Ytterbium.—Blumenfeld and Urbain,[1] in a series of analyses of the sulfate $Yb_2(SO_4)_3.8H_2O$, find Yb = 173.54. This may be rounded off to 173.5.

Uranium.—Hönigschmid,[2] from analyses of the bromide UBr_4, finds U = 238.18. The value 238.2 may properly be adopted.

At the meeting of the International Congress of Applied Chemistry, in 1912, a resolution was passed favoring delay in changes in the table of atomic weights. In accordance with the desire so expressed, no changes have since been made, but several now seem to be necessary. These relate to C, S, He, Sn, Pb, Ra, U, Yt, Pr, Yb, Lu, and U. The reasons for the changes, which are small, may be found in this and the three preceding reports. They are based upon new determinations, which seem to be better than the old.

(Signed) F. W. CLARKE,
T. E. THORPE,
W. OSTWALD.

NOTE.—Professor Urbain, because of an official connection with the military service of France, is debarred from signing any international report during the war. Otherwise he would approve this report.

F. W. C.

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

THE VAPOR PRESSURE OF THALLIUM AMALGAMS.

BY JOEL H. HILDEBRAND AND ERMON DWIGHT EASTMAN.

Received September 3, 1915.

The work presented in this paper is in continuation of the series of investigations undertaken by one of us on the laws of concentrated solutions. The previous papers include vapor pressure measurements on zinc,[3] silver,[4] gold,[4] and bismuth[4] amalgams, and also a discussion of e. m. f. measurements to be found in the literature on the amalgams of zinc, tin, lead, thallium, indium and cadmium.[1] We would refer to the earlier papers for the progress of the work up to this point, as well as for references to the literature.

The experimental procedure was essentially the same as that used in working with bismuth amalgams, so that it is unnecessary to repeat its description here. The thallium used was analyzed for lead, two experiments giving 0.3% and 0.25%, respectively, an amount of impurity far too small to have any effect on these measurements.

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[1] *Compt. rend.*, **159**, 325.

[2] *Z. Electrochem.*, **20**, 452.

[3] J. H. Hildebrand, *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, **22**, 139, 147; *Trans. Am Electrochem. Soc.*, **22**, 319, 335 (1912); THIS JOURNAL, **35**, 501 (1913).

[4] Ermon D. Eastman and J. H. Hildebrand, THIS JOURNAL, **36**, 2020 (1914).

The results of the measurements are summarized in Table I. Under *n* in the third column, are given values of the number of mols of mercury per mol of thallium. (In previous papers this ratio was denoted by *N*. The desirability of using the large letter for the mol-fraction, here $n/(n + 1)$ has suggested the present change.) The letters p and p_0 denote the vapor pressure of mercury over the amalgam and over pure mercury, respectively. Instead of giving the individual readings of the pressures, a number of which were made at each concentration, we report the number of these observations and the "probable error" of the mean values given in the table calculated by the usual formula.

Thallium amalgams are especially interesting because of the existence of one, and, so far as is known, only one compound in the solid state. The freezing-point measurements of Kurnakow[1] show very clearly the separation of a solid compound of the composition $TlHg_2$. We may conclude, furthermore, from the absence of a peak to the melting point curve for this compound, that it is considerably dissociated in the liquid amalgam. The addition of either mercury or thallium to the liquid having a composition corresponding to $TlHg_2$ fails to lower its freezing point very much, indicating that the substance added is already present to a large extent in the liquid, and hence a further addition does not produce the increase in concentration that would be produced if the compound were but slightly dissociated. The existence of $TlHg_2$ in dilute liquid amalgams has been further concluded by G. McP. Smith[2] on the basis of the rate of diffusion of thallium in mercury. However, the application of Raoult's law to the e. m. f. of dilute amalgams has been shown by one of us[3] to indicate the existence of $TlHg_6$, breaking down in some way as the amalgams become more concentrated.

TABLE I.

Wt. Tl.	Wt. Hg.	n.	$n/n + 1$.	No. of obs.	Temp.	p/p_0 obs.	Prob. error.	p/p_0 calc.
1.673	36.408	22.1	0.957	6	329.0	0.955	0.0003	0.952
1.163	18.70	16.35	0.942	5	327.4	0.938	0.0004	0.935
1.673	17.68	10.74	0.915	5	328.3	0.901	0.0004	0.901
1.163	9.554	8.35	0.893	5	327.5	0.875	0.0004	0.874
3.207	16.10	5.12	0.836	5	322.9	0.803	0.0003	0.803
3.207	9.069	2.87	0.742	5	327.5	0.690	0.0003	0.691
4.162	8.097	1.978	0.664	5	326.1	0.602	0.0004	0.603
3.207	5.029	1.590	0.614	5	327.6	0.548	0.0005	0.550
7.390	7.196	0.990	0.497	6	325.2	0.433	0.0006	0.433
7.720	4.033	0.531	0.347	10	327.1	0.293	0.0011	0.293
7.221	1.796	0.253	0.202	8	324.0	0.166	0.0016	0.166

It will be seen from the measurements in Table I, and from their graphic

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[1] *Z. anorg. Chem.*, **30**, 86 (1902).

[2] THIS JOURNAL, **36**, 847 (1914).

[3] *Loc. cit.*

representation in Fig. 1, that the relative vapor pressures of the amalgams, p/p_0, are always less than the apparent mol-fraction of mercury in the amalgam, instead of equal to it, if Raoult's law held in its simplest form. The deviation is in the direction that we should expect if a compound were formed reducing the mol-fraction of free mercury. If the formation of $TlHg_2$ in the liquid were complete, then there would be $n - 2$ mols of free mercury and Raoult's law would give $p/p_0 = (n - 2)/(n - 1)$. This equation makes p/p_0 much less than is found by experiment, so that we next assumed that this same compound is formed partially. Representing by z the number of mols of $TlHg_2$ formed from 1 mol of thallium and n mols of mercury, we would have present in the solution $1 - z$ mols of thallium and $n - 2z$ mols of mercury, the total number of mols being $n - 2z + 1$. Since the three substances are in equilibrium according to the equation $Hg + 2Tl = TlHg_2$, we can apply the mass-law, using mol fractions for concentrations, obtaining the equation

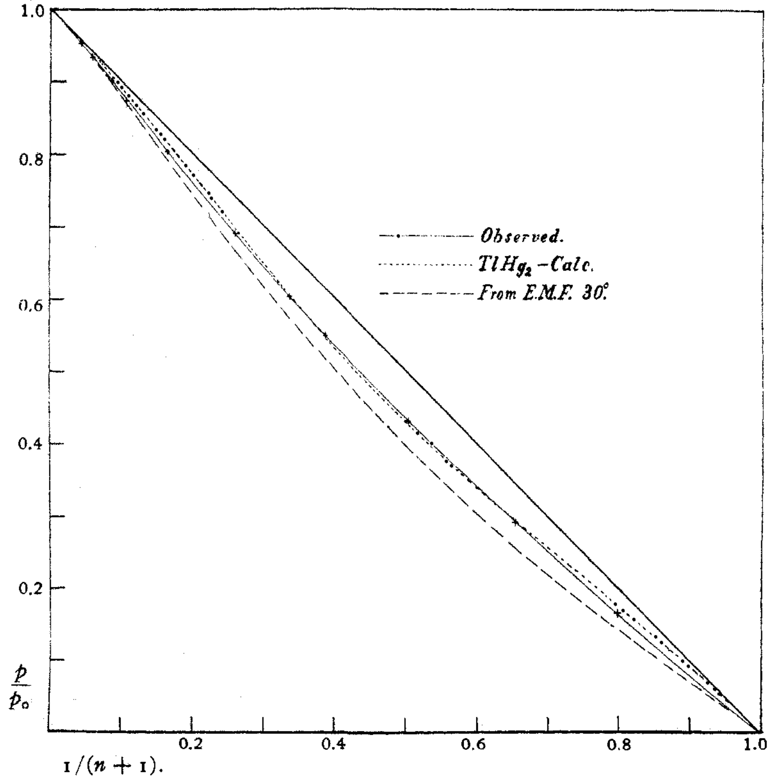

Fig. 1.

$$(1 - z)(n - 2z)^2 = Kz(n - 2z + 1)^2 \qquad (1)$$

By Raoult's law in its corrected form we have

$$\frac{p}{p_0} = \frac{n - 2z}{n - 2z + 1}. \qquad (2)$$

From these two equations it is possible to eliminate z, giving p/p_0 in terms of K and n. It is mathematically simpler, however, to assign values to z and solve separate simultaneous equations for p/p_0 and n. For this purpose we can combine the above equations, obtaining

$$\frac{p}{p_0} = \frac{Kz}{1 - z},$$

and to get n we can transpose Equation 2, getting

$$n = 2z + \frac{1}{(p_0/p) - 1}.$$

In Fig. 1 the dotted curve gives the resulting values putting K = 1.3. It is obvious that there is an approximate, but by no means perfect, agreement with the experimental values. The actual pressures are less than given by the equation, probably at the concentrated, and certainly at the dilute, end of the curve. A change in the value assumed for K would not help matters. Making the curve fit at the ends would throw it off at the middle.

It is not unreasonable, however, that there should be this deviation from the simple assumption of $TlHg_2$. The well-known analogy between thallium and the alkali metals makes it natural to consider the possibility of compounds containing more mercury than $TlHg_2$, for in addition to the very stable $NaHg_2$ and KHg_2, there exist solid compounds containing several more atoms of mercury per atom of alkali metal. It is not unlikely, therefore, that some higher thallium-mercury compound exists in the liquid amalgam, and it may be added that the freezing-point measurements of Kurnakow are not numerous enough to exclude even the possibility of its existence in the solid form. The existence of, say, $TlHg_5$, would explain the deviation from the calculated curve in the dilute amalgams.

A quite different explanation would be that Raoult's law, even when modified to account for chemical reactions in the solution, is not able to express the vapor pressure accurately. This kind of deviation has been discussed in connection with bismuth amalgams, also in a paper by one of us on the entropy of vaporization,[1] and will be again referred to later.

It is very important to compare the results of the above vapor pressure measurements with the measurements of the e. m. f. between thallium amalgams of different concentration, published by Richards and Wilson,[2] and Richards and Daniels.[3] The evidence as to the constitution

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[1] Joel H. Hildebrand, THIS JOURNAL, **37**, 970 (1915).

[2] *Pub. Carnegie Inst. Wash.*, **118**; *Z. physik. Chem.*, **72**, 129 (1910).

[3] *Trans. Am. Electrochem. Soc.*, **22**, 343 (1912).

of thallium amalgams afforded by the former measurements has been already presented by one of us[1] by a method which may be outlined briefly as follows:

If one mol of thallium combines with m mols of mercury in an amalgam containing, altogether, one mol of thallium and n mols of mercury, then there would be present $n - m$ mols of free mercury and one mol of compound, or a total of $n - m + 1$ mols. Applying Raoult's law to this we get

$$\frac{p}{p_0} = \frac{n - m}{n - m + 1}. \tag{3}$$

Now, it has been shown in the first papers on amalgams that the following exact equation applies to the e. m. f. of concentration cells of this type:

$$\nu EF = RT \int n \, d \ln p \tag{4}$$

Here ν denotes the valence of the metal dissolved in the mercury. The other letters have their usual significance in this connection. Integrating this with the aid of the preceding relation between n and p we obtain the expression

$$\nu EF = RT \, m \ln \frac{n_2 - m}{n_1 - m} - RT(m - 1) \ln \frac{n_2 - m + 1}{n_1 - m + 1}. \tag{5}$$

This formula has been applied to the measurements of Richards and Wilson in the earlier papers, and has been shown to give very good agreement when m is 5 or 6, indicating the presence of $TlHg_5$ or $TlHg_6$ in the most dilute amalgams. Since then, however, the single measurement reported by Richards and Daniels has been considered. They find, at 30°, an e. m. f. of 76.3 mv. between a pair of amalgams containing 3.736% and 21.722% of thallium, respectively. Calculated by the equation for an ideal solution,

$$\nu EF = RT \ln \frac{n_2 + 1}{n_1 + 1},$$

this should be 40.0 mv., and calculated for $TlHg_2$, by putting $m = 2$ in Equation 5, we get 81.0 mv. We could conclude from this evidence that in the most concentrated amalgams even $TlHg_2$ is somewhat dissociated.

Where several partly dissociated solvates exist together in solution the application of Raoult's law to the integration of Equation 4 becomes exceedingly complicated, and with no external evidence for the formula of any of these solvates except $TlHg_2$, any such calculation would not be worth the time and labor it would involve.

It is possible, however, to make a further and exact comparison between vapor pressure and e. m. f. data, and we shall find that the devia-

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[1] Hildebrand, This Journal, **35**, 501 (1913).

tion from Raoult's law is of the same type in both cases, the difference being due only to the difference in temperature at which the two sets of measurements were carried out.

In the discussion of the results with bismuth amalgams we have shown that the equation of Van Laar[1] for the vapor pressure of liquid mixtures can be used very satisfactorily as an empirical equation, probably to fit any type of vapor pressure curve. We will write it as follows:

$$\frac{p}{p_0} = \frac{n}{n+1} e^{\frac{b}{(1+cn)^2}} = \frac{n}{n+1} 10^{\frac{a}{(1+cn)^2}} \tag{6}$$

where a, b, and c are constants and e the base of natural logarithms. It was found that the observed vapor pressures were given very closely indeed on putting $a = -0.0960$ and $c = 0.263$ in this equation. The values shown in the last column of Table I were thus obtained and may be regarded as the "smoothed out" observations given in the seventh column of the same table. The close agreement attests the accuracy of the experimental work. If this form of vapor pressure equation is used to integrate the fundamental e. m. f., Equation 4, one obtains the following equation:

$$\nu EF = RT \ln \frac{n_2+1}{n_1+1} + 0.4343 \frac{a}{c} RT \left[\frac{1+2cn_2}{(1+cn_2)^2} - \frac{1+2cn_1}{(1+cn_1)^2}\right] \tag{7}$$

This equation is found to fit the results of Richards and his co-workers very accurately when we take $a = -0.1791$ and $c = 0.345$, the simplified expression being then, for 30°,

$$E = 0.06012 \log \frac{n_2+1}{n_1+1} + 0.06069 \left[\frac{1+0.69n_1}{(1+0.345n_1)^2} - \frac{1+0.69n_2}{(1+0.345n_2)^2}\right]$$

The first term of the right-hand member of this equation represents the e. m. f. of the ideal solution, obeying Raoult's law in its simplest form.

TABLE II.

% Tl.	n.	E (mv. at 30°). Observ.	E (mv. at 30°). Calc.
0.1575	644.6		
		10.09	10.39
0.2294	442.3		
		22.61	22.61
0.5249	192.7		
		37.13	37.07
1.846	54.08		
		...	...
3.736	26.204		
		76.31	76.32
21.722	3.6649		

The figures in Table II give the results in millivolts between each pair of concentrations.[2] It will be seen that the agreement between the calculated and observed values is excellent throughout the entire range of

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[1] *Z. physik. Chem.*, **72**, 723 (1910); **82**, 599 (1913).

[2] A slight error made throughout in the values for n in the earlier papers has been here corrected, which accounts for the slight differences. The influence on the values for e. m. f. is negligible.

concentration represented by the data. The graphic comparison is perhaps more striking, as given in Fig. 2. The four curves give the deviation of the e. m. f. from Raoult's law according to the assumption of complete formation, first, of $TlHg_6$, second, of $TlHg_2$, third, according to the actual measurements from the Harvard laboratory at 30°, and fourth, calculated from the values of a and c which fit the vapor-pressure measurements at 327°.

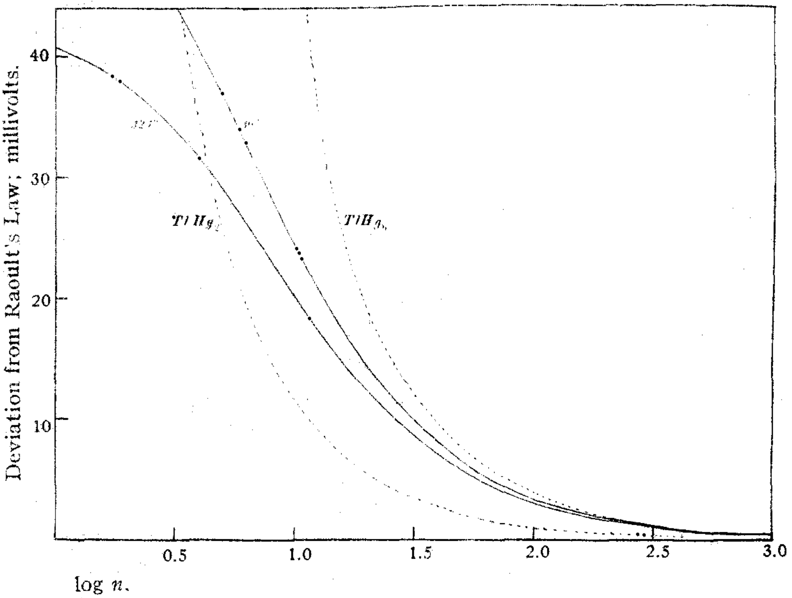

Fig. 2.

By means of empirical Equation 6 we can also plot the vapor-pressure curve which would be obtained at 30°, using for the purpose the values of a and c which give the e. m. f. curve at that temperature, according to Equation 7. The result is seen in the broken curve in Fig. 1. The difference between the curve at high and at low temperature, as would be expected, is in the direction of greater solvation at the lower temperature. The substantial agreement as to type justifies the belief that we now have, at both temperatures, very accurate information on both the vapor pressure and the free energy of dilution of thallium amalgams.

One more fact remains to be pointed out in connection with the e. m. f. equation. In previous publications objection has been made to the Cady equation

$$\nu EF = RT \ln \frac{c_2}{c_1} + U,$$

where U is the heat of dilution, on the ground that any exact correction must be made by altering the term RT ln c_2/c_1 so as to make it an exact expression of the free energy of dilution, as is the case with the term we have used,

$$\nu \mathrm{RT} = \int n\, d \ln p.$$

It is hard to see how the integration of this could give any such expression as is found in the Cady equation. It must be noted, however, that, contrary to first impressions, the logarithmic term need not be the only one resulting from the integration of the differential. If the vapor-pressure equation used to connect p and n in making the integration contains an exponential term, as is the case with the van Laar equation (6), then an equation of the Cady type is obtained. It is important to note that the van Laar equation and the Cady equation are equivalent to each other, for the exponent in the van Laar equation is intended as an expression for the partial heat of dilution. From the exhaustive tests of the Cady equation by Richards and his co-workers it is evident that this equation, and therefore the van Laar equation as well, corrects for part, but not all, of the deviation from the simple law of the ideal solution. In fact, it would be rather surprising if these equations were to be found exact, as the correcting term should undoubtedly be a free energy term and not a heat term, the other terms being free energy terms. That this is true of the van Laar equation will be more evident if it is written in the equivalent form,

$$\mathrm{RT} \ln p/p_0 = \mathrm{RT} \ln \mathrm{N} + \Delta\overline{\mathrm{H}},$$

where $\Delta\overline{\mathrm{H}}$ is the partial molal heat of mixing.

In conclusion, it may be announced that one of us is testing a new equation which promises to form the necessary addition to the previous treatment by means of Raoult's law which will make possible an adequate treatment of the theory of solutions. The new expression uses a work term in place of the heat term, the work being that done by expansion against the internal pressure K, when one mol of a liquid having a molal volume, V, in the pure state is mixed with an infinitely large amount of solution in which its molal fraction is N and its partial molal volume is $\overline{\mathrm{V}}$. The equation may be written either

$$\mathrm{RT} \ln \frac{p}{p_0} = \mathrm{RT} \ln \mathrm{N} + \mathrm{K}(\overline{\mathrm{V}} - \mathrm{V}),$$

or

$$\frac{p}{p_0} = \mathrm{N}e^{\frac{\mathrm{K}}{\mathrm{RT}}(\overline{\mathrm{V}} - \mathrm{V})}$$

Experimental proof of the value and scope of this equation will be deferred till a future publication.

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