

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE SURFACE ENERGY OF MERCURY AND THE ENERGY RELATIONS AT THE INTERFACE BETWEEN MERCURY AND OTHER LIQUIDS.¹

BY WILLIAM D. HARKINS AND WARREN W. EWING.

Received September 24, 1920.

Introduction.

The measurement of interfacial tension offers a convenient method for determining the energy relations—free energy, latent heat, total energy of surface formation, and work of adhesion—between liquids insoluble, or slightly soluble, in each other. While considerable is known concerning these relations in the case of liquids, but little is known about the energy relations existing between solids and liquids at their interface. Such knowledge would be of special value in connection with problems concerning lubrication and the flotation of ores. It is difficult to measure either the force or the work of adhesion between a solid metal and a liquid, but the adhesional work may be determined from measurements of surface tension provided the metal is in the liquid state. Among the metallic elements mercury and gallium² have freezing points lower than the boiling points of ordinary liquids. Some of the low melting alloys also possess this characteristic.

This paper gives the energy relations obtained by measuring the surface tension of mercury at various temperatures, the interfacial surface tension between mercury and various liquids and vapors at 20°, and the interfacial surface tension between mercury and 4 organic liquids at different temperatures between 0° and 60°.

Surface Energy Relations of Mercury in a Vacuum.

Since the values found in the literature³ vary by a hundred ergs per square centimeter, it was thought best to make a new determination of the surface tension of mercury in a vacuum. Also it is necessary to know the surface tension of mercury at several temperatures if the total energy relations at the interfaces is to be calculated.

A new form of apparatus was constructed for measuring the surface tension of mercury *in vacuo*. Fig. 1 represents the final form of the apparatus used.

The carefully purified mercury was distilled from Flask A into Reser-

¹ A similar paper on the energy relations at the interface between water and organic liquids will be presented in THIS JOURNAL, by Harkins and Cheng. For the preliminary work on mercury see the preceding paper by Harkins and Grafton.

² We hope to work on the surface energy relations of both liquid and solid gallium in this laboratory.

³ Cenac, *Ann. chim.*, [VIII] 29, 298 (1913).

voir B after the system had been evacuated by means of a mercury condensation pump, with the pump still running. The spirals C, C' permitted the reservoir to be raised so that the mercury flowed over and dropped from the tip T. The height of B was adjusted so that a drop formed in 2 minutes. Determinations were made in which the time of formation of the drop was varied between one and five minutes and it was found that the weight of the drop is independent of the time whenever the period is greater than 1.5 minutes. When 10 drops had fallen into D, the tube was sealed off and another 10 drops collected. The sealed portions of the tube containing the mercury were broken and the mercury weighed in a weighing bottle. A constriction was made in the capillary tube at E to control the speed of drop formation. In the dia-

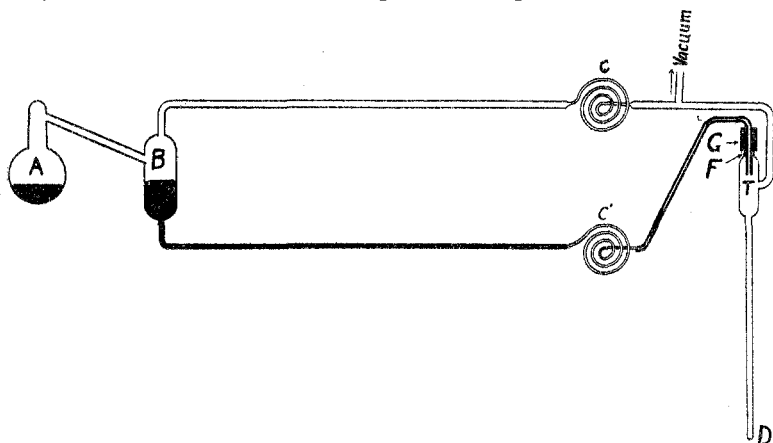


Fig. 1.—Apparatus for the determination of the surface tension of mercury in a vacuum produced by a mercury diffusion pump.

gram F represents a ground glass joint and G a mercury seal. It was found necessary to have the portion of the capillary tube above the tip perfectly smooth and clean. Any roughness of the glass or the presence of a particle of dust caused the mercury column to break apart at that point, so that many tubes had to be tried before a satisfactory one was found. A 2-stage mercury condensation pump was used in producing the vacuum, and the system was evacuated for 2 hours before starting the collection of drops. The pressure was so low that no pressure could be detected by the use of a McLeod gage. The results obtained are given in Table I. The surface tensions, Col. 2, are calculated from the equation $\gamma = mg/2\pi r\psi(\tau/v^{3/4})$ and the latent heats from the Clapeyron equation $l = -T \Delta\gamma/\Delta T$.

The following results indicate that the Ramsay-Shields constant is 0.96 instead of the normal 2.12 for mercury, or the entropy of surface formation for the area occupied by a molecule is 0.0135×10^{-14} ergs.

TABLE I.—THE FREE ENERGY, LATENT HEAT, AND TOTAL ENERGY OF SURFACE FORMATION OF MERCURY *in Vacuo*.^a

(All values in ergs per sq. cm.)

Entropy of surface formation = 0.22 ergs per degree per cm².

1. Temp. ° C.	2. Free energy of surface formation.	3. Latent heat of surface formation.	4. Total energy of surface formation.	5. $\frac{\Delta\gamma/\Delta T}{\gamma_0}$
0	480.3	60.1	540.4	0.00046
10	478.3	62.3	540.6
20	476.1	64.5	540.6
30	474.2	66.7	540.9
40	471.3	68.9	540.2
50	469.4	71.1	540.5
60	467.1	73.3	540.4

^a Instead of the value 480.3 dynes at 0° as given here, Cenac found 460 or 467, according as the correction used was that determined by calculations by Lohnstein or by the experiments of Rayleigh. Cenac, Cantor (*Wied. Ann.*, 1894, p. 423) and Siedentopf (*Diss. Göttingen*, 1897) obtained the value 0.0005 for $\frac{\Delta\gamma/\Delta T}{\gamma_0}$ instead of 0.00046 as given above.

Apparatus and Experimental Procedure.

The interfacial tensions were measured by means of the drop-weight apparatus devised in this laboratory for measuring the surface tension of liquids in air, but in a slightly modified form. Since mercury does not wet glass, the drops form and fall from the circumference of the bore and not from the circumference of the tube. Also, because of the high density of mercury, it is not possible to cause the drops to form slowly enough if the mercury siphons through the tube under the influence of gravity. A third difficulty, not met with in making similar measurements with water, is that the mercury surface adsorbs very readily any water in the organic liquid, the dry organic liquid dissolving enough moisture from the air in a few minutes to appreciably change the interfacial surface tension.

To overcome the first of these difficulties a tip made from a metal which mercury wets was first tried, but it was found that with a metal such as platinum enough of the metal dissolved in the mercury to change its surface tension. Glass tips were, therefore, used in all measurements recorded. To insure a sharp edge to the bore of the tube at the end where the drop broke off, the bore was filled with Woods metal before grinding. All the tips used had a diameter of 1.2 mm. to 1.4 mm., and this was accurately measured.

To control the speed of flow of mercury, a very small constriction (B, Fig. 2) was made in the siphon. After considerable practise it was found possible to make a constriction so small that with a head of mercury of 2 centimeters in the reservoir A, a drop weighing one g. would take 5 minutes to form at the end of the tip C. In practise suction was applied

at D until the drop was so large that it would fall in about one minute after the suction was released. The constriction was so small that sulfuric acid could be forced through under pressure only very slowly, and so small, too, that a small particle of dust was found to clog the bore completely, thus ruining the tube for further use.

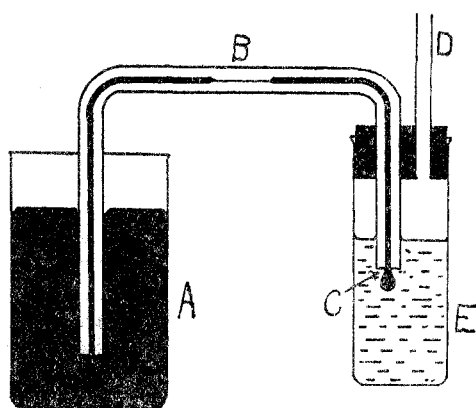


Fig. 2.—Glass parts of apparatus for the determination of the surface tension (interfacial tension) between other liquids and mercury. For a figure showing the metal parts see THIS JOURNAL, 37, 1636-76 (1915).

In purifying the liquids used great care was exercised both in drying the liquids and in keeping them from contact with moist air during the experiment. It was found that the same portion of liquid could not be used for running a second set of drops, since in changing the liquid from the weighing bottle (Fig. 2, E) to another weighing bottle, in

order to remove the mercury, enough moisture was taken up from the air to change the interfacial surface tension markedly.

Purification of Liquids.

The liquids used were purified by the methods given below.

Mercury.—Commercial mercury was distilled and this was then purified by electrolysis and repeated distillations according to the method recommended by the Bureau of Standards.¹

The alcohols were treated with freshly burned quicklime for several days, distilled off, fractionally distilled and dried over metallic calcium for 2 weeks.

The hydrocarbons and also alcohol-free ether were purified by heating for several hours, in a flask containing mercury and fitted with a reflux condenser, until the black precipitate which appeared at first no longer formed. They were then fractionally distilled and dried over metallic sodium for 2 weeks.

Oleic and undecylinic acids were distilled *in vacuo*.

Carbon disulfide and di-amyl amine were fractionally distilled and the distillates dried over freshly fused potassium hydroxide.

Aniline was fractionally distilled 2 times, finally with zinc dust and hydrogen, and the colorless product was dried over potassium hydroxide.

Acetone was fractionally distilled and dried over calcium chloride.

The halogen compounds were distilled and kept over mercury, redistilled and always used immediately after the redistillation.

¹ Bur. Standards, *Bull.* 4, 10 (1907).

Carefully purified aromatic hydrocarbons and ether contained an impurity, presumably a sulfur compound, which caused a black precipitate to form in the presence of mercury. After refluxing several hours with mercury, this impurity was removed.

The Interfacial Tensions at the Phase Boundary Between Mercury and Another Liquid.

TABLE II.—THE INTERFACIAL TENSION AND ADHESION BETWEEN MERCURY AND ORGANIC ACIDS.

(Liquids arranged in order of adhesional work against mercury.)

(Values in ergs per sq. cm. Temperature 20°.)

1.	2.	3.	4.	5.	6.	7.	8.
	Free surface energy of liquid.	Free interfacial energy against mercury.	Adhesional work against mercury (W_A)	Cohesional work against itself. (W_C)	Difference. (4)—(5)	Adhesional work against water.	Difference. (4)—(7)
	γ_l .	γ_i .	$\gamma_{Hg} + \gamma_l - \gamma_i$.	$2\gamma_l$.	S	$\gamma_{H_2O} + \gamma_l - \gamma_i$	$\frac{W_A Hg}{W_A H_2O}$
					$W_A - W_C$.		
Acetone.....	26.1	390	112	52.2	60
Hexane.....	18.4	378	116	36.9	79	40	76
Ethyl ether.....	21.8	379	119	43.6	75	73	46
Octane.....	21.7	375	123	43.5	79	44	79
Di-amyl Amine.....	24.6	371	130	49.2	81
Propyl alcohol.....	23.7	368	132	47.4	85	96	36
Nitro-ethane.....	34.9	378	133	69.8	63
Ethyl alcohol (G).....	22.4	364	134	44.8	89	85	39
Secondary octyl alcohol....	27.0	359	144	54.0	90
Carbon tetrachloride (G)...	26.6	362	146	53.3	93	56	90
Toluene.....	29.0	359	147	58.0	89	67	80
Benzene.....	28.8	357	148	57.6	90	67	81
<i>m</i> -Xylene.....	29.0	357	148	38.0	90	64	84
<i>o</i> -Xylene.....	29.0	359	149	38.0	91	67	82
<i>p</i> -Xylene.....	27.0	361	151	54.0	97	64	87
Chloroform (G).....	27.1	357	151	54.3	97	67	84
Undecylinic acid.....	30.6	353	154	61.2	93	103	51
<i>iso</i> -Butyl alcohol.....	22.8	343	156	45.6	110	94	62
Octyl alcohol (G).....	27.5	352	157	55.0	102	92	65
Methylene chloride (G)....	26.5	341	165	53.0	112	71	94
Nitrobenzene.. (G).....	43.4	350	169	86.8	82	91	78
Ethylidene chloride (G)....	24.6	337	170	49.2	121
Carbon disulfide.....	31.4	336	171	62.8	108	56	115
Aniline.....	42.6	341	177	85.2	92	110	67
Water (G).....	72.8	375	178	145.6	32	145.6	32
Oleic acid.....	32.5	322	187	65.0	122	90	97
Ethyl iodide (G).....	28.2	322	191	56.4	135	63	128
Ethylene bromide (G).....	38.7	326	193	77.4	116	75	118
Methyl iodide (G).....	35	304	207	70	137
Acetylene tetrabromide (G)	49.6	320	213	99.3	114	84	129
Mercury.....	476.0	...	(952)	952	...	178	774

Values marked (G) obtained by Dr. E. H. Grafton.

Adsorption of Vapors on a Mercury Surface.

Preliminary experiments were made on the surface tension of mercury in air saturated with vapors of volatile liquids. The results are only approximate as the only precaution taken to control the concentration of the vapor was to let the apparatus stand for an hour at $20^{\circ} \pm 0.1$ with a few drops of the liquid in the bottom of the weighing bottle (Fig. 2, E). In benzene vapor the surface tension was found to be about 394, in ether vapor about 389 and in carbon disulfide vapor about 370 ergs per sq. cm. This shows a lowering of the free-surface energy of mercury of 80 to 100 ergs per sq. cm. and gives values approximating those found in liquids. This indicates a *strong positive adsorption* of these vapors on a mercury surface.

An attempt was made to measure the adsorption of nonyllic acid in water solution by mercury but the results were not concordant. The solution could not be kept from creeping up into the tube and thus displacing the mercury. The same difficulty was met with in the case of some of the organic liquids. Monochloro-acetone in particular would displace the mercury for a distance up into the tube of from 1 to 2 cm. This is probably caused by the attractive forces between the liquid and glass being stronger than the forces keeping the mercury in contact with the glass. The interfacial tension against benzaldehyde could not be determined because in it a white skin formed about the mercury drop and supported the drop until it became abnormally large. The skin then broke letting the drop fall through.

Accuracy of the Experimental Work.

As has been stated, in all of this work the mercury was dropped down from the sharp inside edge of the capillary tube, or from what is called an open tip. This method, as was found by Harkins and Brown, is not so accurate as that in which what is termed a closed tip is used, so the results should not be expected to attain the precision better than 0.1% such as was obtained in work on water and other liquids in their work. The precision attained in the present work seemed to be of the order of 1%—that is, results on the same liquid agreed to within 1% even after long periods of standing, provided the liquid was kept carefully sealed in the interim, though opening the bulb to the ordinary air of the laboratory would often allow enough moisture to be absorbed to cause a lowering of several per cent. in the interfacial tension. However, such manipulation as this is inexcusable.

Two important sources of error have been mentioned in the previous section. First, the organic liquid may creep up the capillary tip between the mercury and the wall of the glass capillary, as was the case with monochloro-acetone, and with an aqueous solution of nonyllic acid. However, in such cases the results obtained were altogether irregular and

erratic, with a variation as large as 25%. The very regular results obtained in connection with the data presented here give a reasonable basis to the assumption that this error was avoided. In order to do

this, however, it was necessary to use a small tip, with a diameter less than 2 mm. in order to give a bulging drop, so that the mechanical forces would cause the mercury to press tightly against the edge of the tip. Second, there was no evidence of the formation of a quasi-solid film except with benzaldehyde, where the results were *entirely erratic* and *abnormally high*, and in the case of the halogen derivatives, which gave very consistent and low results. In all other cases the mercury remained extremely bright, and consistent results were obtained. Attempts to obtain the interfacial tension by dropping the liquid upward through the mercury failed, since with the experimental arrangements at hand it was found impossible to control the drop sufficiently well. The results obtained *in vacuo* are believed to be the most accurate thus far obtained with mercury. Any small differences noted in the data of the preceding and of the present paper are not due to the drop weight method as employed, but to the later removal of impurities, small traces of which may change the values greatly.

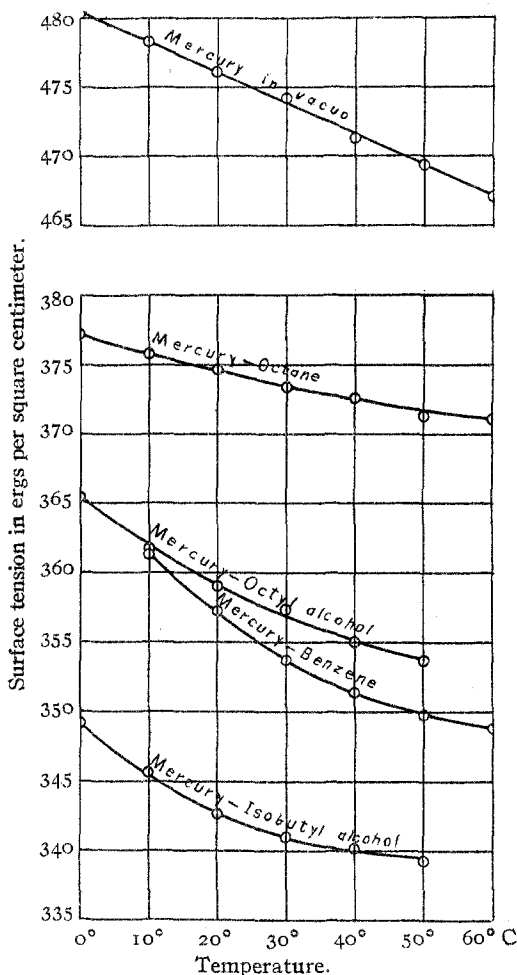


Fig. 3.—The free surface energy (or surface tension) of mercury *in vacuo* and at the interface with other liquids.

Discussion of Results.

The data presented in the tables of this and of the preceding paper indicate that the adhesional work between a mercury surface and the surface of an organic liquid is always greater than that between the organic

TABLE III.—THE ADHESIONAL WORK AND ENERGY AND THE SURFACE TENSION AT THE INTERFACE BETWEEN MERCURY AND VARIOUS ORGANIC LIQUIDS.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
Temp. °C.	Free surface energy of mercury. γ_{Hg} .	Free surface energy of organic liquid. γ_l .	Free interfacial energy against mercury. γ_i .	Adhesional work against mercury. $\gamma_{Hg} + \gamma_l - \gamma_i$.	Cohesional work against itself. $2\gamma_l$.	Difference (5)—(6) $W_A - W_C$.	Adhesional work against water. $\gamma_{H_2O} + \gamma_l - \gamma_i$.	Difference (5)—(8) $\frac{W_A Hg^-}{W_A H_2O}$.	Free interfacial surface per degree. $\left(\frac{\Delta\gamma}{\Delta T}\right)_i$.	Latent heat of interfacial surface formation. $l_i = T \frac{\Delta\gamma}{\Delta T}$.	Total energy of interfacial surface formation. $E_i = \gamma_i + l_i$.	Total adhesional energy, $E_a = \gamma_{Hg} + \gamma_l - \gamma_i + l_i$.
<i>iso</i> -Butyl Alcohol.												
0	480	24.3	349.1	155	49	106	0.48	130	479	106
10	478	23.5	345.6	156	47	109	0.31	87	433	153
20	476	22.7	342.7	156	45	111	0.21	62	405	184
30	474	22.0	341.0	155	44	111	0.14	42	383	206
40	471	21.3	340.2	152	43	109	0.09	28	358	217
50	469	20.5	339.3	151	41	110	0.05	16	355	230
<i>Secondary Octyl Alcohol.</i>												
0	480	27.9	365.4	143	56	87	95.4	48	0.38	104	469	93
10	478	27.2	361.7	143	54	89	92.7	50	0.33	93	455	108
20	476	26.3	359.0	143	53	90	89.9	53	0.25	73	432	132
30	474	25.5	357.3	143	51	92	87.2	56	0.20	61	418	147
40	471	24.7	355.0	141	49	92	84.5	56	0.13	41	396	170
50	469	23.8	353.6	140	47	93	81.8	58	0.10	32	386	181
Octane.												
0	480	23.7	377.2	127	47	81	48.0	79	0.16	44	421	145
10	478	22.7	375.8	126	45	81	46.1	80	0.14	40	416	151
20	476	21.8	374.7	123	44	79	43.8	79	0.12	35	410	158
30	474	20.8	373.4	121	42	79	41.9	79	0.11	33	406	163
40	471	19.8	372.6	118	40	78	40.0	78	0.09	28	401	169
50	469	18.8	371.3	117	38	79	38.2	79	0.08	26	397	174
60	467	17.9	371.1	114	36	78	36.2	78	0.06	20	391	181
Benzene.												
10	478	30.4	361.3	147	61	86	69.1	78	0.50	142	503	106
20	476	28.9	357.2	148	58	90	66.7	81	0.37	108	465	144
30	474	27.6	353.7	148	55	93	64.6	83	0.26	79	433	177
40	471	26.3	351.4	146	53	93	62.2	84	0.16	50	401	208
50	469	24.9	349.8	144	50	94	59.7	84	0.14	45	395	214
60	467	23.6	348.8	142	47	95	57.2	85	0.09	30	379	230

¹ NOTE.—The derived values given in Cols. 10 to 13 inclusive, should not be expected to represent more than an approximation, since their calculation involves a differential. The values given in these columns are presented in order to represent only the general order of magnitude of the quantities involved. On the other hand, the data of Cols. 2 to 9, are, it is believed, quite accurate, probably within 1 or 2% in the case of the larger numbers.

² This is the entropy of interface formation.

substance and water, and also greater than that between the organic liquid and itself, or the cohesive surface work. A second point of interest is that for about half of the substances investigated, the *difference* between the adhesional work against mercury and that against water is nearly constant, and between 80 and 90 ergs. This is true for such liquids as the paraffin hydrocarbons, benzene, toluene, and xylenes, carbon tetrachloride, chloroform, and nitrobenzene, so the *work of attraction is by no means entirely specific*. On the other hand the adhesional work is specifically high toward water in the case of the alcohols, water itself, organic acids, acetone and ether, while that toward mercury is very high in the case of the compounds containing iodine, bromine, and sulfur, and somewhat high for oleic acid, which indicates that the specific effects are very marked.

The values for $W_A - W_C$ or of S , the *spreading coefficient*, are all large, which would indicate that if what may be termed the Neuman triangle principle is applicable to spreading all of these liquids should spread on a *pure* mercury surface. That they often do not spread is not surprising, when it is considered that a mercury surface in ordinary air is always covered by a film of water and other vapors, as may be seen by consulting the preceding section of this paper. It will be seen that this spreading coefficient *increases* with the temperature for *iso*-butyl alcohol, *secondary* octyl alcohol, and benzene, but *decreases* for octane.

Table III shows that the *adhesional work decreases* rapidly with increase of temperature, while the *total adhesional energy increases*.¹ The latent heat of the interface between mercury and another liquid decreases rapidly as the temperature increases, while the latent heat of most ordinary surfaces increases with the temperature, and the total energy of interface formation also decreases, though not so rapidly.

Since the halogen and sulfur atoms in organic compounds show a specifically high attraction for the mercury surface, it is to be expected that at such an interface the molecules should be oriented in such a way that the halogen or sulfur atoms are turned toward the mercury.

CHICAGO, ILL.

¹ It is evident that at higher temperatures the adhesional energy must also decrease.