ing to the excess heat of reaction with potassium and indeed probably does the reverse.

Acknowledgments.—We are indebted to T. J. Neubert and S. Gordon for suggesting this problem and for guiding the work in its early stages. We are indebted to Dwight Hutchison and Louis Pobo for having performed the mass spectrometry.

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Thermodynamic Properties of Dilute Alkali Metal Amalgams[1]

BY HAROLD L. FRIEDMAN AND KENNETH SCHUG[2]

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The thermodynamic properties of ternary amalgams containing Na with K, Rb, Cs or Sr have been investigated by an equilibrium method. The results, together with independent data for Na amalgam, yield properties of the binary amalgams of K, Rb, Cs and Sr. When combined with data from other sources these provide information on the formation of the alkali metal amalgams from the elements and the deviations from Raoult's law of these solutions. For the process M(Hg, Hyp. 1 molal) = M^+(gas) + e^-(gas), ΔH decreases from Li to Cs, but ΔS increases strongly, becoming +30 e.u. for Cs. This and several other amalgam properties are consistent with the hypothesis that the alkali metals are ionized in the amalgams and that only the electron tends to enter the mercury phase from the gas phase. Then the positive ions tend to escape the amalgam, the more so the larger the ion, but this tendency is overcome by the forces leading to electroneutrality of the phase. The detailed form of the activity coefficients in the amalgams is consistent with a Brönsted specific ion interaction between the electrons and the positive ions in the amalgam in a way similar to that first suggested by C. Wagner. The temperature coefficients of the activity coefficients reflect the large entropy effects in solvation.

Introduction

The amalgam partition method[2] for the investigation of the energetics of non-aqueous solutions of electrolytes involves the equilibrium interchange of two metal species, M_1 and M_2, between an amalgam phase (Hg) and an electrolytic solution phase (es)

$$\frac{1}{z_1}\,M_1^{z_1+}\,(\text{es}) + \frac{1}{z_2}\,M_2(\text{Hg}) = \frac{1}{z_1}\,M_1(\text{Hg}) + \frac{1}{z_2}\,M_2^{z_2+}\,(\text{es}) \qquad (1)$$

in which z_1^+ and z_2^+ are the ionic charges in the electrolytic solution. Equilibrium concentration measurements in such a system, when suitably extrapolated to zero solute concentration in each phase, lead to the standard free energy change of reaction (1), ΔF_1^0. If the free energies of M_1(Hg) and M_2(Hg) are known, ΔF_1^0 leads to the relative ΔF_f^0 of $M_1^{z_1+}$(es) and $M_2^{z_2+}$(es). In the present work, however, we employ electrolytic solutions in water, in which the ionic free energies are known, and the objective is to obtain the thermodynamics of M_2(Hg), with M_2 = K, Rb, Cs and Sr, from measurements on reaction (1) with M_1 = Na. For this purpose the thermodynamics of Na(Hg) obtained by Bent and Swift[3] from measurements on e.m.f. cells will be used as a basis.

It was found early in the present work that the e.m.f. experiments which lead to the currently accepted[4] ΔF_f^0 of Cs^+(aq) had given temperature coefficients which were inconsistent with our amalgam partition results, as well as with the accepted entropy of Cs^+(aq).[4] It is planned to discuss this discrepancy in a report on the redetermination of ΔH_f^0 of Cs^+(aq) which is now in progress, but for this paper the value, $\Delta F_f^0(Cs^+aq) = -70.3$ kcal./mole, based upon the calorimetric investigation of Rengade[5,6] will be used.

Likewise some of our own experimental results are clearly in need of refinement but the discussion of amalgam properties which is presented here is based upon magnitudes and correlations which are firmly established by the data in their present form.

Part of the data for reaction (1) comes from a series of investigations by G. M. Smith and his associates, made many years ago.[7,8] The results of their experiments as well as ours may be expressed as concentration products for reaction (1)

$$R(M_1/M_2) = (m_1/m_{1w})^{1/z_1} \times (m_{2w}/m_2)^{1/z_2} \qquad (2)$$

and with appropriate activity coefficients we obtain

$$-\Delta F_1^0/2.303RT = \log R(M_1/M_2) - \log\,[\gamma_1^{1/z_1}/\gamma_2^{1/z_2}] + \log\,[f_1^{1/z_1}/f_2^{1/z_2}] \qquad (3)$$

which is used in the reduction of the data. The sum of the first two terms on the right of eq. 3 appears in the presentation of the data and is designated $\log R'(M_1/M_2)$. A glossary of the symbols used in eqs. (2) and (3) and in the rest of the paper is given here

m_{iw} = molality (moles/kg. of solvent) of species i in the aqueous phase
m_i = molality of species in the amalgam phase
ΔF_i^0 = Gibbs free energy increase for reaction i with each product and reactant in hypothetical one molal standard state
f_i = stoichiometric activity coefficient of species i in the amalgam phase, hyp. 1 M std. state
γ_i = ionic activity coefficient of species i in the aqueous phase, hyp. 1 M std. state
$\bar{\gamma}_i$ = ionic activity coefficient of species i in the amalgam phase

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(1) (a) This research supported by the U. S. Atomic Energy Commission. (b) From the thesis submitted by Kenneth Schug to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) K. Schug and H. L. Friedman, THIS JOURNAL, **76**, 3609 (1954).

(3) H. E. Bent and E. Swift, *ibid.*, **58**, 2216 (1936).

(4) F. D. Rossini, D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, 1952, Washington, D. C.

(5) E. Rengade, *Ann. chim. phys.*, [8] **14**, 540 (1908).

(6) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

(7) G. M. Smith and T. R. Ball, THIS JOURNAL, **39**, 179 (1917).

(8) (a) G. M. Smith and S. A. Braley, *ibid.*, **39**, 1545 (1917); (b) L. S. Wells and G. M. Smith, *ibid.*, **42**, 185 (1920).

I = ionic strength, molal scale, in aqueous soln.
β_{ix} = Guggenheim interaction parameter for ions i and x in aqueous solution
α = $[\log(f_1/f_2)]/(m_1 + m_2)$ for reaction (1) for a particular temp., and pair of solutes
B_{ii} = $[\log f_i]/m_i$ for the binary amalgam of metal i
F^{rel} = $2.303RTB_{ii}\ m/2$, the free energy due to solute-solute interaction, in a quantity of solution containing one mole of solute at molality m

Experimental

Equilibration.—The amalgam and aqueous solutions were equilibrated in 15-ml. screw cap bottles which were turned end-over-end about 40 times a min. for about 30 min. in a constant temperature bath. The solutions came in contact only with the glass of the bottle and a Teflon film, 0.08 mm. thick, placed under the screw cap. The phases were sampled within a minute of the time that the rotation of the bottles was stopped. The amalgam sample was washed with a small amount of water and decomposed with 1 ml. of 6 M HCl. Comparison with more elaborate procedures showed that all of the alkali metal was extracted from the amalgam in this way.

Analysis.—Aqueous chloride solutions derived from the aqueous and amalgam phases were analyzed with a Beckman flame photometer attachment (model No. 9200) and a Beckman model DU spectrophotometer. This flame photometer employed H_2 at a pressure of 5.5 p.s.i. and O_2 at a pressure of 20 p.s.i. and was operated at minimum slit width in order to obtain maximum resolution and to reduce errors from background radiation. Calibration curves (percentage transmission reading *vs.* molal concentration) were constructed on the basis of results with stock solutions prepared from the fused chlorides. For each curve, 100% transmission was made to correspond to a 0.01 (or 0.001) molal solution, and the curve covered the range from 0.01 (or 0.001) to 0.001 M (or 0.0001 M). The standard solution corresponding to 100% transmission was used to adjust the sensitivity of the flame photometer in the analysis of unknowns. With this precaution it was found possible to analyze independently prepared solutions of a given electrolyte to 0.5%.

Emission lines of the following wave lengths were used in the analyses: Na, 5890 Å.; K, 7680 Å.; Rb, 7800 Å.; Cs, 8521 Å. and Sr, 4607 Å. It was found that with certain mixtures of electrolytes the transmission readings were enhanced over those of the separate solutions of the same concentration. This enhancement was found to arise only in small part from incomplete resolution of the emission lines, and the main cause must be a change in the processes in the flame itself with changing composition. No enhancement was exhibited by the following pairs of metal ions in the flame except when one of the metals was present in great excess (of the order of fifty to one): Li/K, Na/K, Na/Rb, Na/Cs, Na/Sr, K/Sr. On the other hand, marked enhancement occurred with the mixtures K/Rb and K/Cs, even in roughly equimolal mixtures. In the range 0.01 to 0.001 M these corrections amounted to as much as 30%, and experiments requiring the analysis of such mixtures by flame photometry were avoided. Our experience with analyses of mixtures without enhancement suggests 2% as an upper limit for the error in each concentration determined in such a mixture by flame photometry. A photomultiplier attachment, installed in the spectrophotometer during the later phases of this work, made it more difficult to perform analyses within this limit of error.

TABLE I

A TYPICAL AMALGAM PARTITION EXPERIMENT: RUN A-30

Starting materials: 10 ml. H_2O, 5.00 ml. of 0.100 M K_2CO_3 solution, 1.5 ml. Hg and 0.5 ml. 0.15 M sodium amalgam; 25°; 10 min. equilibration time.

(1)	Phase	H_2O		Hg	
(2)	Phase mass, g.	15.0		26.3	
(3)	Anal. sample mass, g.	150		48	
(4)	Ion	Na^+	K^+	Na^+	K^+
(5)	Flame photometer reading. 0.01 M standard	59.7	63.0	57.9[a]	92.2
(6)	Millimolality of anal. sample	3.24	4.16	13.2	8.52
(7)	Mmoles in anal. sample	0.486	0.624	0.633	0.409
(8)	Milli molality in equil. phase	32.4	41.6	24.0	15.5

[a] Used 0.01 M NaCl at 50% transmission as the standard.

Typical Run.—Table I gives the experimental details for a typical sample and summarizes the calculations. The analytical sample mass for the aqueous phase corresponds to ten-fold dilution of the entire aqueous phase. That for the amalgam phase corresponds to dilution of the aqueous extract of the entire amalgam phase to a final mass of 48 g. These figures involve small corrections, not shown, for the losses in phase separation. The appropriate combination of the numbers in row 6 of the table (or row 8) leads to R = 1.99 for this run, in which, according to row 8, the total concentration of alkali metal in the amalgam phase is 39.5 millimolal. A check is provided by noting that 1 mmole of K was taken for the experiment, and 1.033 mmoles of K found in the aqueous and amalgam phases together. A material balance calculation for sodium is not possible because the concentration and amount of sodium amalgam taken are not accurately known. Careful calculations of material balance, as shown here, were made in only a few cases in order to confirm the validity of the analytical methods.

Results

The available data are presented in Figs. 1 to 4 in a form which shows the dependence of log R' upon $m_1 + m_2$ and upon temperature. The effects of the remaining variables are discussed separately.

Analytical Errors.—Straight lines have been fitted to the log R' *vs.* $m_1 + m_2$ data by the method of least squares. The intercepts, slopes and standard deviations are recorded in Table II. The data of Smith and co-workers are more precise than ours, mainly because of the greater accuracy of the gravimetric method they employed for analysis. Thus the standard deviation of 0.006 in log R (1.5% in R) obtained by Wells and Smith[8b] in their Na/K series is smaller than could be expected if the analyses were performed by flame photometry, considering that four concentrations must be determined to fix a single value of R. However the large scale gravimetric method employed by Smith and co-workers does not seem practical when costly elements such as Rb and Cs are involved.

TABLE II

SUMMARY OF REDUCED PARTITION DATA

System	Temp., °C	Intercept = log K	Slope = $-\alpha$	Std. dev	Source of data
Na/K	0	0.11	1.32	0.01	*a*
	14.5	.27	1.26	.02	*a*
	25	.335	1.11	.02	*a*
Na/Rb	0	− .03	0.75	.03	*a*
	14.5	.065	1.87	.02	*a*
	25	.23	1.14	.01	*a*
Na/Cs	0	− .62	4.1	.02	*a*
	14.5	− .28	1.26	.02	*a*
	25	− .165	2.34	.01	*a*
Na/Sr	0	− .50	0.6	.04	*a*
	14.5	− .55	0.8	.02	*a*
	25	− .70	2.6	.02	*a*
Na/K	15	.246			*b*
	20	.287			*b*
	25	.328	1.22	.006	*c*
	30	.363			*b*
Na/Sr	15	− .59		.01	*d*
	20	− .61		.01	*d*
	25	− .64	−0.22	.01	*d*
	30	− .67		.01	*d*

[a] Present work. [b] Reference 7. [c] Reference 8b. [d] Reference 8a.

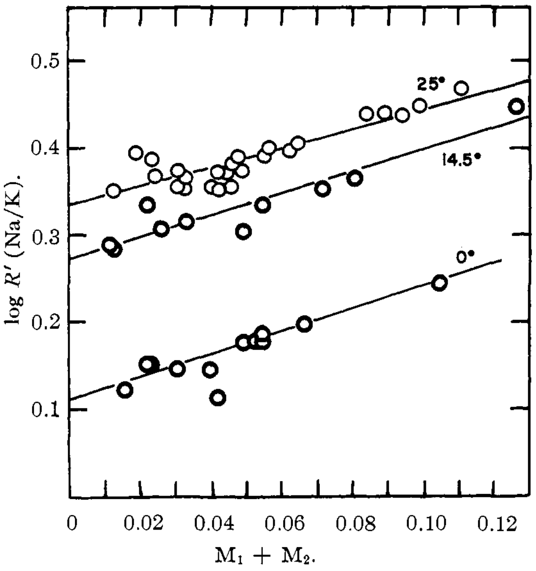

Fig. 1.—Carbonate media.

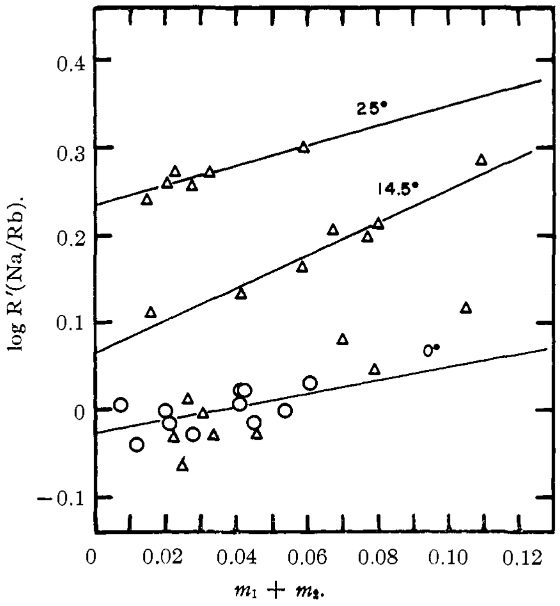

Fig. 2.—Carbonate media O; chloride media Δ.

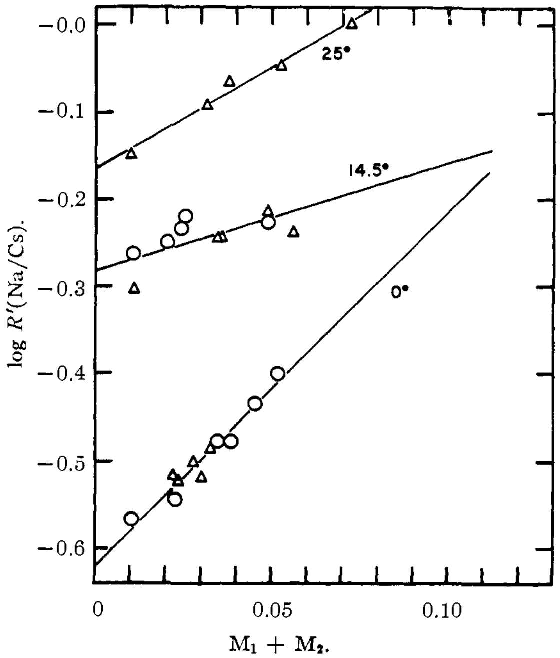

Fig. 3.—Carbonate media O; chloride media Δ.

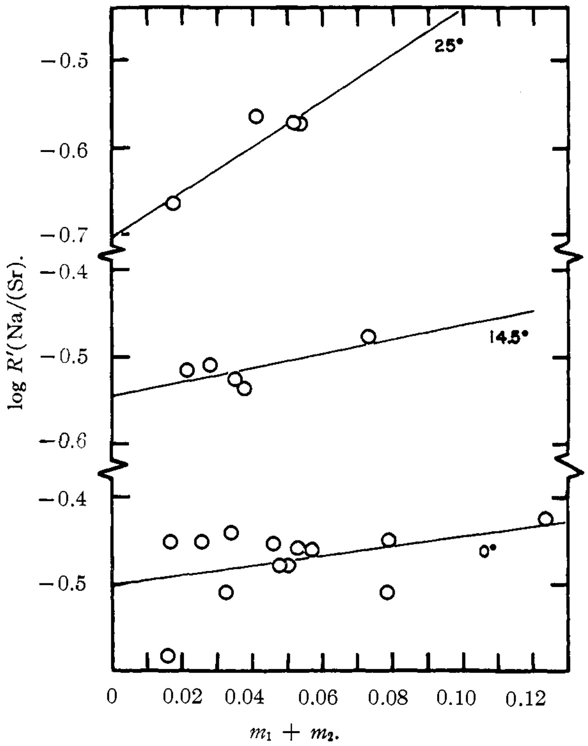

Fig. 4.—Chloride media.

Equilibrium.—The present results are consistent with those of Wells and Smith[8b] in which equilibrium was approached from both directions. Investigation of the approach to equilibrium in connection with the present work indicated that equilibrium was substantially complete within 15 min. (Fig. 5). This refers, of course, to the equilibrium in reaction (1). The oxidation of the amalgams by water was a slower reaction which reached at most 20% of completion during the 20 to 35 minutes allowed for reaction (1).

Aqueous Activity Coefficients.—For the aqueous concentration range employed here, 0.05 to 0.20 *M*, Guggenheim's empirical equation[9] for the ionic activity coefficients

$$\log \gamma_i = -Az_i^2\sqrt{I}/(1+\sqrt{I}) + 2\sum_{x}\beta_{ix}m_{xw} \qquad (4)$$

is sufficiently accurate and will be used for the estimation of the activity coefficients of positive ions. The summation is over all of the negative ions, each of molality m_{xw}, in the solution. The parameter β_{ix} measures the specific interaction between the $M_i^{z_i+}$ ion and the X^{z-} ion, and is supposed to be independent of composition so that it may be determined from the behavior of solutions of a single electrolyte.

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[9] E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, **51**, 747 (1955).

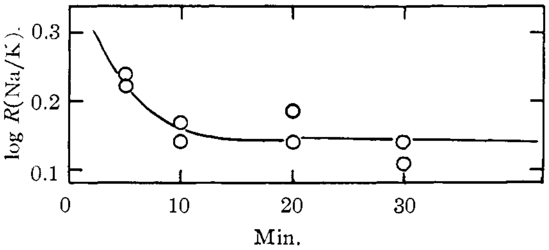

Fig. 5.—Approach to equilibrium, chloride media, 0°; $M_1 + M_2 = 0.022 \pm 0.003$; data obtained by Mr. P. E. Peterson with analysis by a gravimetric method.

In the simplest case, $z_1 = z_2 = 1$ and the aqueous activity coefficient term of eq. 3 is

$$-\log(\gamma_1/\gamma_2) = 2I(\beta_{1x} - \beta_{2x}) \qquad (5)$$

which is independent of m_{1w}/m_{2w} at constant I. Moreover, the correction is small as shown by the β values in Table III. For NaCl–KCl at 25° these lead to 0.044 for the coefficient of I in eq. 5, whereas the data of Smith and Ball[7] and Wells and Smith[8b] yield values of about 0.03. The disagreement is probably not significant since the amalgam partition value depends heavily upon data at $I = 0.2\ M$ and above, and the solutions contain some OH^- which tends to cancel the effect of the Cl^-. For the ionic strengths (*ca.* 0.05 M) employed in the present work it appears that $\log(\gamma_1/\gamma_2) = 0$ within the experimental error, and this has been assumed for the Na/K, Na/Rb and Na/Cs systems in Cl^- media in reducing the data.

However, discrepancies are observed in comparing data for $CO_3^=$ media with those for Cl^- media. It was found that these discrepancies could be resolved by assuming that $\log(\gamma_1/\gamma_2)$ had the values 0.04 for Na/K, 0.03 for Na/Rb and 0.076 for Na/Cs in carbonate media. The Na/K correction is consistent with the approximate values found for Na_2CO_3 and K_2CO_3 (Table III). The assumed $\log(\gamma_1/\gamma_2)$ values are independent of temperature and composition for the small ranges of these variables dealt with here.

TABLE III

THE GUGGENHEIM PARAMETER, β_{ix},[a] FOR AQUEOUS SOLUTIONS, 25°

M^{z+} X^{z-}	Na^+	K^+	Rb^+	Cs^+	Sr^{++}
Cl^-	0.065	0.043	0.026	0.000	0.27[b]
OH^-	.026	.056	...	.152	...
$CO_3^=$	.08[c]	.009[d]	...	...	...

[a] For the calculation of $\log_{10} \gamma_i$. This equals Guggenheim's β divided by 2.303. Values taken from ref. 9 except as noted. [b] Calculated from data of R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948). [c] Calculated from data of C. E. Taylor, *J. Phys. Chem.*, **59**, 653 (1955). [d] Calculated from data given in Landolt-Börnstein, "Tabellen," III Erganzungsband, 1936, T 3, p. 2147.

For the system Na/Sr the situation is less satisfactory because the ion-atmosphere effect no longer cancels out in the activity coefficient ratio. Now the Guggenheim equation yields for the aqueous activity coefficient term of equation 3.

$$\log(\gamma_{Na+}/\gamma_{Sr++}^{1/2}) = A\sqrt{I}/(1 + \sqrt{I}) + (2\beta_{NaCl} - \beta_{SrCl})m_{Cl^-} \qquad (6)$$

In this case the corrections are too large to neglect and have been applied to the data using eq. 6 as a basis but without taking into account the small variation of the correction arising from variation in the $(Na^+)/(Sr^{++})$ ratio at constant ionic strength. Typical values of the correction are: ionic strength/correction to log R, 0.12/–0.116, 0.22/–0.138, 0.25/–0.142, 0.28/–0.144. These corrections were applied to the data of Smith and Braley as well. Smith and Braley[8a] did investigate the dependence of R(Na/Sr) upon aqueous concentration, but only the lower end of the concentration range they investigated was in the range of validity of eq. 7. In this small region of overlap the agreement is satisfactory.

Amalgam Activity Coefficients.—It is observed in both the earlier work and the present work that R' depends upon $m_1 + m_2$, but is independent of m_1/m_2. This is shown by the two sets of data of Table IV, in which the observed log R' is compared with that calculated from the data of Table II. Because of this independence, R' for the alkali metal pairs is a function only of the total amalgam molality and the temperature, as shown in Figs. (1–3). For Na/Sr, R' is also practically independent of the total amalgam concentration, as is shown clearly by the more precise data of Smith and Braley.[8a]

TABLE IV

Na-K, 25°, data of Wells and Smith (each value is the average of 6 runs).

Total amalgam mm.	17.5	16.8	17.3
(Na)/(K)	4.4	2.2	1.1
Log R' obsd.	.345	.343	.343
Log R' calcd.	.348	.349	.349

Na–Cs, 0°, present work

Total amalgam mm.	22.5	23.6	30.8	33.4	28.7
(Na)/(Cs)	0.11	0.21	0.64	2.34	8.25
–Log R' obsd.	.516	.520	.518	0.485	0.499
–Log R' calcd.	.529	.526	.496	.485	.504

Thermodynamic Properties of the Amalgams.—The intercept of each of the curves in Figs. (1) to (4) gives log K and the slope gives α for that system, referring to reaction (1). These constants are recorded in Table II. The ΔF_1^0 values derived from log K are plotted in Fig. 6, giving lines of slope ΔS_1^0. With the aid of literature data[3,4] ΔF_1^0 and ΔS_1^0 at 25° are reduced to values for the reaction

$$M(c) \longrightarrow M(Hg, hyp.\ 1\ M) \qquad (7)$$

and these are presented in Table V.

The activity coefficient function, α, for the ternary amalgams can also be reduced to functions for the binary amalgams by making use of the known activity coefficients of Na amalgams and the theory presented in a later section of this paper. Values of B_{ii} derived in this way are presented in Table V, along with values of the excess functions.

We define the free energy of the real amalgam relative to a hypothetical amalgam of the same concentration, in which Henry's law is obeyed, by

$$F^{rel} = F(\text{real amalgam}) - F(\text{Henry's law amalgam}) \qquad (8)$$

TABLE V

PROPERTIES OF BINARY AMALGAMS

Solute method	Li E.m.f.	Na E.m.f.[c]	K A.P.	K E.m.f.[d]	Rb A.P.	Rb E.m.f.[e]	Cs A.P.	Cs E.m.f.[f]	Sr A.P.
ΔF_7°, kcal., 25°	−20.2[a]	−18.43	−22.85	−22.95	−22.98	−22.84	−26.35	−24.1	−46.62
ΔS_7°, e.u.	1.5[a]	− 5.3	−10.5	−11.6	−15.4		−17.5	−48	−18.0
ΔH_7°, kcal.	−19.8	−20.0	−26.0	−26.4	−27.6		−31.6	−38.9	−52.0
B_{11} 0°	.....	3.190	5.83	6.32	4.7		11.4		....
14.5°	.....	3.102	5.62	6.01	6.8		5.6		....
25°	2.3[b]	3.045	5.27	5.86	5.3		7.75		....
$F^{\rm rel}/m$, kcal., 25°	1.5	2.08	3.9		3.6	.....	5.3	....	....
$S^{\rm rel}/m$, e.u.	.....	− 2	0		80	.....	75	....	....
$H^{\rm rel}/m$, kcal.	.....	− 1.5	7.8		28	.....	28	....	....

[a] G. N. Lewis and F. G. Keyes, THIS JOURNAL, **35**, 340 (1913). [b] G. Spiegel and H. Ulich, *Z. physik. Chem.*, **A178**, 187 (1937). [c] Reference 3. [d] H. E. Bent and E. S. Gilfillan, THIS JOURNAL, **55**, 3989 (1933). [e] G. N. Lewis and W. L. Argo, *ibid.*, **37**, 1983 (1915). [f] H. E. Bent, G. S. Forbes and A. F. Forziati, *ibid.*, 61, 709 (1939).

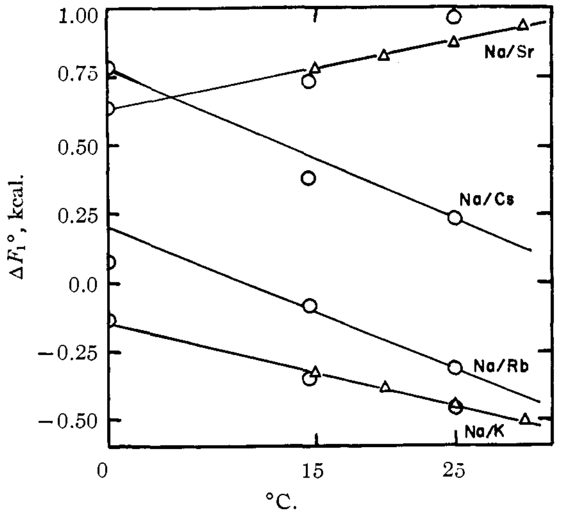

Fig. 6.—Present work O; Smith and co-workers Δ.

In each case F is the total free energy of the quantity of solution containing one mole of solute at the same molality. The amalgam activity coefficients also measure deviations from Henry's law, and we have the relations, for 1 = solute and 3 = solvent, M = kg./mole of solvent

$$F^{\rm rel} = \bar F_1^{\rm rel} + \bar F_3^{\rm rel}/mM = RT \ln f_1 + \bar F_3^{\rm rel}/mM$$

$$m\, d\bar F_1^{\rm rel} + \frac{1}{M}\, d\bar F_3^{\rm rel} = 0$$

which give

$$F^{\rm rel} = 2.303RTB_{11}\, m/2$$

This definition makes $F^{\rm rel}$ a measure of the solute–solute interactions in the dilute solution.[10] The temperature dependence of $F^{\rm rel}$ is shown in Fig. 7, leading to lines of slope $S^{\rm rel}/m$, where $S^{\rm rel}$ is analogous in definition and significance to $F^{\rm rel}$. $H^{\rm rel}$ may be calculated in a similar way and is the relative apparent molal enthalpy of the solution. These quantities are recorded in Table V. It is clear that accurate values of the relative functions, especially $S^{\rm rel}$ and $H^{\rm rel}$ cannot be obtained from these data, but that the trends and extraordinarily large values for the heavier alkali metals are definitely established.

Discussion

Two aspects of these results will be discussed here. One is the solvation of the alkali metals in mercury, derived from the energetics of formation of the amalgams. The second is the solute–solute interaction in amalgams, derived from the activity coefficients. The goal is to interpret both sets of phenomena in terms of a single model for the amalgams.

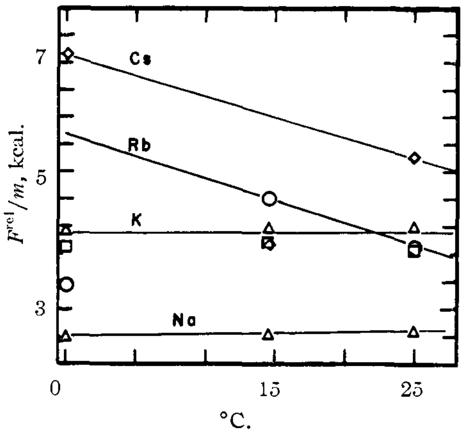

Fig. 7.—Δ, e.m.f. data; □,O,◇, amalgam partition data.

Solvation.—The most striking feature of the energetics of amalgam formation from the elements is the enormous entropy decrease found for the heavier alkali metals.[11] In order to discuss this and other aspects without complications arising from the difference in interaction between the atoms in the various crystalline alkali metals, the energetics of solvation from the gas phase have been calculated from the data of Table V with the aid of values for the energetics of the gaseous species from the NBS Thermochemical Tables.[4] The calculations pertain to the process

$$\mathrm{M(Hg)} \longrightarrow \mathrm{M(g)} \qquad (9)$$

involving the ideal-dilute state in solution, the ideal gaseous state and the same volume concentration in each phase.

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[10] For other uses of the excess functions for dilute solutions see H. S. Frank and A. L. Robinson, *J. Chem. Phys.*, **8**, 933 (1940); G. Scatchard, *Chem. Revs.*, **44**, 7 (1949), and C. Wagner, "Thermodynamics of Alloys," Addison–Wesley Press, Inc., Cambridge, Mass., 1952. The present specialized nomenclature is offered to avoid confusion with functions which measure the excess relative to *ideal* solutions.

[11] First noted for K(Hg) by H. E. Bent and E. S. Gilfillan, THIS JOURNAL, **55**, 3989 (1933).

The Barclay–Butler plot[12] for eq. 9 is shown in Fig. 8. Evidently the expected positive slope is obtained, which in itself is consistent with the formulation of the process as eq. 9, as would be appropriate if the alkali metal were not ionized in the amalgams. A suitable model corresponding to this process would be that in which the electron of the alkali metal serves to bind a number of mercury atoms to the alkali metal ion, binding a larger number of mercury atoms more tightly as we proceed from Na to Cs as the solute. However, on this model it is difficult to understand why Li and Sr lie so far from the other metals on this plot.

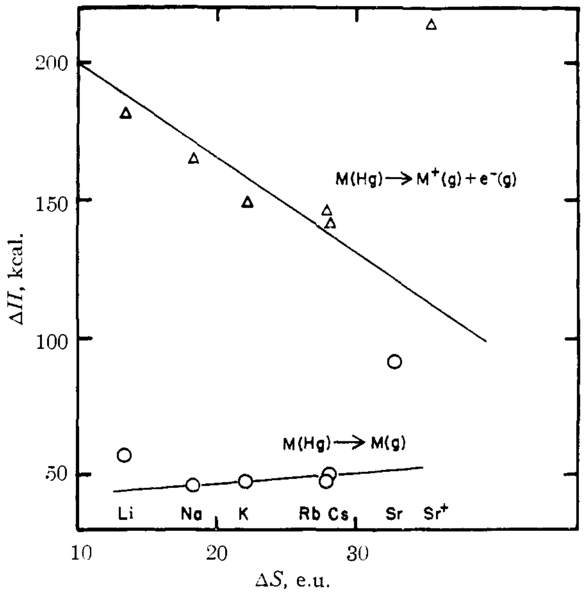

Fig. 8.—Barclay–Butler plots. In the process M(Hg) → M^+ (g) + e^-(g) the translational entropy of the electrons in the gas phase has been neglected in the calculation of ΔS. Unless this is done the calculated ΔS depends upon the choice of the (identical) volume concentration of the two phases at which the calculation is made. ΔS calculated in this way will be the value for the positive ions alone if the entropy of the electrons in the metal phase is approximately zero, as seems usually to be the case.

On the other hand there is independent evidence that the alkali metals are ionized in amalgams. The behavior of the activity coefficients may be understood on this basis, as shown in the following section. Wagner[13] has concluded that the alkali metals are ionized in amalgams by analogy with the behavior of other alloys. The interpretation of the conductivity data is not straightforward, as shown by the observations that addition of Li to Hg causes an increase in conductivity, while addition of K to Hg causes a decrease,[14] but leads to the conclusion[15] that the alkali metals are completely ionized in amalgams. The same conclusion is also reached on the basis of the magnetic properties of the amalgams, since the paramagnetic contribution expected from the un-ionized atoms is not found, even in dilute amalgams.[16]

Because the alkali metals are completely ionized in the amalgams the Barclay–Butler plot should be made of the energetics of the reaction

$$M(Hg) \longrightarrow M^+(g) + e^-(g) \qquad (10)$$

The reason is that M(Hg) is more precisely represented as $M^+(Hg) + e^-(Hg)$. Then the Barclay–Butler plot for eq. 10 (Fig. 8) is essentially a plot for the solvation of the alkali metal ions, the electrons being represented by a constant term in both the entropy and the enthalpy. However, the negative slope which this plot exhibits is contrary to the general theory,[12] which in simplest terms is, the greater the ΔH of desolvation, the stronger the forces binding the solute to the solvent; the stronger these forces, the greater the restriction of motion in the solution and, thus, the greater the ΔS of desolvation.

The anomalous Barclay–Butler plot for reaction (10) suggests that the forces between the solute ions and the solvent do not play a determining role in the generation of the observed entropy trend. A simple (although perhaps extreme) elaboration of the complete ionization model for the amalgams which produces this behavior is one in which the driving force for the solution of the alkali metals in mercury is the solvation of the electrons, with the alkali metal ions dragged into the mercury phase by the forces leading to electroneutrality. This is reasonable if the alkali metal ions exhibit little more affinity than rare gas atoms for the components of the mercury structure, but upon entering the mercury phase disrupt the structure, the more so the larger the alkali metal ion.

This extreme model has the following features which are consistent with the observations. (a) Because ΔH for the desolvation of the positive ions is negative the theory leading to positive slopes for Barclay–Butler plots does not apply. (b) ΔH for reaction (10) shows only a 30% decrease from Li to Cs, implying that the main enthalpy change originates in an effect which is common to all of the alkali metals. By way of contrast, the hydration energy of Li^+ is nearly twice that of Cs^+. (c) The trend in entropy change for reaction (10) indicates that Cs^+ has the greatest disruptive effect on the structure of the liquid mercury, resulting in the greatest loss of freedom of the mercury atoms. The explanation may be similar to that advanced for aqueous solutions of the rare gases,[12] namely, that the unbalance of solvent–solvent molecule forces in the neighborhood of an indifferent solute leads to the formation of solid-like aggregates of solvent in this neighborhood. The analogy of the hydrogen bonding which is the cause of this complicated behavior in aqueous solutions is provided by the directional forces about the mercury atom which are responsible for mercury having a relatively open structure in both the solid and the liquid.[17] (d) This model suggests that the alkali metals in amalgams should be surface-active, because one of the

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(12) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 504 (1945).

(13) C. Wagner, *ibid.*, **19**, 626 (1951).

(14) G. Borelius, in "Handbuch der Metallphysik," G. Masing, Ed., Akademische Verlagsgesellschaft, Leipzig, 1935, Vol. 1, part 1, p. 344.

(15) G. N. Lewis and T. B. Hine, *Proc. Nat. Acad. Sci.*, **2**, 634 (1916); C. Wagner, *Z. physik. Chem.*, **B15**, 347 (1932).

(16) W. Frank and H. Katz, *Z. anorg. Chem.*, **231**, 63 (1937); W. Klemm and B. Hauschulz, *Z. Elektrochem.*, **45**, 346 (1939).

(17) J. S. Lukesh, W. H. Howland, L. F. Epstein and M. D. Powers, *J. Chem. Phys.*, **23**, 1923 (1955).

ionic solute components seeks to escape the phase. It has been reported that the alkali metals in mercury are indeed surface active, and K more so than Na.[18]

In some quantitative respects too, the comparison of the model and the data is satisfactory. Thus if it is assumed that the solvation energy of Li^+ is zero, then the introduction of Cs^+ into the mercury phase is endothermic by some 40 kcal./mole. The amount of mercury "frozen" by a mole of Cs^+ may be estimated as the difference in solvation entropy of Cs^+ and Li^+, 17 e.u., divided by the molal entropy of fusion of Hg, 2.4 e.u., giving 7 moles of Hg frozen. The heat of fusion of Hg is 4 kcal. for 7 moles, so introduction of a mole of Cs^+ into the Hg phase must break Hg–Hg bonds to the extent of 44 kcal., corresponding to the vaporization of 3 moles of Hg. Assuming that in the vaporization of a molecule of Hg, 3 Hg–Hg bonds are broken as a net result (for coördination number 6), then the introduction of a Cs^+ into the Hg phase breaks 9 Hg–Hg bonds. The crystal radius of Cs^+ is 1.69 Å., and the metallic radius of Hg is 1.57 Å.[19] so it is not unreasonable that a Cs^+ breaks somewhat more bonds than if it just displaced one Hg atom, but on the other hand it seems unlikely that it is big enough to break many more than 9 bonds, and therefore it is unlikely that the solvation of Li^+ is very endothermic.

If the solvation energy of Li^+ is zero, the values for the other alkali metals are therefore reasonable, and ΔH for the solvation of the electron is -180 kcal./mole. This is much larger than the energy corresponding to the work function for Hg or any other metal, but it seems that the comparison may not be pertinent.[20] Another difficulty is encountered in the comparison with the solvation in Hg of $Sr^{++} + 2e^-$, for which $\Delta H = -480$ kcal. The use of -180 kcal. for the contribution from one electron leads to -120 kcal. for the ΔH of solvation of Sr^{++}, in striking contrast to the small positive values assumed for the alkali metals. This difficulty has not been resolved.

Solute–Solute Interaction in Amalgams.—The activity coefficient ratios in the amalgams depend upon concentration according to

$$\log (f_1/f_2) = \alpha(m_1 + m_2) \qquad (11)$$

As pointed out above, α is independent of m_1/m_2 as well as of $m_1 + m_2$.

In the binary amalgams which have been investigated by e.m.f. cell methods (Li,[21] Na,[3] K[11]), it is found that

$$\log f_i = B_{ii}m_i \qquad (12)$$

within the experimental error up to 0.1 molal in each case. The form of eq. 12 suggests that in the ternary amalgams the activity coefficients will show the usual[22] concentration dependence

$$\begin{aligned} \log f_1 &= B_{11}m_1 + B_{12}m_2 + \dots \\ \log f_2 &= B_{21}m_1 + B_{22}m_2 + \dots \end{aligned} \qquad (13)$$

with terms of higher powers in the concentrations being of negligible magnitude in the concentration range in which eq. 11 is valid.

If eq. 13 is accepted as valid, useful relations may be derived between the coefficients of equations 11 and 12. As a consequence of the choice of molality concentration scales, it is true[23] that $B_{12} = B_{21}$. Then the following relations are obeyed

$$B_{12} = B_{21} = (B_{11} + B_{22})/2 \qquad (14)$$

$$\alpha = (B_{11} - B_{22})/2 \qquad (15)$$

These relations between the properties of a ternary amalgam and the corresponding binary amalgams differ from the results of a theory proposed by Wagner[13] which leads to

$$B_{12} = B_{21} = \sqrt{B_{11}B_{22}} \qquad (16)$$

instead of (14). In choosing (14) and (15) rather than (16) for the reduction of the data the following points have been considered: (a) The model on which Wagner's theory is based, with only a slight modification, yields (14) instead of (16), as shown below. (b) In the thallium–alkali metal ternary amalgams investigated by Wagner, eq. 16 does give a much better correlation with binary amalgam properties than (14). (c) Equation 16 is incompatible with the observation that α is independent of m_1/m_2 in the alkali metal ternary amalgams. Referring to Table IV, Wagner's theory leads one to expect log R'(Na/K) to vary by 0.025 unit for the range of m_1/m_2 investigated, and log R'(Na/Cs) to vary by more than 0.06 unit. In both cases the observed erratic variation of log R', which is attributed to the imperfection of the experiments, is considerably less than the uniform variation expected from this theory.

The "A.P." B_{ii} values in Table V have been evaluated from the experimental data by means of eq. 15 and the B_{11} values for Na amalgams calculated from the data of Bent and Swift.[4] The other "e.m.f." B_{ii} values in Table V have been provided for comparison.

The structural interpretation of these data requires an atomistic theory of the amalgams. Wagner's suggestion that a modified Brönsted specific action principle applies to the ion–electron interaction is adopted here. Wagner also assumed that the activity coefficient of each solute depends only upon the chemical potential of the electrons, and that this is, in turn, determined by the concentrations of the solutes. His result (eq. 16) is also obtained if it is assumed that the activity coefficients of the solutes depend only upon the *concentration* of the electrons, and this is determined by the concentrations of the solutes. But eq. 14 is obtained if we formulate the chemical potentials in the way appropriate to completely dissociating solutes (for the alkali metals as 1–1 electrolytes)

$$\begin{aligned} \mu_1 = \mu_{1+} + \mu_{e-} = \mu_1^\circ + RT(\ln m_1 + \ln \bar{\gamma}_1 + \\ \ln(m_e/m_e^\circ) + \ln \bar{\gamma}_e) \\ \mu_2 = \mu_{2+} + \mu_{e-} = \mu_2^\circ + RT(\ln m_2 + \ln \bar{\gamma}_2 + \\ \ln(m_e/m_e^\circ) + \ln \bar{\gamma}_e) \end{aligned} \qquad (17)$$

The concentration of electrons in pure Hg is m_e°,

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[18] R. J. Johnson and A. R. Ubbelohde, *Proc. Roy. Soc.* (*London*), **A206**, 275 (1951); P. P. Pugachevich, *C. A.*, **47**, 8443 (1953); L. Convers, *J. chim. phys.*, **36**, 175 (1939).

[19] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

[20] E. A. Guggenheim, "Thermodynamics," North Holland Publishing Co., 1950, p. 332.

[21] G. Spiegel and H. Ulich, *Z. physik. Chem.*, **A178**, 187 (1937).

[22] H. L. Friedman, *J. Phys. Chem.*, **59**, 161 (1955).

[23] H. A. C. McKay, *Trans. Faraday Soc.*, **49**, 237 (1953).

and this appears in eq. 17 because the form of the empirical activity coefficient, eq. 12, makes it convenient to choose pure Hg as the standard state for the electrons rather than hyp. 1 molal solution. In addition the following assumptions are made

$$m_e = m_e^\circ + m_1 + m_2 \tag{18}$$

$$\ln \bar{\gamma}_1 = b_{1e}(m_e - m_e^\circ),\ \ln \bar{\gamma}_2 = b_{2e}(m_e - m_e^\circ),$$
$$\ln \bar{\gamma}_e = b_{e1}m_1 + b_{e2}m_2 + b_{ee}(m_e - m_e^\circ) \tag{19}$$

The assumptions of eq. 19 have been formulated by analogy with the Brönsted specific action principle for aqueous solutions of electrolytes,[9] except for the b_{ee} term, which represents the electron–electron interaction resulting from the operation of Fermi–Dirac statistics.[24] An ionic strength term does not appear in these formulas because of the presumably high and nearly constant value of the ionic strength in dilute amalgams, although it has been suggested that such an effect may be of importance in other types of metallic solutions.[25] Further simplification may be achieved by noting that $b_{e1} = b_{1e}$ and $b_{e2} = b_{2e}$ are required by the McKay relations[23]

$$\partial \ln \bar{\gamma}_i / \partial m_j = \partial \ln \bar{\gamma}_j / \partial m_i$$

which apply to charged as well as neutral components of a system.

The stoichiometric coefficients may then be calculated for the case, $m_1 + m_2 \ll m_e^\circ$

$$\ln f_1 = \frac{\mu_1 - \mu_1^\circ}{RT} - \ln m_1 = (2b_{e1} + b_{ee} + 1/m_e^\circ)m_1 + (b_{e1} + b_{ee} + b_{e2} + 1/m_e^\circ)m_2 \tag{20}$$

$$\ln f_2 = \frac{\mu_2 - \mu_2^\circ}{RT} - \ln m_2 = (b_{e1} + b_{ee} + b_{e2} + 1/m_e^\circ)m_2 + (2b_{e2} + b_{ee} + 1/m_e^\circ)m_2$$

Equations 20 are of the form of eq. 13, and the values of the coefficients are consistent with eq. 11, 14 and 15, as may easily be verified.

This agreement with experiment is not obtained if the model is generalized to allow for incomplete ionization of the solutes or direct positive ion interaction. On the other hand terms involving solute–ion *vs.* mercury–atom or –ion interaction have the same form as those for solute–ion *vs.* electron, and if such additional interactions exist, they are included in the interaction coefficients already formulated.

Finally we obtain for the binary amalgams

$$F^{\mathrm{rel}} = RT(2b_{e1} + b_{ee} + 1/m_e^\circ)m/2 \tag{21}$$

We can use this equation to test the consistency of the model and the observations if we calculate values of the coefficients b_{e1} and b_{ee} from the model. A rough mathematical approximation is made by using the equation for the chemical potential of an electron gas at 0°K.

$$\mu_e = 600\,V^{-2/3}\ \text{kcal./mole} \tag{22}$$

which is nearly unchanged from 0° to 300°K.[26] In this equation, V is the molar volume of the gas in cc. The effect of the potential fields in the metal is neglected. The effective volume, **V**, available to the electrons is an extensive property so we have

$$\mathbf{V} = n_1 V_1 + n_3 V_3 \tag{23}$$

in which V_i is defined as $(\partial \mathbf{V}/\partial n_i)_{n_j}$, and n_1 and n_3 are numbers of moles of solute and solvent, respectively. Then the molar volume of the electron gas in the amalgam is

$$V = (m_1 V_1 + V_3/M)/m_e \tag{24}$$

where M is kg./mole of solvent. Substitution of (24) into (22) and differentiation yields expressions for b_{ee} and b_{e1} which, for low solute concentration and constant V_1 and V_3, reduce to

$$b_{ee} = (2\mu_e^\circ/3RT - 1)/m_e^\circ \tag{25}$$

$$b_{e1} = -2\mu_e^\circ V_1 M/3RTV_3 \tag{26}$$

The following values of the parameters are assumed: m_e° = 1 mole/kg. M/V_3 = 0.013 kg./cm.³, the density of Hg. $-V_1$ = molal volume of the positive ions of the solute, calculated from crystal radii. (It is assumed that the space occupied by these ions is not accessible to the electrons.) Then μ_e°, the value obtained from eq. 22 for pure Hg is 33 kcal./mole and RTb_{ee} = 21 kcal./mole molal. The remaining results are shown in Table VI.

TABLE VI

CALCULATION OF F^{rel}

Solute	Li	Na	K	Rb	Cs
$V_.$, cm.³/mole	−0.6	−2	−6	−8	−11
RTb_{e1}, kcal.	0.2	0.6	1.7	2.2	3.1
F^{rel}/m, kcal.	11.2	11.6	12.7	13.4	14.5

These results indicate that activity coefficients of the magnitude and solute dependence found may be consistent with the complete dissociation model, which in other respects also is consistent with the data. Although a more quantitative comparison of the results of such a crude calculation with the data would not be significant, the calculation suggests that the large deviations from Henry's law arise from the fact that the electrons, which are a component of the solute as well as the solvent, obey Fermi–Dirac statistics, and that the solute dependence is caused by the compression of the electron gas by the solute ions which, having noble gas electron structures, are relatively repellent to it.

These effects, according to this calculation, lead to temperature independent values of F^{rel} and to judge by other applications of the electron gas model to metals, inclusion of potential energy effects will not change this. Thus, the large values of S^{rel} which are observed for the heavier alkali metals would probably not be calculated from this model even if the potential field from the positive ions were accounted for. However, the explanation given for the solvation entropies of the alkali metals, involving frozen patches of solvent around the solute ions, suggests that if these frozen patches interfere with each other, S^{rel} will increase as the concentration increases, as observed. Such a structural effect does not seem to be inconsistent with the model, although it does reduce its simplicity.

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(24) The necessity of accounting for this effect by a separate term was pointed out to the authors by Prof. Carl Wagner.

(25) N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys," Oxford University Press, London, 1936, pp. 86 ff.

(26) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1940.