The hydration of curd fibers of sodium palmitate, salted out by saturated sodium chloride, was again confirmed, using urea, as two moles of water to one equivalent of soap.

Thick cellophane membranes kept at 90° tend to become impermeable even toward ordinary ions.

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The Surface Tension of Mercury and of Water in Contact with Saturated Vapors of Organic Liquids[1]

BY F. E. BARTELL, LEE O. CASE AND HENRY BROWN

Introduction

It was predicted by Gibbs[1a] that if the surface tension of mercury were measured in contact with a saturated vapor of another liquid, as with water vapor, the value of this surface tension would be equal to the interfacial tension of mercury against liquid water (σ_{12}) plus the surface tension of liquid water in contact with its own vapor (σ_{23}). If σ_{13} be taken to represent the value of the surface tension of mercury against the saturated vapor of the other liquid, then

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \tag{1}$$

This relation obtains because a film of liquid is adsorbed or is condensed on the mercury from the saturated vapor. Gibbs believed that at saturation vapor pressures the condensed film would be of such thickness that its interior would have the properties of a phase in mass.

The thermodynamic condition that governs the application of equation (1) is that the surface tension of the mercury in the presence of its own vapor, σ_1,[2] must be greater than the sum of σ_{12} and σ_{23}.

Previous Results for Films on Mercury.—The experimental data previously used by Iredale[3] to test equation (1) for mercury surfaces indicate that this equation holds for saturated water vapor in contact with mercury but not for other saturated vapors against mercury. The measured surface tension value of mercury in the presence of the saturated vapor was in every case (except for water) greater than the sum of the interfacial

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[1] The material presented in this paper is from a portion of a dissertation submitted by H. Brown to the Graduate School of the University of Michigan, in partial fulfilment for the Degree of Doctor of Philosophy, 1932.

[1a] Gibbs, "Collected Works of J. Willard Gibbs," Longmans, Green and Co., New York, 1928 Vol. I, p. 235, *cf.* p. 258.

[2] In the designation of surface and interfacial tensions, the use of the symbol σ with two numbers for a subscript represents the surface or interfacial tension between two phases mutually saturated with each other and in equilibrium in contact with each other. In case only one number appears as a subscript, the symbol then stands for the surface tension of a pure liquid in contact with its own vapor and air.

[3] Iredale, *Phil. Mag.*, [6] **49**, 603 (1925).

tension value of mercury against the other liquid, and the surface tension value of the liquid, *i. e.*, $\sigma_{13} > \sigma_{12} + \sigma_{23}$. For benzene the measured value, σ_{13}, was greater by 3.1%, for methyl acetate 4.3%, for ethyl alcohol 7.5%, and for methyl iodide 3.0%. These deviations were considered to be greater than could be accounted for by experimental error.

Iredale[3] attempted to explain these results on the basis that Gibbs deduced his relation on the assumption that the films formed on the surface from the saturated vapors were sufficiently thick to have the properties of a phase in mass, whereas the films actually formed were probably monomolecular in thickness and that it did not follow that the tension of such films would be the same as that of liquid in mass (*i. e.*, σ_{13} would not necessarily equal $\sigma_{12} + \sigma_{23}$).

The fact that for all but the water system, $\sigma_{13} > \sigma_{12} + \sigma_{23}$ indicates that from the thermodynamic standpoint equilibrium was attained with the water films and not with films of other liquids.

In searching for causes for the discrepancies, it seemed to us possible that traces of capillary active impurities might have been present in the various liquids used. This would be especially serious in the determination of σ_{12} values since very minute traces of an impurity capable of reacting with the mercury surface can cause an appreciable lowering of the interfacial tension. The fact that water can be more readily obtained in a pure state than can the other liquids mentioned, seemed significant. Another possible source of error might lie in the effect of temperature variations. It is true that so far as the measurements of σ_{12} are concerned, variations of even two or three degrees would be of little effect owing to the small temperature coefficient (about 0.2 dyne per degree)[4]. But in the measurement of σ_{13} isothermal conditions are obviously necessary in order that no evaporation or condensation with respect to the film shall be brought about by temperature differences in the system.

It seemed advisable to carry out new measurements of σ_{12} and σ_{13} using liquids that could be obtained in a very pure state and which were known to be without chemical action on the mercury. The method which was selected as the most reliable for the measurements with mercury was the drop weight method as developed by Harkins and co-workers and as used with mercury by Harkins, Grafton and Ewing,[5] by Iredale[6] and by Micheli.[7]

Experimental Work with Films on Mercury

The measurements of the surface tension of mercury in the presence of the saturated vapors (σ_{13}) were carried out at the same time as the interfacial tension measurements for mercury in contact with the liquids (σ_{12}). In both cases the drop weight method was employed.

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(4) Harkins and Ewing, THIS JOURNAL, **42**, 2539 (1920).

(5) Harkins and Grafton, *ibid.*, **42**, 2534 (1920); Harkins and Ewing, *ibid.*, **42**, 2539 (1920).

(6) Iredale, *Phil. Mag.*, [6] **45**, 1088 (1923); **48**, 177 (1924).

(7) Micheli, *ibid.*, [7] **3**, 895 (1927).

The *interfacial* tension measurements have already been described in a previous paper.[8] The measurements of the *surface* tension of the mercury in the presence of the saturated vapors of the organic liquids were carried out in the following manner. Two or three drops of the pure organic liquid were distilled directly into two of the drop weight apparatus cups which were then covered with ground-glass plates and allowed to stand for about one hour in the thermostat before measurements were started. The drop weight apparatus was provided with a small bulb[9] in which a few drops of the liquid could be placed to aid in saturating the vapor space.

In making the measurements of σ_{13} it is very important to place the drop weight apparatus cup in position with a clamp (a test-tube clamp is convenient) because the heat of the hand would cause vaporization of liquid with subsequent supersaturation and condensation on the cooler portions of the apparatus, *i. e.*, on the tip and the drop. This, of course, would cause erratic results and would completely invalidate the measurement. Even if the hand is touched for a moment to the cup a blur appears on the tip showing condensation due to distillation.

Seven or eight drops were usually collected in each cup. The drops were allowed to form in the course of about three minutes and then by lowering the head of mercury by means of a ratchet and pinion they were allowed to detach in the course of about two minutes.

In the measurements of σ_{13}, the surface tension of mercury against saturated vapors, it was found that while the organic vapors condensed very readily on the mercury to give the tension equal to $\sigma_{12} + \sigma_{23}$, in the case of water vapor it was necessary to allow the drops of mercury to form very close to the water surface in the cup, and to allow about five minutes for the detachment of the drop after it had formed. By operating in this manner reproducible results were obtained and the measurements of σ_{13} for water gave the value equal to $\sigma_{12} + \sigma_{23}$. Iredale had already made the observation that water vapor did not readily condense on mercury surfaces. Very recently Cassel and Salditt[10] found that the surface tension of mercury when measured in the presence of different partial pressures of water vapor in the absence of air at 50° remained unaffected (*i. e.*, the same as *in vacuo*), even when the water vapor pressure was 62 mm.

The method of purification of the liquids used has been given in the preceding paper.

Discussion of Results for Films on Mercury

In Table I (A) are given the measurements made of σ_{13}, and also in the same table are summarized the data to test equation (1).

From a comparison of column 3 with column 6 of the table it will be seen that the relation $\sigma_{13} = \sigma_{12} + \sigma_{23}$ holds within 0.5% and less (the average deviation is about 0.3%) which is within the experimental error for all the films measured. This indicates that all the films formed were in true equilibrium and that equation (1) holds when correct data are used.

It will be observed that equation (1) represents in fact Antonoff's rule[11] which is usually stated in the following form: the interfacial tension between two liquids mutually saturated with each other is equal or approximately equal to the difference between the surface tensions of the two phases, each in contact with the vapor of the other phase.[12] This rule

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(8) THIS JOURNAL **55**, 2419 (1933).

(9) For a sketch of the apparatus see Ref. 8.

(10) See Cassel and Salditt, *Z. physik. Chem.*, **A155**, 321 (1931).

(11) Antonoff, *J. Chim. phys.*, **5**, 372 (1907).

(12) It has been stated by Harkins (Alexander, "Colloid Chemistry," The Chemical Catalog Co.,

TABLE I

THE SURFACE TENSION OF MERCURY IN THE PRESENCE OF SATURATED VAPORS IN AIR AT 25°, TABLE (A)

To test the equation, $\sigma_{13} = \sigma_{12} + \sigma_{23}$, for films on mercury compare col. 3 with col. 6

	(A)			(B)		
	(1) Uncorr. drop weight, g.	(2) $f\{r/V^{1/3}\}$	(3) Surface tension (Hg-vapor) σ_{13} (dynes/cm.)	(4)[a] Interfacial tension (Hg-liquid) σ_{12} (dynes/cm.)	(5)[b] Surface tension of liquid σ_{23} (dynes/cm.)	(6) $\sigma_{12} + \sigma_{23}$ = (4) + (5)
Water	0.1299	0.7294	447.6	374.0	72.0	446.0
Ethyl alcohol	.1156	.7238	401.3	376.6	22.0	398.6
n-Propyl alcohol	.1149	.7235	399.1	376.5	23.3	399.8
n-Butyl alcohol	.1142	.7231	397.1	373.1	24.2	397.3
Isoamyl alcohol	.1142	.7231	397.1	374.0	23.9	397.9
Hexane	.1154	.7236	398.4	380.1	18.0	398.1
Heptane	.1151	.7235	399.8	378.5	19.8	398.3
Benzene	.1131	.7226	393.3	364.4	28.2	392.7
Toluene	.1123	.7222	390.8	362.9	28.0	390.9
n-Propylbenzene	.1129	.7226	392.7	363.0	28.5	391.5
n-Butylbenzene	.1129	.7226	392.7	362.4	28.7	391.1
Nitrobenzene	.1133	.7228	393.7	349.4	42.8	392.2

[a] Bartell, Case and Brown, THIS JOURNAL, **55**, 2419 (1933).

[b] The surface tensions of the organic liquids σ_{23} were taken from Hennaut-Roland and Lek (International Bureau of Physical Chemical Standards), *Bull. soc. chim. Belg.*, **40**, 177 (1931); *Chem. Abstracts*, **25**, 5322 (1931), and from the "International Critical Tables," Vol. IV.

was based on results of a limited experimental study. Reynolds[13] in a series of measurements by the capillary rise method found that the rule held closely. Examination of the systems used by him shows that for these cases σ_1 was greater than $\sigma_{12} + \sigma_{23}$. For one system, however, carbon bisulfide and water, he made the observation that the rule did not apply, and he attributed this to impurities in the carbon bisulfide. As a matter of fact, the rule should not apply to the system carbon bisulfide and water because for this system $\sigma_1 < \sigma_{12} + \sigma_{23}$ and as Hardy[14] had already pointed out for such systems, no continuous *liquid* film of the organic liquid can form on the surface of the water.

In a recent paper Antonoff[15] reiterates that his rule is of universal application, and that the reason other investigators (Hardy, Harkins) obtained exceptions to his rule was because of their failure to obtain equilib-

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New York, 1926, Vol. I, p. 216) that Antonoff's rule does not apply to the calculation of the interfacial tensions of mercury in contact with other liquids. It was shown above that equation (1) (which embodies Antonoff's rule) does hold for mercury in contact with other liquids. It appears that in the cases which have been cited as indicating failure of Antonoff's rule when applied to mercury, the surface tension of mercury saturated with an organic liquid or with water was, apparently by mistake, assumed to be the same as that of mercury in a vacuum or in an inactive gas at ordinary pressures, probably because of the extremely low solubility of the liquids in mercury.

(13) Reynolds, *J. Chem. Soc.*, **119**, 466 (1921).

(14) Hardy, *Proc. Roy. Soc.* (London), **A86**, 610 (1912); **88**, 313 (1913).

(15) Antonoff, *Kolloid-Z.*, **59**, 7 (1932).

rium conditions in the measurements of σ_{13} and σ_{23}. We believe, however, that the work of Hardy and the later experimental work of Harkins (with water against carbon bisulfide and against methylene iodide) has definitely shown that Antonoff's rule is not of general applicability in that it does not hold for cases in which $\sigma_1 < \sigma_{12} + \sigma_{23}$.

Discussion of Results for Films on Water

For films on water surfaces in equilibrium with their supporting phase and the saturated vapor phase the measurements made by Harkins and co-workers[16] are generally held to be the most accurate. Their measurements were made by the drop weight method.

The result they obtained for the systems benzene, isoamyl alcohol and *n*-heptyl alcohol with water are striking,[17] in view of the fact that for these systems the measured value of σ_{13} was found to be less than the sum of $\sigma_{12} + \sigma_{23}$. In these systems $\sigma_1 > \sigma_{12} + \sigma_{23}$ and yet these results would indicate that equation (1) does not hold. However, the difference between the values of σ_{13} and $\sigma_{12} + \sigma_{23}$ in these cases seems greater than one might reasonably expect. In the case of *n*-heptyl alcohol, for example, the value of the surface tension of the dry liquid at 20° is given by Harkins as 26.97, whereas the International Bureau of Physical Chemical Standards[18] gives 24.42 dynes/cm. For the interfacial tension of benzene against water Harkins and Humphrey[19] have obtained lower results with the capillary rise method than with the drop volume, but Harkins has accepted the value given by the drop volume method.

In view of these facts it was decided to make measurements for a few systems of organic liquids with water. The capillary rise method was used for both the surface tension and interfacial tension measurements. When these measurements were made it was found that equation (1) held closely for all the cases studied, including benzene with water, for which system measurements were carried out at both 20 and 25°. The results are given in Table II.

The surface tension measurements were carried out in an apparatus of the Richards[20] type. It is an absolutely essential precaution, necessary in making measurements with this apparatus of the surface tension of water saturated with an organic liquid, *i. e.*, in equilibrium with the saturated vapor, that the ground glass joint above the capillary tube be kept moist with the organic liquid to ensure the saturation of the vapor space with respect to the organic liquid. Otherwise a mercury seal at this joint

[16] Harkins, "Colloid Symposium Monograph," 1928, Vol. VI, p. 23.

[17] We need not consider the systems carbon bisulfide and methylene iodide with water because for these systems $\sigma_1 < \sigma_{12} + \sigma_{23}$ and no stable film registering the tension $\sigma_{12} + \sigma_{23}$ could form, *i. e.*, equation (1) does not apply.

[18] Hennaut-Roland and Lek, *Bull. soc. chim. Belg.*, **40**, 177 (1931); *Chem. Abstracts*, **25**, 5322 (1931).

[19] Harkins and Humphrey, THIS JOURNAL, **38**, 236, 242 (1916).

[20] Richards and Coombs, *ibid.*, **37**, 1656 (1915).

TABLE II

SUMMARY OF THE VALUES OBTAINED BY THE CAPILLARY RISE METHOD FOR THE INTERFACIAL TENSION OF WATER AGAINST ORGANIC LIQUIDS (σ_{12}), AND THE SURFACE TENSION AGAINST THE SATURATED VAPORS (σ_{13})

Liquid	(1) Temp., °C.	(2) Interfacial tension of water against org. liq., σ_{12}	(3) Surface[a] tension of org. liq., σ_{23}	(4) $\sigma_{12} + \sigma_{23}$ = (2) + (3)	(5) Surface tension of water satd. with org. liq. obs., σ_{13}
Benzene	20	34.21	28.82	63.03	63.01
Benzene	25	33.91	28.23	62.14	62.12
Toluene	25	35.68	27.97	63.65	63.70
n-Propylbenzene	25	39.08	28.52	67.60	67.98
n-Butylbenzene	25	40.64	28.72	69.36	69.09
Nitrobenzene	25	25.15	42.76	67.91	67.70
Carbon tetrachloride	25	43.50	26.15	69.65	69.66

[a] The surface tension of the dry organic liquid and the surface tension of the organic liquid when saturated with water were not appreciably different for the above organic liquids.

must be used, and a small receptacle with some of the organic liquid must be kept in the vapor phase above the capillary tube.

The radius of the capillary was calculated over the part of the tube used, by measurements of the rise of conductivity water and also of pure benzene, accepting 72.79 at 20° and 72.08 at 25° as the surface tension of pure water, and 28.23 as the surface tension of pure benzene at 25°. The value of the radius over the part of the capillary that was used was 0.019465 cm. with water and 0.01946 cm. with benzene. The capillary tube was one selected for its uniformity of bore.

The interfacial tension values were measured with the Bartell–Miller[21] capillary rise apparatus. It is in general more difficult to apply the capillary rise method to the measurement of interfacial tensions (liquid–liquid) than to the measurement of surface tensions (liquid–vapor) because contact angles at the solid–liquid–liquid interface are more prevalent than at the solid–liquid–vapor interface.

However, it is believed that for the systems studied in this work (Table II) the interfacial contact angle was approximately zero. In the first place, the water had a markedly higher adhesion for the walls of the capillary than did the organic liquids. (A soft glass capillary was used because water exhibits a higher degree of adhesion for soft glass than for Pyrex.) Furthermore, the capillary was coated with a water film before the organic liquid was allowed to enter. Under these conditions, the water film seemed to be stable in the presence of the organic liquid; in fact, the measurements were limited to the systems listed in Table II for this reason.

The radius of the capillary of the interfacial tension apparatus was de-

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[21] Bartell and Miller, THIS JOURNAL, **50**, 1961 (1928).

termined by the use of mercury threads. The value obtained was 0.03249 cm. It has been the practice in the use of this latter method to obtain the radius of the capillary by calculation from measurements for water against benzene, because of the advantage of obtaining the radius at a fixed point, accepting as a standard the value of 35.00 dynes/cm. at 20° or 34.71 dynes at 25° for the interfacial tension of water against benzene (the values obtained in Harkins' laboratory by the drop volume method). By this method the radius obtained was 0.03324 cm.—*a discrepancy of about 2.3%.*

This discrepancy is not due to impurities in either the water or the benzene, because repeated measurements were made; the water used was fresh conductivity water and the benzene was highly purified (the directions were given in a preceding paper). It must be that either the interfacial tension values for water against benzene stated above are in error, or else an interfacial contact angle of about 12° existed in the system during the measurement. The evidence obtained in working with this system (*i. e.*, constancy of the position of the meniscus in the capillary, and the reproducibility of the measurements) lead us to believe that the discrepancy is not due to an interfacial contact angle, but is due instead to an error in the value stated above for the interfacial tension of water against benzene.

In favor of the lower value for the interfacial tension between water and benzene, *i. e.*, 33.91 at 25° against 34.71 given by Harkins by the drop volume method, it may be mentioned that for the interfacial tension between water and toluene and other organic liquids such as chlorobenzene and nitrobenzene we have obtained values which check fairly closely with Harkins' values by the drop volume method, and at the most the values are only about 0.2 of a dyne lower, whereas with benzene the discrepancy is 0.8 of a dyne (2.3% discrepancy).

The values given in Table II agree closely (when corrected to the same temperature) with the values obtained by Reynolds[13] for the same systems. The latter also found excellent agreement in the application of equation (1) to the system water and amyl alcohol, whereas Harkins did not. (The amyl alcohol used by Reynolds was probably isoamyl alcohol though he did not designate which of the amyl alcohols he used.) Reynolds' value for the surface tension of dry amyl alcohol (24.4 dynes/cm. at 18° or corr. to 20° = 24.2) agrees closely with that given by the International Bureau of Physical Chemical Standards[22] for isoamyl alcohol (24.32 at 20°), which differs from the value given by Harkins (23.73 at 20°).

The results in Tables I and II show that equation (1) applies when the initial condition that $\sigma_1 > \sigma_{12} + \sigma_{23}$ holds. This is evidently because a film is formed on the surface of the liquid of higher surface tension which lowers the tension to the value $\sigma_{12} + \sigma_{23}$ at saturation vapor pressures. Whether this film is the thick film of Gibbs,[1] or the monomolecular film of Rayleigh,

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[22] *Loc. cit.*, Table I, Ref. *b*.

Devaux and Langmuir, is an important question which, on the basis of existing data,[23] cannot be answered definitely as a general case.

Summary

1. Measurements by the drop weight method were made of the surface tension of mercury in contact with saturated vapors of organic liquids. Different values from those existing in the literature were obtained for some of the liquids, and also values were obtained for a number of liquids for which no previous values appear to have been recorded.

2. Measurements by the capillary rise method were made of the interfacial tension of water in contact with organic liquids, and of the surface tension of water saturated with organic liquids and in contact with the saturated vapor.

3. The results show that when a film is spontaneously formed on the surface of a liquid (*e. g.*, mercury or water), the surface tension of the liquid supporting the film registers at saturation vapor pressures a tension, σ_{13}, the value of which is equal to the sum given by the interfacial tension of the liquid against the liquid constituting the film, σ_{12}, plus the surface tension of the film liquid, σ_{23}, that is, $\sigma_{13} = \sigma_{12} + \sigma_{23}$ at saturation vapor pressures when the initial condition (the condition for film formation) $\sigma_1 > \sigma_{12} + \sigma_{23}$ is fulfilled. In other words, the so-called Antonoff's interfacial tension rule holds for these systems, contrary to the results of some previous investigators.

[23] For evidence of multimolecular films *cf.* Cassel [*Trans. Faraday Soc.*, **28**, 177 (1932)] and for monomolecular films *cf.* Rideal, "Introduction to Surface Chemistry," Cambridge University Press, 1930, pp. 61, 83; Adam, "Physics and Chemistry of Surfaces," Oxford University Press, 1930, p. 29.

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Properties of Electrolytic Solutions. V. The Conductance of Some Amido Salts in Liquid Ammonia[1]

BY CHARLES A. KRAUS AND WILLIAM W. HAWES[2]

I. Introduction

This and the three succeeding papers of the present series deal with the influence of ionic constitution on the properties of electrolytic solutions. They are particularly concerned with the influence of the constitution of anions upon the dissociation of their alkali metal salts in liquid ammonia.

It is known that some electrolytes are stronger than others; for example, the dissociation constants of acids and bases in water and in other solvents extend over a wide range of values. Similarly, salts of the less electropositive metals are generally less highly dissociated in a given solvent than

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[1] This and the succeeding paper of this series formed the subject matter of the Edgar F. Smith Birthday Lecture delivered by the senior author at the University of Pennsylvania, May 23, 1930.

[2] Metcalf Fellow in Chemistry.