paper on double salts (*6*).

Van't Hoff and Meyerhoffer first turned their attention to the systems $MgCl_2$-H_2O, KCl-$MgCl_2$-H_2O, and $CaCl_2$-$MgCl_2$-H_2O and the minerals bischofite, carnallite, and tachhydrite. Solution compositions and phase transitions were determined over a wide temperature range (from below 0° to 200°C), the former by chemical analysis and the latter by simple heating and cooling curves. The tachhydrite paper (contribution IV) contains the first direct geologic application (*25*). Below 21.95°C tachhydrite was found to decompose to bischofite and calcium chloride:

$$\underset{\text{tachhydrite}}{2MgCl_2 \cdot CaCl_2 \cdot 12H_2O} \rightleftharpoons \underset{\text{bischofite}}{2MgCl_2 \cdot 6H_2O} + CaCl_2 \cdot 6H_2O + 6\,H_2O$$

Tachhydrite is found within anhydrite in the carnallite zone. Van't Hoff and Meyerhoffer (contribution IV) remark (*25*, p. 40):

> With respect to the formation of natural salt deposits, it is especially important to realize that the temperature 21.95 represents a lower limit, and that the occurrence of tachhydrite indicates a temperature above this limit.

After this preliminary work, Van't Hoff addressed himself to the important reciprocal system KCl-$MgCl_2$-K_2SO_4-$MgSO_4$-H_2O previously studied by Löwenherz in 1894 (*23*). In 1897 Löwenherz (*26*) had pointed out some large discrepancies in his own determinations. Van't Hoff carefully repeated the experiments and found that they were due to the rimming of sylvite by carnallite and hence to the lack of equilibrium between sylvite and the solution (*25*, p. 55). Water vapor pressures of the saturated solutions were reported next in contribution VI, which also contains the remarks (*25*, p. 57):

> Finally, the vapor pressures . . . may be connected with the atmospheric humidity existing during the formation of the evaporites. . . .

The next five papers (contributions VII–XI) were concerned with the Löwenherz system saturated with respect to NaCl at 25°C. They dealt with the minerals halite, sylvite, carnallite, bischofite, epsomite, picromerite (schoenite), aphthitalite, thenardite, and bloedite and led up to a review of the evaporation of seawater at 25°C. The sequence of precipitates found was halite → epsomite → hexahydrite → sylvite → carnallite → bischofite. The absence of kieserite, loeweite, kainite, and langbeinite was blamed on the lack of temperature variation. These conclusions were to be modified frequently during the progress of the work.

The first check was made in terms of the vapor pressures of the saturated solutions at 25°C (contribution XIX).

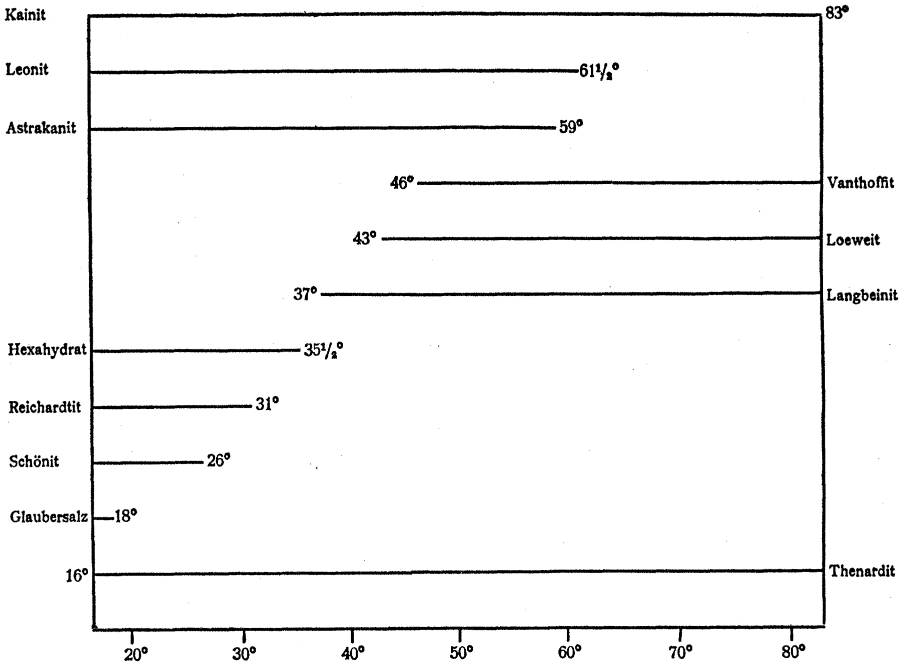

Fig. 2. Temperature grid (in degrees Celsius) for common marine evaporite minerals [copy of original diagram of Van't Hoff (*29*)]. For the current mineral names, see (*30*). [Courtesy of Vieweg und Sohn, Braunschweig]

This result pointed to the stable existence of kainite at 25°C (contribution XXI) and the replacement of sylvite by kainite in the evaporation sequence.

Meanwhile, Van't Hoff decided to look at the calcium-bearing phases as well, such as gypsum (contribution XVIII), anhydrite (contribution XXIV), glauberite (contributions XV and XLII), syngenite (contribution XX), and polyhalite. The presence of these relatively insoluble compounds did not affect the compositions of the saturated solutions, but it was important to determine which of the phases was stable for a specific set of conditions. The glauberite field was not intersected by evaporating seawater at 25°C, but that of gypsum was. The phase relations between gypsum, bassanite, and anhydrite occupied Van't Hoff and his collaborators for a number of years (*27*). Hardie (*28*) has reviewed their results for the gypsum-anhydrite transition and compared them with subsequent determinations (*28*, pp. 187–188). It is indicative of Van't Hoff's brilliance as an experimenter that his values for the transition temperature are closest to the presently accepted set of values.

Next Van't Hoff returned his attention to the more soluble salts, but to those phases that were not found at 25°C. Langbeinite was encountered at 37°C (contribution XXV), loeweite at 43°C (contribution XXVI), vanthoffite at 46°C (contribution XXXI), and at 83°C kainite decomposed to a mixture of kieserite plus sylvite (contribution XXXII). In this manner, Van't Hoff constructed a table of metamorphic changes for evaporite minerals [contribution XXXII in (*25*, p. 327) and (*29*)], based on a very accurate temperature calibration (see Fig. 2) (*30*). Apparently, Van't Hoff decided that 83°C was a natural upper limit for his investigations, and he next determined vapor pressures and compositions of the saturated solutions at that temperature (contributions XXXIV and XXXV). With this framework erected, it was possible to discuss mineral assemblages as they change from 25°C to 83°C (contribution XXXVI). Van't Hoff distinguished three intervals: 25° to 37°C, 37° to 55°C, and 55° to 83°C. The first interval is characterized by the disappearance of picromerite, epsomite, and hexahydrite; the second by the appearance of langbeinite, loeweite, and vanthoffite; and the third by the disappearance of bloedite, leonite, and kainite. This temperature grid of Fig. 2 is based on the following dehydration reactions:

$$\underset{\text{mirabilite}}{Na_2SO_4 \cdot 10H_2O} \rightleftharpoons \underset{\text{thenardite}}{Na_2SO_4} + 10\,H_2O$$

at 18°C in the presence of halite; at 16°C in the presence of halite, bloedite, and aphthitalite.

$$\underset{\text{picromerite}}{K_2Mg(SO_4)_2 \cdot 6H_2O} \rightleftharpoons \underset{\text{leonite}}{K_2Mg(SO_4)_2 \cdot 4H_2O} + 2\,H_2O$$

at 26°C in the presence of halite, bloedite, and aphthitalite.

$$\underset{\text{epsomite}}{MgSO_4 \cdot 7H_2O} \rightleftharpoons \underset{\text{hexahydrite}}{MgSO_4 \cdot 6H_2O} + H_2O$$

at 31°C in the presence of halite and bloedite.

$$\underset{\text{hexahydrite}}{MgSO_4 \cdot 6H_2O} \rightleftharpoons \underset{\text{kieserite}}{MgSO_4 \cdot H_2O} + 5\,H_2O$$

at 35.5°C in the presence of halite and bloedite.

$$\underset{\text{leonite}}{K_2Mg(SO_4)_2 \cdot 4H_2O} + \underset{\text{hexahydrite}}{MgSO_4 \cdot 6H_2O} \rightleftharpoons \underset{\text{langbeinite}}{K_2Mg_2(SO_4)_3} + 10\,H_2O$$

at 37°C in the presence of halite and kainite.

$$2\,\underset{\text{bloedite}}{Na_2Mg(SO_4)_2 \cdot 4H_2O} \rightleftharpoons \underset{\text{loeweite }(31)}{Na_4Mg(SO_4)_4 \cdot 5H_2O} + 3\,H_2O$$

at 43°C in the presence of halite, kieserite, and leonite; at 59°C in the presence of halite and thenardite.

$$\underset{\text{bloedite}}{Na_2Mg(SO_4)_2 \cdot 4H_2O} + 2\,\underset{\text{thenardite}}{Na_2SO_4} \rightleftharpoons \underset{\text{vanthoffite}}{Na_6Mg(SO_4)_4} + 4\,H_2O$$

at 46°C in the presence of halite and aphthitalite.

$$30\,\underset{\text{leonite}}{K_2Mg(SO_4)_2 \cdot 4H_2O} + 3\,\underset{\text{loeweite}}{Na_4Mg_2(SO_4)_4 \cdot 5H_2O} \rightleftharpoons 18\,\underset{\text{langbeinite}}{K_2Mg_2(SO_4)_3} + 8\,\underset{\text{aphthitalite}}{NaK_3(SO_4)_2} + 2\,\underset{\text{thenardite}}{Na_2SO_4} + 135\,H_2O$$

at 61.5°C in the presence of halite.

$$\underset{\text{kainite}}{KMgClSO_4 \cdot 3H_2O} \rightleftharpoons \underset{\text{kieserite}}{MgSO_4 \cdot H_2O} + \underset{\text{sylvite}}{KCl} + 2\,H_2O$$

at 83°C in the presence of halite.

The solution compositions were chosen so as to give the highest temperatures at which mirabilite, picromerite, epsomite, hexahydrite, bloedite, leonite, and kainite and the lowest temperatures at which langbeinite, loeweite, and vanthoffite can be expected in a marine evaporite. The temperatures reported were based either on vapor pressure measurements or on volume changes to determine the direction of reaction. Solids were identified by chemical analysis and by microscopic observations.

Similar grids have been erected during the last 20 years for metamorphic rocks for the temperature interval from 200° to 800°C based mainly on silicate reactions. The comparison is startling: Van't Hoff's grid is much more closely spaced. This is in part due to the fact that among salt mineral assemblages simple dehydration reactions are much more common and solid solution is much less extensive than among silicates.

The crucial test for experimentalists, a comparison of all stable experimental assemblages with naturally occurring assemblages, was not possible until a complete list of natural assemblages became available. When the latter was published (*32*), Van't Hoff (*29*) immediately drew up a comparison. He scored very well because of the 230 or so possible assemblages only 14 were unexpected, and most of these could be accounted for, whereas 66 of the expected 103 had actually been described. This result must be judged a major triumph for Van't Hoff's approach and for his care and tenacity. It certainly has not been surpassed since. Van't Hoff extended his studies to include some equilibria below 25°C (contribution XXXIX) and then embarked upon an investigation of borate minerals, which occupied him during most of the remaining years of his life.

Van't Hoff summarized his contributions in two small volumes (*11, 29*), the first dealing with the more soluble salts and the second with the calcium-bearing phases and the borate minerals. The first volume (*11*) contains a section on secondary changes, in which the effects of adding water are considered, and a section on temperature determinations based on mineral assemblages. The second volume (*29*) extends these applications and also lists the remaining tasks.

The correspondence between experiments and nature was characterized as follows (*29*, p. 42):

> These results correlate with natural relationships qualitatively, but not at all quantitatively, which indicates that salt deposits are not formed by simple evaporation of seawater.

Van't Hoff continues (*29*, p. 77):

> The discrepancy is twofold, because the original amount of anhydrite in nature is much larger than the amount of overlying halite and because the latter contains considerably more anhydrite than it should. If one assumes that during evaporation seawater is added, the relationship between the total amount of anhydrite and halite is not changed. . . . The thickness of the lower gypsum and anhydrite beds as compared with that of the halite beds requires an additional assumption: either that not only was seawater added, but brine was lost, or that gypsum-bearing river water was added, as Winther has suggested.

In the summary, Van't Hoff states (*29*, p. 75):

> In concluding these investigations I am fully aware of having made but a step, and at the outset I had not intended to do more, as we were dealing essentially with a chemical point of view. I restricted myself deliberately, but always kept in touch with natural occurrences, either through personal contacts, for which I am indebted to Misters Kubierschky and Precht, or through repeated visits to the mines. . . . However, in order to achieve the desirable integration with the natural occurrences, an extensive study is still needed to bridge chemistry and geology. A significant contribution in this direction could be made by the association for the study of natural salt deposits, which was formed at the suggestion of Mr. Rinne.

The last remark points directly to the fate of Van't Hoff's investigations in Germany. The "Association for the Study of Natural Salt Deposits" was formed in 1906 with the express aim of continuing the work and broadening its base. Van't Hoff himself considered his task nearly completed and was glad that its continuation was assured. He included an account of the history of the association and its first two annual reports in his last paper (*25*, contribution LII). The completion was timely, because Meyerhoffer, his chief collaborator, had died in 1906 and Van't Hoff himself was ordered in the spring of 1908 to cease all experimental work for medical reasons. There was still time to finish the summary (*29*) and a move to the suburbs where he hoped to continue his work on fermentation. But illness hampered his progress and he died on 1 March 1911.

Absence of Theory in the Marine Evaporite Study

In contemplating Van't Hoff's contribution as a whole, one must be impressed by the resourcefulness in experimental techniques, by the almost dogged persistence with which the originally conceived project was pursued, and by the virtual absence of new theory. It is remarkable, for instance, that, although Van't Hoff was familiar with the phase rule and had even lectured on it (*33*), he did not use it in a single instance throughout his study of salt deposits. His attitude is best summarized in this quotation (*33*, pp. 4252–4253):

> It is a pity that gradually a certain exaggeration has developed with respect to the consequences of the phase rule, regardless of the importance of its content. . . . The large significance of the phase rule lies not so much in its value as a guide during the investigation, but rather as a pedagogical tool for the treatment and classification of chemical equilibria.

This extremely cautious stand is perhaps understandable, if we remember that in his "law of the incompatibility of condensed systems" Van't Hoff had been concerned with phase-rule problems at a time when he was still ignorant of the phase rule. Also, in his work on optically active substances he dealt with cases that are particularly difficult to handle with the standard phase rule application. It is a pity that he did not trust Gibbs's thermodynamics more and that he did not use the geometric methods based on Gibbs's free energy surfaces, which were introduced on the continent by Van Rijn van Alkemade (*17*) in Van't Hoff's own journal. Van't Hoff's influence was so strong that this attitude persisted for over half a century in evaporite studies. As late as 1915, one of his students, A. E. Boeke, in a much admired text on chemical petrology, says (*34*, p. 101):

> However, we should not forget that the representation of the relationships by zeta surfaces is only an image of experience, which has been derived from the thermodynamics of isotropic bodies (gases and liquids) and extended, perhaps not with complete justification, to the crystalline state.

The question of why Van't Hoff, who had made his reputation by introducing theory into the largely empirical field of chemistry, abandoned theoretical work altogether is difficult to answer. Fischer (*24*) mentions that many of Van't Hoff's friends interpreted his Berlin period as a time of rest, and perhaps even of exhaustion. In contrast, Fischer suggests that Van't Hoff felt he had completed the theoretical framework and that it was now necessary for him to return to observation and experiment before further generalizations were possible. I would prefer a slightly different interpretation. The effort was so massive and uncompromising that there could have been little thought of rest for Van't Hoff. It is true, however, that he concerned himself very little with theory, or, for that matter, with any other problem outside the chosen task. This is very unusual behavior for a man with the breadth of interests Van't Hoff had demonstrated earlier. Could it be that he had committed himself to a problem that was very much larger than he had anticipated and that once committed, he felt obliged to complete it? Van't Hoff himself gives some hints in this direction (*35*, pp. 73–74):

> For me the work we began once again was only in part connected with salt deposits, but the increasing fascination and the magnitude of the problems slowly displaced other thoughts. . . . At first, everything went smoothly beyond expectation. . . . But our hopes were not fulfilled and a visit to the Neu-Stassfurt salt mines with Mr. Precht made it clear, that at the moment we had more to learn from geology and mineralogy than vice versa.

Even at the end, he showed little sign of mental exhaustion and lost originality, as he tackled an entirely different and equally taxing new problem, that of fermentation, and he was stopped only by failing health.

Van't Hoff and His Disciples

Van't Hoff's disciples, foremost among them d'Ans, Boeke, Jänecke, and Rinne, continued to work entirely in his spirit. They refined the edifice and continued to keep Germany in the forefront of research on evaporites. A certain narrowing of the outlook was inevitable. This is clearly expressed in the introduction to Jänecke's book on salt deposits (*36*, p. vi):

> While in a book on the origin of coal deposits the geologic parts of their formation must be stressed more than chemical questions, the opposite is true for potash deposits. Here the physical-chemical aspects of precipitation and transformation are much more important for their genesis than geologic considerations. . . . furthermore, with respect to the purely geologic processes there can hardly remain any differences of opinion, ...

In other words, the problem could now be reduced to a purely chemical question and contact with natural deposits was no longer essential. Fortunately, this attitude was not universal, and in the books by Lotze, Borchert, and Braitsch (*37*) the authors preserved a careful balance between laboratory data and geologic arguments. However, even the most recent experimental studies, such as those of Autenrieth, Baar and Kühn, and Braitsch and Herrmann, clearly show their debt to Van't Hoff (*38*). The first radical departure from Van't Hoff's approach was made by another physical chemist, Sillen (*39*), when he applied the phase rule to problems of the composition of seawater.

The impact of Van't Hoff's work on other branches of geology is fairly easy to assess. He did not influence the study of sedimentary rocks in general, which remained descriptive and free of physical chemistry. This attitude remained unchallenged until the paper of Krumbein and Garrels (*40*) appeared. Van't Hoff's true heirs are Day and Allen, Goldschmidt, and Bowen, who studied igneous and metamorphic rocks (*41–43*). As late as 1911, Rinne (*44*) complained that Van't Hoff's monumental contribution remained unappreciated. After reiterating the fact that mineral formations from aqueous solutions and from silicate magmas follow the same laws, a viewpoint arrived at half a century earlier by Scheerer, Sorby, and Bunsen, he said (*44*, p. 183):

> A survey of the petrologic literature shows that this thought of Bunsen . . . has been accepted only very rarely by petrologists. The fate of the physical-chemical studies of the Zechstein salts by Van't Hoff demonstrates this very clearly. In this study . . . petrology possesses the first example of a fundamental, systematic, and experimentally exact study and insight into the conditions of formation of a large rock unit, arrived at through precise physical-chemical reasoning. . . . Nevertheless, this monumental contribution has hardly been noticed by the leading petrologists. . . .

Van't Hoff and Igneous Petrology

As mentioned earlier (*41–43*), Van't Hoff's true heirs in the field of experimental petrology are the men who initiated research on the high-temperature behavior of silicates. A. L. Day, a physicist working at the U.S. Geological Survey, spearheaded this effort in 1900. Day was trained at Yale and the University of Berlin and had spent the three previous years as an assistant at the Physikalisch-Technische Reichsanstalt, Charlottenburg, Berlin (1897–1900). Although he must have known Van't Hoff personally, he seems to have developed his program in igneous petrology independently. He came to it by way of his background in high-temperature gas thermometry acquired in Berlin (*45*) and the geologic problems presented to him by his Survey position. C. D. Walcott was then the director of the U.S. Geological Survey and he was also Secretary of the newly founded Carnegie Institution of Washington (1902), as well as a member of its committee on geophysics. This committee submitted a comprehensive report on the need for a Laboratory of Geophysics in Washington, D.C. (*46*). Walcott had asked Van't Hoff, among others, to comment on the proposal and Van't Hoff answered (*46*, p. 65):

> . . . an investigation in that direction might prove of the highest value, if made in a systematic way and continued for some years.
>
> The special problem, which I mean, deserves attention, is the physical chemistry of high temperatures applied to the chief constituents of the earth's crust, silicates in the first instance. To express myself more clearly, I add that two great problems concerning geophysics may in the present state of our knowledge be solved, via., the evaporation of complex solutions, which have produced systematic deposits, such as salt layers, etc.; and secondly, the cooling down of molten masses, that have produced the volcanic and plutonic formations.
>
> With the first problem, by far the easier one as regards apparatus, etc., I have been occupied for more than six years, and a series of twenty-six publications in the *Annals of the Prussian Academy of Sciences* (1897–1902) shows how far these researches have been carried out.

In March 1903, Walcott requested Van Hise and Becker to assemble further supporting material to justify the establishment of the proposed geophysical laboratory. Van Hise reported (*47*, p. 174):

> Van't Hoff, Ostwald, and others, seeing that there was a great unoccupied field between physics and chemistry, began the occupation of it. The great results reached by these men placed their names very high in the roll of those who have contributed fundamental ideas to science.

And he reiterated his conviction (*47*, p. 174):

> The purpose of a geophysical laboratory is to take possession of the vacant ground between geology and physics and geology and chemistry. So long as geology remained a descriptive science, it had little need of chemistry and physics; but the time has now come when geologists are not satisfied with mere descriptions. They desire to interpret the phenomena they see in reference to their causes—in other words, under the principles of physics and chemistry.

Again using Van't Hoff as the shining example, he said (*47*, pp. 179–180):

> Another class of investigations is the artificial production of minerals and rocks from aqueous solutions. This involves a study of natural solutions, both those of the sea and those in openings of rocks, in order to determine the conditions under which minerals crystallize from such solutions. Already the study of natural solutions with reference to the crystallization of salt and gypsum has been undertaken by Van't Hoff. This great chemist has reached many important results, but he points out that very much remains to be done. . . .

These statements seem to have been sufficient justification for the trustees of the Carnegie Institution. As a first step they made direct grants to Becker and Day of the U.S. Geological Survey. The grants were renewed the next year (1904), and Day reported (*48*, pp. 225–226):

> The investigation of the lime-soda feldspar group which was begun in the Geological Survey has been finished, after nearly three years' work upon it. The investigation has shown that the lime-soda feldspars form a continuous series of mixed crystals capable of stable existence in any proportion of the two component minerals.

The results were published as *Carnegie Institution of Washington Publication No. 31* with an introduction by G. F. Becker and optical studies by J. P. Iddings (*41*). This exquisite contribution to experimental petrology is both a worthy successor to Van't Hoff's work and a counterpart to it in the high-temperature field. Its impact, however, was much more immediate and extensive, probably because it addressed itself to a different audience within geology, one willing and eager for this new language in igneous petrology.

The trustees of the Carnegie Institution also expressed their confidence in Day's work, both by renewing his grant of $17,500 per annum and by appropriating, in December 1905, $150,000 for a geophysical laboratory with Day as its director. Of his last year's work at the U.S. Geological Survey, Day reported (*49*, p. 177):

> With the work of the present year our studies of mineral fusion and solution in the laboratory may be said to have passed beyond the preliminary stage. It has been found thoroughly practicable to study several of the important problems in mineral formation by applying the principles and methods of physics and physical chemistry at the temperature where the formation actually occurs, and to carry out the quantitative determinations with an accuracy entirely comparable with the more conventional physical and chemical research at ordinary temperatures.

and he listed the 12 papers published during the previous year by members of his laboratory, which included Allen, Sheperd, White, and Wright, all subsequently members of the Geophysical Laboratory's original staff. The Geophysical Laboratory was constructed during 1906–1907 and occupied during the last few days of June 1907. With its opening, the future of experimental petrology was assured. Igneous rocks were the primary concern of investigators at the Geophysical Laboratory at first, and in N. L. Bowen the Geophysical Laboratory could boast of the most famous geologic experimentalist. Bowen built directly upon the work of Day and Allen and became, through his mastery of both classical petrology and modern experimental approaches, its most effective proponent.

The founding of the Geophysical Laboratory was, of course, not a direct result of Van't Hoff's efforts on behalf of evaporites, but its indebtedness to his general approach and his success in both physical chemistry and experimental petrology is obvious in the statements of Van Hise and the Geophysics Committee. Day himself does not directly pay tribute to Van't Hoff, but Van't Hoff [in (*35*), p. 76] refers to a thank-you note from Day which he received in 1906 and in which Day told him of the founding of the Geophysical Laboratory. To Van't Hoff this institution, devoted to the study of silicates, was analogous to the "Kaliverband" (the Association for the Study of Natural Salt Deposits), which was to continue with the study of evaporite deposits where he left off.

Van't Hoff and Metamorphic Rocks

One further influence of Van't Hoff on geology remains to be traced: that on the study of metamorphic rocks. In his classic memoir on the contact metamorphism of the Kristiania region, Goldschmidt clearly formulated his debt to Van't Hoff (*42*, pp. 123–124):

> The fundamental law which governs the relationship between chemical composition and mineral assemblage of contact rocks is the *phase rule*. If we have as starting materials a certain number of compounds, for instance, those of a shale, then we can calculate the number of minerals to be found in the products of contact metamorphism. However, in its most general formulation, the phase rule of Willard Gibbs[1] cannot be applied with ease and confidence, if we are dealing with a system of many different substances. For our needs, in considering hornfels derived from shales, the following substances are important: silica, alumina, magnesia, and lime. Systems of four components present severe difficulties, if treated with the most generalized phase rule. I prefer, for reasons of simplicity, to apply the phase rule in a special form, namely, in the form of the laws of the formation of double salts.[2] These laws are contained within the phase rule, but they are especially suited to interpret the reactions of contact rocks. *We consider that part of a rock which is in a reactive state as a saturated solution, that is, a solution saturated with respect to the relevant contact minerals*; the minerals produced by the contact metamorphism we consider as *precipitates* of that solution. . . .
>
> [1] From the point of view of the mineralogist, Willard Gibbs' phase rule seems to me to have the following formulation: The maximum number *n* of solid minerals which can coexist simultaneously and stably is equal to the number *n* of individual components contained in these minerals (if one disregards the singular temperatures of transition points).
>
> [2] Van't Hoff's laws of double salts can be found in the following publications: "Studies in chemical dynamics," Leipzig, 1896; "Lectures on formation and decomposition of double salts," Leipzig, 1897; "Lectures in theoretical and physical chemistry," Braunschweig, 1898.

This quotation illustrates how difficult it was for even the most enlightened geologists to cope with the phase rule, perhaps because it was formulated in such abstract and mathematical language. Goldschmidt obviously preferred the more tangible result of Van't Hoff and he proceeded to analyze the mineral assemblages of his hornfelses in the light of the "law of the incompatibility of condensed systems." His approach was so obviously successful that it became a landmark in the study of metamorphic rocks and an important step toward Eskola's eventual formulation of the facies principle (*50*).

Conclusions

Van't Hoff's work constitutes the first systematic contribution to experimental petrology. At all times, the problem was perceived as geologic in nature and the laboratory results were checked against natural assemblages whenever possible. The phase rule was not used, nor, for that matter, was chemical thermodynamics, except for the Van't Hoff equation. However, the work of Van't Hoff and Van Deventer was indirectly involved in the evolution of phase theory by Roozeboom, Van Rijn van Alkemade, and Schreinemakers. Meyerhoffer himself wrote the first text explicitly devoted to the phase rule.

The impact of Van't Hoff's study was enormous, but it was restricted to those geologists willing and able to cope with chemistry. Foremost among them were igneous petrologists who had long since accepted chemical arguments for classification purposes. I consider the Geophysical Laboratory program to be the most direct heir of the Van't Hoff approach. Although the shape of that program was formulated independently by Van Hise, Becker, Day, and others, the inspiration they derived from Van't Hoff's successes is clearly acknowledged. The study of the fusion of plagioclases by Day and Allen (*41*), which directly led to the authorization for the Geophysical Laboratory, was the igneous counterpart of Van't Hoff's low-temperature experimental petrology. On metamorphic petrology, too, Van't Hoff left his mark, with V. M. Goldschmidt acting as his disciple. The interpretation of the Kristiania contact rocks was explicitly based on Van't Hoff's double salt law in preference to the phase rule.

Sedimentologists remained unaffected and continued their preoccupation with description and classification. Chemical arguments remained subordinate in their work and of an elementary nature, underscoring the chasm between "hard" rocks and "soft" rocks. This gulf is only now beginning to close as a result of the blossoming of experimental petrology and geochemistry since World War II. At last the generality of the point of view of Gibbs is being accepted. If Van't Hoff's contribution had been appreciated fully at the time, this could have happened 70 years earlier.

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