single step from the Second Law of thermodynamics directly to the differential equation of the desired relation.

4. In connection with the application of the engine to the subject of chemical equilibrium, the following points have been brought out:

(*a*) Contrary to the statement of T. B. Robertson, the Mass Action Law is not an expression of the condition for equilibrium in a system whose equation of state is $p(v - d) = RT$.

(*b*) The derivation of the Law of the Constancy of the Solubility Product for a solute which dissociates in solution does not involve any assumption regarding the nature of the law which regulates the equilibrium between the undissociated molecules and their products of dissociation. Consequently the theoretical basis for the Solubility Product Law in the case of strong electrolytes is not destroyed by the fact that they do not obey the Mass Action Law, as inferred by Stieglitz.

5. It is shown that many of our equations which contain the van't Hoff i, involve an unnecessary number of assumptions and that each equation can be split up into two simpler equations, one involving only the ions, the other only the unionized molecules. The advantage of so doing is illustrated by a consideration of the experimental data of Noyes and Sammet on the solubility of orthonitrobenzoic acid.

URBANA, ILLINOIS, January 15, 1910.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS: THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS (FIRST PAPER).

A STUDY OF THE REACTION, $KHg_m + Na^{\cdot} \rightleftarrows K^{\cdot} + NaHg_n + (m-n)\,Hg$.

BY GEORGE MCPHAIL SMITH.

Received February 16, 1910.

It has previously been shown[1] that the alkali metals exist, in liquid mercurial solution, in the form of compounds of the general formula $MeHg_n$, containing only one atom of the amalgamated metal to the molecule. It has also been shown that a mixed solution, containing the chlorides of sodium and potassium, reacts readily with either sodium or potassium amalgam, with the rapid establishment of an equilibrium. The same has been found to be the case with sodium and rubidium, and sodium and caesium amalgams, when treated with the corresponding mixed solutions.[2]

The present paper is the outcome of a more detailed study of the first

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[1] Ueber die relative Beständigkeit bzw. die Konstitution der verdünnten Amalgame der Alkali-bzw. Erdalkalimetalle. G. McP. Smith, *Z. anorg. Chem.*, 58, 381 (1908).

[2] *Loc. cit.*

of these reactions. In subsequent investigations the alkali earth and other amalgams will be included.

Experimental Method.[1]—Approximately equimolal liquid sodium and potassium amalgams were prepared, and after filtration through chamois skin on the filter pump, they were at once filled into small sealing bottles, whose necks were then drawn into capillaries and sealed off. At intervals, the measured salt solutions, which had previously stood in the thermostat in stoppered Erlenmeyer flasks, were tared on a balance, and the desired quantities of amalgam were poured into them directly from the opened capillaries.[2] The flasks were then restoppered and put back into the thermostat, and the capillary necks of the sealing bottles were at once re-sealed. The reaction mixtures were agitated for a given time in the thermostat, after which they were taken out, one at a time, and treated as follows:

The aqueous solution was decanted and the amalgam was washed by passing it through a row of 5 beakers, each of which contained about 50 cc. of distilled water; the wash water was decanted each time before the amalgam was poured into the next beaker. In this way each amalgam was washed thoroughly in the course of 1 minute, and the chemical action of the wash water was negligible. The amalgams were finally decomposed with hydrochloric acid, and the extracts were analyzed. The experimental results are given in Table I.[3]

In the reversible reaction,[4]

$$\mathrm{KHg}_m + \mathrm{Na}^{\cdot} \rightleftarrows \mathrm{K}^{\cdot} + \mathrm{NaHg}_n + (m-n)\mathrm{Hg},$$

as carried out in these experiments, free mercury was present in such quantity that its concentration may be taken as constant. We have therefore a heterogeneous equilibrium of the second order, and if $[\mathrm{KHg}_m]$ and $[\mathrm{NaHg}_n]$, $[\mathrm{Na}^{\cdot}]$ and $[\mathrm{K}^{\cdot}]$ represent the relative molal concentrations at equilibrium, then the equilibrium constant,

$$\mathrm{K} = \frac{k_1}{k_2} = \frac{[\mathrm{KHg}_m] \times [\mathrm{Na}^{\cdot}]}{[\mathrm{NaHg}_n] \times [\mathrm{K}^{\cdot}]}.$$

[1] The mercury used in the preparation of the amalgams was purified by the ordinary methods, after which it was distilled under reduced pressure in a current of air. The salts were of Kahlbaum's manufacture, and the water employed was obtained by redistilling the distilled water of the laboratory, after having acidified it slightly with sulphuric acid.

[2] In all cases the interaction of the amalgam and the solvent-water was infinitesimal and it will be neglected in what follows.

[3] The five solutions employed in the first 10 experiments contained, respectively, 14.6150 g. NaCl + 9.3200 g. KCl, 7.3075 g. NaCl + 18.6400 g. KCl, 14.6150 g. NaCl + 4.6600 g. KCl, 3.6538 g. NaCl + 18.6400 g. KCl, and 7.3075 g. NaCl + 9.3200 g. KCl; they were made up, one after another, in the same 250 cc. measuring flask.

[4] The values of *m* and *n* are not known for the compounds in solution; they may have several values in the case of the crystalline compounds. For references to the literature, see *loc. cit.*

TABLE I.[1]

No.	t°.	Time. Min.	Molal concentration of mixed solution at start.		Volume of aqueous solution used. cc.	Metallic solution used.	Resulting amalgam gave on analysis.		It therefore contained.		Which is equivalent to
			NaCl.	KCl.			NaCl+KCl.	K_2PtCl_6.	K.	Na.	
1	24.0	40	1.00	0.50	100	50.5 g. K-amalgam	0.3485	0.2182	0.0350	0.1110	0.447% K
2	24.0	40	1.00	0.50	100	50.7 g. Na- "	0.3834	0.2034	0.0326	0.1265	0.290% Na
3	24.0	40	0.50	1.00	100	50.0 g. K- "	0.3593	0.5537	0.0888	0.0749	0.432% K
4	24.0	40	0.50	1.00	100	50.0 g. Na- "	0.4055	0.5540	0.0888	0.0929	0.290% Na
5	24.2	40	1.00	0.25	100	50.1 g. K- "	0.3324	0.1300	0.0208	0.1151	0.433% K
6	24.2	40	1.00	0.25	100	50.6 g. Na- "	0.3752	0.1131	0.0181	0.1340	0.289% Na
7	24.2	40	0.25	1.00	100	50.3 g. K- "	0.3482	0.7418	0.1190	0.0478	0.400% K
8	24.2	40	0.25	1.00	100	50.2 g. Na- "	0.4166	0.7838	0.1257	0.0697	0.287% Na
9	24.1	50	0.50	0.50	100	50.1 g. K- "	0.3345	0.3679	0.0590	0.0874	0.415% K
10	24.1	50	0.50	0.50	100	50.9 g. Na- "	0.3908	0.3577	0.0574	0.1108	0.289% Na
11	24.	30	2.00	2.00	50	50. g. K- "	0.3299	0.3173	0.0509	0.0918	......
12	24.	30	2.00	2.00	50	50. g. Na- "	0.3166	0.2846	0.0456	0.0904	......
13	17.	30	2.00	2.00	50	50. g. Li- "	0.0599	0.0540	0.0087	0.0171	......

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[1] Samples of the amalgams were taken beforehand from the sealing bottles and analyzed. They gave: Na = 0.29 per cent. and K = 0.45 per cent., respectively.

Experiments 11 and 12 are taken from the paper already cited. In the case of Experiment 13 (which is taken from *Am. Chem. J.*, 37, 517 (1907)), the alcoholic filtrate from the potassium chloroplatinate was evaporated to dryness and the residue tested spectroscopically for lithium, of which not a trace could be detected.

Now, in the case of Experiments 1 and 7, for example,

$$\frac{\frac{0.0350}{39.10}[\mathrm{Na}^{\cdot}]_1}{\frac{0.1110}{23.00}[\mathrm{K}^{\cdot}]_1} = \mathrm{K} = \frac{\frac{0.1190}{39.10}[\mathrm{Na}^{\cdot}]_7}{\frac{0.0478}{23.00}[\mathrm{K}^{\cdot}]_7};$$

whence

$$\frac{]\mathrm{Na}^{\cdot}]_1}{[\mathrm{K}^{\cdot}]_1} \bigg/ \frac{]\mathrm{Na}^{\cdot}]_7}{[\mathrm{K}^{\cdot}]_7} = 7.90.$$

And, starting with 100 cc. of solution and taking into account the changes in concentration during the reaction, we have at equilibrium in the case of these two experiments the molal relations:

$$\frac{(\mathrm{NaCl})_1}{(\mathrm{KCl})_1} \bigg/ \frac{(\mathrm{NaCl})_7}{(\mathrm{KCl})_7} = \frac{\frac{2.3000 - 0.1110}{2.3000}}{\frac{1.9550 + 0.1887}{3.9100}} \Bigg/ \frac{\frac{0.5750 - 0.0478}{2.3000}}{\frac{3.9100 + 0.0813}{3.9100}} = 7.73.$$

From the approximate equation, 7.90 = 7.73, it follows roughly that

$$\frac{[\mathrm{Na}^{\cdot}]_1}{[\mathrm{K}^{\cdot}]_1} : \frac{[\mathrm{Na}^{\cdot}]_7}{[\mathrm{K}^{\cdot}]_7} = \frac{(\mathrm{NaCl})_1}{(\mathrm{KCl})_1} : \frac{(\mathrm{NaCl})_7}{(\mathrm{KCl})_7};$$

i. e., in mixed sodium and potassium chloride solutions, the ratios which exist between the relative ion concentrations of sodium and potassium in the different solutions are identical with those which exist between the relative molal concentrations of the two salts in the respective solutions. It is therefore permissible to substitute the latter values in the calculation of the equilibrium constant. The results are given in Table II:[1]

TABLE II.[2]

No.	Amalgam at start.	At equilibrium, $[\mathrm{KHg}_m] : [\mathrm{NaHg}_n]$.	From the relative molal concentrations at equilibrium, $[\mathrm{Na}^{\cdot}] : [\mathrm{K}^{\cdot}]$.	Total molal concentration of mixed salt solution.	$\frac{[\mathrm{KHg}_m] \times [\mathrm{Na}^{\cdot}]}{[\mathrm{NaHg}_n] \times [\mathrm{K}^{\cdot}]}$.
1	Potassium...	15.64 : 84.36	0.9517 : 0.5482	1.50	0.322
2	Sodium......	13.12 : 86.83	1.0083 : 0.4916	1.50	0.311
3	Potassium...	41.08 : 58.92	0.4674 : 1.0325	1.50	0.316
4	Sodium......	36.00 : 64.00	0.5227 : 0.9773	1.50	0.315
5	Potassium...	9.03 : 90.97	0.9500 : 0.3000	1.25	0.314
6	Sodium......	7.22 : 92.78	1.0046 : 0.2454	1.25	0.318
7	Potassium...	59.42 : 40.58	0.2294 : 1.0207	1.25	0.329
8	Sodium......	51.49 : 48.51	0.2821 : 0.9678	1.25	0.309
9	Potassium...	28.43 : 71.57	0.4620 : 0.5380	1.00	0.341
10	Sodium......	23.35 : 76.65	0.5147 : 0.4853	1.00	0.323
11	Potassium...	24.61 : 75.39	1.9207 : 2.0798	4.00	0.302
12	Sodium......	22.90 : 77.10	2.0233 : 1.9762	4.00	0.303
13	Lithium.....	23.05 : 76.95	2.0 : 2.0	4.00	0.292

Mean value: $K = 0.315$

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[1] In the calculation of the molal concentrations at equilibrium, if sodium amalgam was started with, for example, then the potassium in the resulting amalgam came

It is interesting to compare with the above the equilibrium constants calculated from previously published results[1] obtained in the action of mixed sodium and rubidium, and sodium and caesium chloride solutions upon sodium and rubidium, and sodium and caesium amalgams, respectively. In these cases the solutions were double molal in respect to each salt in the mixture, so that the concentration changes may be disregarded in calculating the values of the equilibrium constants. The results are given in Table III:

TABLE III.

No.	t°.	Time. Min.	Amalgam at start.	At equilibrium $[MeHg_m]:[NaHg_n]$.	At start and at equilibrium $[Na^\cdot]:[Me^\cdot]$.	$\frac{[MeHg_m]\times[Na^\cdot]}{[NaHg_n]\times[Me^\cdot]}$.	Mean.
1	23	30	Rubidium	27.39 : 72.60	2.0 : 2.0	0.377	0.37
2	23	30	Sodium	26.35 : 73.64	2.0 : 2.0	0.358	
1	24	30	Caesium	32.95 : 67.05	2.0 : 2.0	0.491	0.48
2	24	30	Sodium	32.44 : 67.55	2.0 : 2.0	0.480	

From the foregoing we see that, in the case of the general reaction,

$$NaHg_n + (m - n)Hg + Me^\cdot \rightleftarrows MeHg_m + Na^\cdot,$$

the equilibrium constant is equal to 0.31, 0.37 and 0.48, respectively, when Me stands for K, Rb and Cs, in the order named.

Previous studies of the ionization of salts have led to the conclusion that at any definite concentration salts of the same ionic type have approximately the same degree of ionization. It has also been shown by experimental investigations that the degree of ionization of each salt in such a mixture as KCl + NaCl, in which there is a common ion, is the same as if that salt were alone present with an ion concentration equal to the sum of those of the two separate salts.[2] It therefore follows that, in such a mixed solution,

$$\frac{[Na^\cdot]}{[K^\cdot]} = \frac{\alpha_1(NaCl)}{\alpha_2(KCl)} = \frac{(NaCl)}{(KCl)}.$$

The present investigation offers, through an independent method, a

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from the solution, and the equivalent amount of sodium must have entered the solution from the amalgam. The chemical action of the solvent water was negligible, as can be seen from the figures given in the last column of Table I.

[2] In regard to experiments 11, 12 and 13, see footnote under Table I. Experiment 13 is evidently unreliable, owing to the low lithium content of the amalgam at the start and to the different temperature. Of the first 10 experiments, the 9th is the least reliable. The source of error is suggested in the last column of Table I, where it is seen that the equivalent potassium content found was greater than that in experiment 7, which was performed 1 day earlier; owing to traces of oxidation in the meantime, the amalgam should have shown a lower potassium content. The mean value of K is not affected, however, if *both* experiments are left in the table.

[1] *Loc. cit.*

[2] For references to the literature on this subject, see A. A. Noyes and J. Johnston, THIS JOURNAL, 31, 987 (1909).

striking confirmation of the above conclusions, and, *moreover, it shows that they hold good even in the case of very concentrated solutions.*

URBANA, ILL., February, 1910.

CONCERNING THE CORRECTION OF THE APPARENT WEIGHT OF A SALT TO THE VACUUM STANDARD.

BY THEODORE W. RICHARDS AND GREGORY P. BAXTER.

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The tendency to adsorb gases possessed by finely divided carbon is well known, and there can be no question that other substances also possess, although to a much smaller degree, this same tendency. Therefore the possible effect of adsorbed gases upon the weights of the substances entering into very precise determinations, such as those concerning the atomic weights, is worthy of careful consideration. The idea is by no means new, for Marignac nearly seventy years ago investigated several salts with regard to the possibility of such adsorption, and found in most cases very slight, if any, evidence of an appreciable effect.[1] The topic has been recently revived by Guye and Zachariadès in a brief paper, in which are recorded, without details, a number of extraordinary results very different from those of Marignac.[2] The new investigators interpret their figures to mean that the error from this source is in many cases a serious one, rendering illusory the weighing of most powdered salts more accurately than to within one one-hundredth of one per cent.

The experiments of Guye and Zachariadès have been repeated, as far as potassium chloride is concerned, by Alexander Scott, with results confirming Marignac's rather than those of the new investigators. Scott was unable to find any important adsorptive effect, even in finely powdered potassium chloride.[3] His discussion of the matter seems to leave little need of further remark, except for the fact that Guye and Zachariadès specifically mention the recent Harvard investigations upon atomic weights, and their paper might convey to some the impression that these authors believe their results to concern the work at Harvard. It is very easy to show, however, upon the basis of the evidence in the paper, that, whether the interpretation by the two investigators at Geneva is correct or not, in any case their results can have no relation whatsoever to the Harvard work, and do not render necessary appreciable corrections in any of the Harvard investigations.

Guye and Zachariadès weighed successively in air and in vacuum a number of materials which, as they say, "were chosen especially as having served in the determinations of atomic weights in the chemical

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[1] Marignac, *Oeuvres Completes*, **1**, 44; also *Bibl. Univ.*, 46, 373 (1843).

[2] Guye and Zachariadès, *Compt. rend.*, 149, 593 (1909).

[3] Alexander Scott, *Proc. Chem. Soc.*, **25**, 286 (1909).