Certain of the bands of biacetyl occur, as would be expected, at longer wave lengths than similar bands for the other ketones hitherto investigated. Since absorption coefficients in the absorption regions below 2000 Å. are, generally speaking, very high, it probably would be possible to use these bands for a semi-quantitative as well as a qualitative estimate of the amount of biacetyl present along with acetone and ethyl methyl ketone.

In conclusion the author wishes to express his appreciation to Dr. W. A. Noyes, Jr., who suggested this problem.

Summary

The absorption spectrum of biacetyl vapor has been investigated with a vacuum grating spectrograph between 2000 and 1550 Å. Absorption regions are found which correspond in general to those in acetone and ethyl methyl ketone, although they are displaced to longer wave lengths as would be expected due to the juxtaposition of two carbonyl groups. A prominent frequency difference of about 1220 cm.$^{-1}$ is found in the upper state, although the presence of another difference almost exactly half as great renders the interpretation ambiguous. Certain bands occur at wave lengths sufficiently displaced from those in acetone and ethyl methyl ketone to permit them to be used for the identification of biacetyl in the presence of these other substances.

Providence, R. I. Received May 6, 1938

[Contribution from the Department of Chemistry, Stanford University]

Phase Rule Studies of Soap Systems.
I. Applicability of the Phase Rule

By J. W. McBain, R. D. Vold and M. J. Vold*

The purpose of this introductory paper is to justify the application of the phase rule to soap systems.

It has been shown[1] that many colloid systems are formed spontaneously from their crystalloidal components, and exhibit properties which are independent of previous history and are solely dependent upon composition and temperature, and that they are thermodynamically stable in the same sense as are crystals or solutions of sugar or salts. It will be shown that therefore the phase rule in its usual form, ($F = C + 2 - P$), must apply to all thermodynamically stable colloid systems, without the introduction of any new variable.

Empirically, it has been found in many contributions since that of McBain and Burnett in 1922 that the behavior of systems of soap, water and electrolytes can be represented quantitatively on the usual Gibbs triangular diagram.[2] A large body of knowledge has been thus assembled and the work of previous authors[3] also has been found to fit into the same systematic description and analysis. The results have led to a greatly clarified understanding of the processes and phenomena of soap-boiling.

The same phases occur for sodium palmitate,[4] potassium laurate,[5] and potassium oleate.[6] The observations of temperatures at which phase changes occur and the analytical data on the composition of separated phases fit into the phase rule diagrams. Similar results have been obtained in experiments on the mixed fatty acids from coconut oil and in the experiments of Elford with commercial oils and fats on a full commercial scale. Ferguson and Richardson[7] likewise found that the phases of commercial soaps are the same as those in soaps from a single fatty acid.

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(1) J. W. McBain and A. J. Burnett, *J. Chem. Soc.*, **121**, 1320 (1922); J. W. McBain, Fourth Colloid Symposium Monograph, **4**, 7 (1926); *Kolloid-Z.*, **40**, 1 (1926); This Journal, **58**, 2610 (1936); **60**, 223 (1938).

(2) See also J. W. McBain and E. Walls, Fourth Colloid Report of the British Association for the Advancement of Science, 1922, p. 244.

(3) F. Merklen, "Études sur la Constitution des Savons du Commerce," Marseilles, 1906; German edition by F. Goldschmidt, Halle-a.S., 1907; T. Richert, Diss., "Über das Aussalzen von Seifen," Karlsruhe, 1911; F. Bätz, Diss., Karlsruhe, 1918; M. Thörl, Diss., Karlsruhe, 1918.

(4) J. W. McBain and G. M. Langdon, *J. Chem. Soc.*, **127**, 852 (1925); also J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. physik. Chem.*, **A147**, 87 (1930); this paper contains an extensive bibliography.

(5) J. W. McBain and M. C. Field, *J. Phys. Chem.*, **30**, 1545 (1926).

(6) J. W. McBain and W. J. Elford, *J. Chem. Soc.*, 421 (1926).

(7) R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, **24**, 1329 (1932).

It was an important finding,[2] confirmed by all subsequent work, that for practical purposes, apart from processes involving graining or salting out, the complex contents of the soap kettle may be regarded as a three-component system of soap, water and electrolyte.[7,8]

All this work together with the papers which presently are being communicated illustrates the utility of the phase rule in giving a comprehensive quantitative description of the behavior of soap systems. The very different methods used in these studies: namely, analysis of separated phases, visual observation of temperatures and concentrations at which phases appear and disappear, observations with the microscope and the polarizing microscope with heating stage,[9] vapor pressures, and dilatometer, are all in complete agreement.

The Phase Rule and Colloids

Theoretically, the phase rule may be regarded as an extension to chemistry of the algebraic principle that n equations are needed for a unique determination of n independent variables. In heterogeneous equilibria the variables are temperature, pressure and composition of the phases, and the relations between them are derived from the thermodynamic criterion of equilibrium that the chemical potential or partial molal free energy of each component must be the same in all phases throughout the system. The phases must be effectively homogeneous, uninfluenced by "capillarity," and in true equilibrium with each other.

No phase is homogeneous on an atomic or molecular scale, and the difficulty is often felt to be accentuated when colloidal particles are present. Büchner[10] has given a satisfactory answer by pointing out that heterogeneity has only a relative and not an absolute meaning and that heterogeneous systems are not necessarily two-phase systems. Even optically heterogeneous colloid systems become homogeneous in the Gibbsian sense if the volume element selected is large compared with the micelle instead of the molecule.

A colloid is thermodynamically a single phase only if its external properties such as vapor pressure, freezing point, distribution ratio, etc., etc., are solely and completely defined by temperature, pressure and composition. Although the effects of capillarity are explicitly excluded in the deduction of the phase rule,[11] yet since temperature, pressure and concentration in a stable reversible colloidal system coincidentally determine the capillary state of the system, there is no effect upon the application of the phase rule to external equilibria.[12]

Attainment of Equilibrium

It is a prerequisite for the legitimate application of the phase rule that true reversible equilibrium is attained and is thereafter independent of time. The same final state should be attainable from higher and lower concentrations or from higher and lower temperatures. Of course, the phase rule applies to reversible metastable equilibria as well, just as it applies to the solubility curve of anhydrous sodium sulfate or even of the slowly hydrolyzing substance ethyl acetate where hydrolysis is slow in comparison with the measurement. It is essential to show not only that the system has been brought into equilibrium but that this has not been displaced or distorted by the method of examination. Mere cooling of a soap system may introduce a phase which only slowly disappears again and may thus be misleading. This is one source of the experimental discrepancies which have been discussed at length in the German literature.[12]

Phases and Nomenclature in Soap Systems

Apart from false "equilibria," much of the denial of the applicability of thermodynamics to soap systems has arisen from the great confusion in the terminology employed in describing them, especially in translation. For clarity, therefore, the phases of soap systems will be listed.[13] It is helpful to refer to the two component diagram of Fig. 1, and to the schematic three component diagram, Fig. 2, where the corners represent soap, water and salt, respectively, and the composi-

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(8) J. W. McBain and A. V. Pitter, *J. Chem. Soc.*, 893 (1926); R. H. Ferguson, *Oil and Soap*, **14**, 115 (1937).

(9) K. MacLennan, *J. Soc. Chem. Ind.*, **42**, 393T (1923).

(10) E. Büchner, "Colloids as One-Phase Systems," in Alexander's "Colloid Chemistry," Vol. I, 1926, Chapter 4, p. 126.

(11) Scientific Papers of J. Willard Gibbs, Vol. I, Longmans, Green and Co., 1906, pp. 62 and 96.

(12) Compare the voluminous literature summarized by Wo. Ostwald and H. Erbring, *Kolloidchem. Beihefte*, **31**, 291 (1930). Likewise, Kruyt and de Jong hesitate to give the name phase to the liquid layers separating out in colloid systems, rejecting the phase rule and terming the process "coacervation," the colloid richer liquid "coacervat" and the liquid poor in colloid "liquide d'équilibre"; H. G. Bungenburg de Jong, "La Coacervation, les Coacervats, et leur Importance en Biologie," Tomes I and II, Actualités Scientifiques et Industrielles No. 397, Herman et Cie., Paris, 1936.

(13) For full descriptions, see J. W. McBain in Alexander's "Colloid Chemistry," Vol. I, 1926, Chapter 5, p. 138; J. W. McBain and M. C. Field, THIS JOURNAL, **55**, 4776 (1933). For examples of German terms, see E. L. Lederer, "Kolloidchemie der Seifen," Th. Steinkopff, Dresden, 1932, p. 299.

tions are proportional to the distances from these corners.

1. **Clear Isotropic Solution. Nigre. Lye.**—It is seen from Fig. 1 that there is only one body of isotropic solution which at sufficiently high temperatures embraces all proportions of soap and water, as they are completely miscible above the true melting point of the soap. Nevertheless in Fig. 2, which refers to a single temperature, it is evident that there is a region, which may be called the isotropic bay region,[14] where two portions of the isotropic solution may exist in equilibrium with each other as separate liquid phases. The one containing much salt with but little soap is called lye, or "Unterlauge," or "dünne Lauge." The other containing a moderate concentration of soap is the soap boilers' nigre, or "Leimniederschlag," "schwärzliche Flüssigkeit," "Leimseife," or "Leim." The isotropic solution in general is commonly called soap solution, "isotrope Seifenlösung," "isotrope homogene Lauge," or "Seifensol."

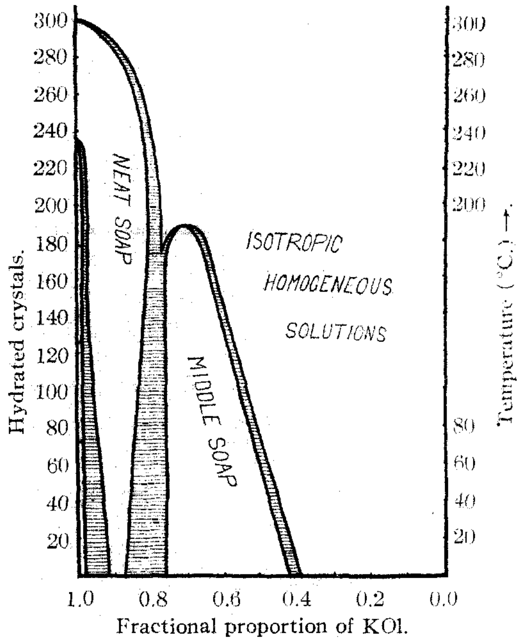

Fig. 1.—Equilibrium diagram for the two-component system potassium oleate–water (from McBain and Elford[6]).

In the middle of the isotropic region some soaps become highly viscous or set to an isotropic jelly.[15] This is not a separate phase and has no separate boundary. The jelly is clear, transparent and elastic, and may flow slowly. It is unfortunate that the term "Seifen-Gallerte" has been employed to designate a wholly different opaque mixture of phases leaving no German term to indicate the true soap jellies. Soap jellies,[15] like middle soap,[4] were previously unknown.

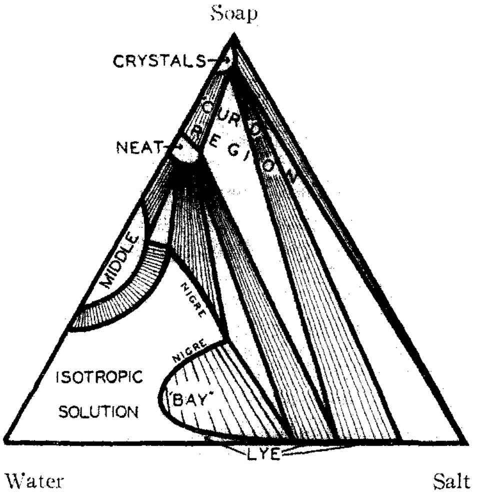

Fig. 2.—Schematic equilibrium diagram for a system soap–salt–water near 100°.

2. **Neat Soap.**—Neat soap is a doubly refracting clear or translucent liquid crystalline soap phase. It includes the soap boilers' fitted and settled soap (while hot), or "geschliffene Kernseife," "Kernseife auf Leimniederschlag," "abgesetzte Kernseife," "klare Seife," or "glatte Kernseife." Curd soap, or "Kernseife auf Unterlauge," is, when hot, the same phase, neat soap; except where the concentration of electrolyte is so high as to cause separation of curd fibers, which anyway appear on cooling (see below).

3. **Middle Soap.**—This is another conic anisotropic liquid or clear doubly refracting liquid crystalline phase, immiscible with neat soap, and of lower soap content. It sometimes has been mistakenly confused with "Leimniederschlag" or nigre which is wholly different.

4. **Crystalline Phases. A. Lamellar Crystals.**—These very thin six-sided transparent colorless crystals, giving a highly developed X-ray pattern, occur sometimes with sodium soaps, or sediments of acid soaps, but more frequently with potassium, ammonium and hydrogen soaps, forming the fig in soft soaps. Since they gen-

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(14) A similar bay is found for gelatin, F. Kellogg and J. W. McBain, *J. Gen. Physiol.*, **12**, 1 (1928). A diagram rather similar to Fig. 2 is also obtained for serum globulin with pseudoglobulin and euglobulin occupying the positions of neat and middle soap; J. W. McBain and E. Jameson, *Trans. Faraday Soc.*, **26**, 768 (1930).

(15) M. E. Laing and J. W. McBain, *J. Chem. Soc.*, **117**, 1506 (1920); *Kolloid-Z.*, **35**, 18 (1924).

erally are not found as a stable phase in the case of sodium soaps they do not appear on any of the phase-rule diagrams in this or the following paper.

B. Curd Fibers.—This second crystalline phase, showing with X-rays[16] a three-dimensional spacing, is the same as the *curd phase* of Vold and Ferguson.[17] It is the common crystalline form of sodium soaps and is the phase which is referred to as hydrated crystals on many of the diagrams. They are white fibers, "Kernfasern," often several centimeters long, but usually consisting of bundles of fibers which are ultramicroscopic except in length. They have been photographed in the ultramicroscope by Zsigmondy and Bachmann[18] and by McBain, Darke and Salmon.[19] Curd fibers may be anhydrous but usually contain water. It is not certain whether they form definite hydrates or are of continuously variable composition. Although submicroscopic fibers may be present, this crystalline phase is sometimes granular in appearance rather than fibrous.

Soap Systems: Multiphase Equilibria

According to the phase rule, in any three component system, three liquid or solid phases may coexist at any one temperature, with vapor, as is shown by the triangles within Fig. 2, whose corners represent the phases in contact; at least one of these four phases will be of continuously variable composition or concentration with change in temperature. Ostwald and Erbring[12] have mistakenly regarded the coexistence of three condensed phases over a temperature range as a disproof of the applicability of the phase rule. The coexistence of pairs of phases, both of variable composition at any one temperature, is likewise shown in Fig. 2 in the areas shaded with tie lines whose ends connect the phases in contact. Five phases of fixed composition are required for any invariant three component system.

Soap curd, or simply **curd** (not to be confused with commercial curd soap boiled on lye, especially not with curd fibers) is a mixture of phases which occurs in the curd region indicated on Fig. 2, and consists of a white, more or less opaque, mass of solid containing curd fibers, with or without solution or liquid crystalline material. Dry curd consists entirely of curd fibers. Curd has been variously designated "geronnener Kern," "kristallines hydratisiertes Gerinnsel," "Gerinnsel," "Koagel," "Kernseife," or "Seifengel"; it is not "Kernseife," which is neat soap. The formation of curd has been called "Erstarrung" or "Gelatinierung," which has been confusing because gelatinization is usually reserved for the formation of true jellies.

Curiously, McBain's suggestion that soap curd may consist of a mixture of definite hydrates of crystalline curd fibers has been regarded[12] (see also Lederer[13]) as evidence that the phase rule does not apply to soap systems. It is supposed that the water content of curd fibers varies continuously, with the *non sequitur* that McBain's suggestion leads to the conception of curd fibers as consisting of an infinite number of phases. The correct alternative is a single phase of continuously variable composition. The confusion may be due to failure to distinguish between curd and curd fibers, the former being the heterogeneous masses indicated in Fig. 2 in the curd region and the latter consisting either of a few definite crystalline hydrates or of one or two series of crystals containing variable amounts of water, as in the zeolites.

Summary

1. It is shown that the phase rule is applicable in its usual form to thermodynamically stable colloid systems in true equilibrium.

2. It is pointed out that the phase rule does in fact describe the actual behavior of soap systems.

3. Since reported discrepancies appear to have been due to misunderstanding of the phases and systems discussed, these are listed and defined.

STANFORD UNIVERSITY, CALIF. RECEIVED APRIL 12, 1938

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(16) S. H. Piper, *J. Chem. Soc.*, 234 (1929); P. A. Thiessen and J. Stauff, *Z. physik. Chem.*, **A176**, 397 (1936); P. A. Thiessen and R. Spychalski, *ibid.*, **A156**, 435 (1931).

(17) R. D. Vold and R. H. Ferguson, communication submitted to THIS JOURNAL.

(18) R. Zsigmondy and W. Bachmann, *Kolloid-Z.*, **11**, 152 (1912).

(19) W. F. Darke, J. W. McBain and C. S. Salmon, *Proc. Roy. Soc.* (London), **A98**, 395 (1921).