for instance, the end-points in the first 2-ratio columns and the ratios between 0.450 and 0.480. Some light is thrown on these by the experiments of Venable and Smithey. The ratio 0.456 would correspond to a hydrolyzed product $ZrO(OH)_2.2ZrO(IO_3)_2$, or to a zirconyl iodate in which $^1/_3$ of the molecules had undergone hydrolysis. Such a product was obtained by these investigators when the precipitation was made in cold, concentrated solutions and the precipitate was freed from the filtrate by suction without washing. The ratio 0.533 corresponds to a product $3ZrO(OH)_2.4ZrO(IO_3)_2$, in which 3 out of 7 molecules had been hydrolyzed. This was obtained when the precipitate was formed from dilute solutions and washed with a limited amount of water at room temperature. The ratio 0.914 corresponds in the same way to $2ZrO(OH)_2.ZrO(IO_3)_2$, in which 2 out of 3 molecules have been hydrolyzed. Here the precipitate was washed with hot water in increased amount. A ratio 1.218, corresponding to $3ZrO(OH)_2.2ZrO(IO_3)_2$, where 3 out of 4 molecules had been hydrolyzed, was obtained after prolonged washing with hot water.

## Summary.

1. The hydrolysis of zirconyl sulfate and chloride has been examined both by relative conductivity and by a precipitation method. The temperatures were 0° and 20°, respectively. Three different dilutions were used and the effect of the time factor noted.
2. There appears to be an initial temperature adjustment on dissolving the salts. Afterwards there is a decrease in the resistance until after about 3 hours an equilibrium or period of very slow change is reached.
3. In the experiments with iodic acid there is also indication of an initial adjustment. The extent of the hydrolysis is indicated. The equilibrium or period of slow change is reached in 2 to 3 hours.

CHAPEL HILL, N. C.

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

# SURFACE TENSION AND MOLECULAR ATTRACTION: ON THE ADHESIONAL WORK BETWEEN MERCURY AND ORGANIC LIQUIDS.[1]

BY WILLIAM D. HARKINS AND E. H. GRAFTON.

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Most of the papers on molecular attraction make use of one of the equations of state in order to calculate the internal pressure of pure substances in the liquid state. It is evident that such equations give a very uncertain basis for the determination of results which represent more

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[1] Published in abstract in *Proc. Nat. Acad. Sci.*, **5**, 569–73 (1919). For similar work with water and organic liquids see Hardy, *Proc. Roy. Soc. London* (A) **88**, 303–33 (1913); Harkins, Brown and Davies, THIS JOURNAL, **39**, 354–64 (1917); and Harkins, Clark, and Roberts, *ibid.*, **42**, 700–12 (1920).

than an approximation. Moreover, they give no indication at all of the magnitude of the attraction between 2 liquids made up of molecules which are unlike. In studying the attraction between 2 dissimilar liquids use will be made of equations which are not only applicable to such a case but are also entirely accurate, since they are based upon thermodynamics alone. The first of these is the equation of Dupré,

$$W_A = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{1,2}$$

where $\gamma_1$ and $\gamma_2$ represent the free surface energies per square centimeter of the 2 liquids, $\gamma_{1,2}$, the free surface energy of their interface, and $-\Delta\gamma$ is the decrease of free energy when the surfaces of the two liquids come together to form an interface. The work done is represented by $W_A$ which represents the amount of work done by the molecular attraction between the 2 surfaces. An equation which is more closely related to the molecular attraction is that derived in an earlier paper from this laboratory,

$$E_A = -\Delta E_s = (\gamma_1 + l_1) + (\gamma_2 + l_2) - (\gamma_{1,2} + l_{1,2}),$$

where $l$ represents the latent heat of a surface, $E_s$ the total surface energy, and $-\Delta E_s$ the total decrease in surface energy per square centimeter when the two surfaces come together. This equation may be put in the form

$$E_A = E_{s_1} + E_{s_2} - Es_{s_{1,2}} = \int_{s_0}^{\infty} F\mathrm{d}s$$

or the integral of the molecular surface attraction is equal to the change in the total surface energy.

This paper will present data from which the adhesional *work* between organic liquids and mercury may be calculated, and the paper which follows will deal with the total adhesional *energy*. Both papers will give extensive data on the surface and interfacial tension and energy relations of mercury.

## Experimental Procedure.

The surface and interfacial tension measurements were made in an apparatus somewhat similar to that used for work on surface tension by Morgan, but in the modified form designed by Harkins and Brown.[1] However, it was found necessary to allow the drop to hang from the inside instead of the outside edge of the capillary tip. The apparatus will be described in the second paper, but some mention will be made here of the experimental difficulties of the work, which are not inconsiderable.

The surface tension was in all cases calculated by the use of the correction curve determined experimentally by Harkins and Brown.[2]

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[1] THIS JOURNAL, **37**, 1656–76 (1915).

[2] *Ibid.*, **41**, 499–524 (1919).

## Surface Tension of Mercury in Air at 20°.

In order to illustrate the character of the results obtained by the method, the data obtained in air are given in Table I. A small constriction was made in the capillary of the tip such that with from one to 1.5 cm. head of mercury the natural period of fall per drop was 30 minutes. In order to shorten this time suction was applied for 0.5 minute, after which it took from 40 to 180 seconds for the drop to fall. The experiments (B), (C), (D), were made 2 months after Experiment A.

Table I.—Surface Tension of Mercury in Air at 20°.

| | Diam. tip cm. | Drop wt. G. | $f\left(\frac{r}{V^{1/3}}\right)$. | Surface tension dynes. |
|---|---|---|---|---|
| A........... | 0.12524 | 0.1345 | 0.7289 | 459.4 |
| B........... | 0.12524 | 0.1359 | 0.7290 | 464.3 |
| C........... | 0.1369 | 0.1475 | 0.7218 | 465.8 |
| D........... | 0.1438 | 0.1519 | 0.7157 | 464.6 |

Table II.—Surface Tension of Mercury in Water.

| | | | | | Corrected wt. drop. |
|---|---|---|---|---|---|
| A........... | 0.12524 | 0.1179 | 0.7234 | 375.4 | 0.1092 |
| B........... | 0.12524 | 0.1176 | 0.7234 | 375.6 | 0.1091 |
| C........... | 0.14375 | 0.1317 | 0.7076 | 374.5 | 0.1221 |
| | | | Average = | 374.8 | |

It will be noted that in spite of the fact that tips of different diameters were used, and that in both tables determinations were made 2 months apart, there is very good agreement between the results.

Table III gives similar results for other liquids. The ether which was used had been standing over sodium for several months, was then distilled off from fresh sodium, allowed to stand over mercury, distilled again, and stored over mercury. On long standing a black residue formed, similar to that formed when ordinary ether is placed over mercury. The ether was redistilled before using. A similar black residue formed in nitro-ethane on long standing in contact with mercury. The liquids used were carefully purified.

Table III.—Surface Tension of Mercury in Different Liquids at 20°.

| | Density. | Diam. tip. cm. | Drop weight. G. | Corrected drop wt. G. | $f\left(\frac{r}{V^{1/3}}\right)$. | Surface tension dynes. | |
|---|---|---|---|---|---|---|---|
| | | | In Ethyl Alcohol. | | | | |
| A....... | 0.7893 | 0.12524 | 0.1120 | 0.1054 | 0.7214 | 364.6 | ..... |
| B....... | ...... | 0.14375 | 0.1255 | 0.1182 | 0.7049 | 364.0 | 364.3 |
| | | | In Ethyl Ether. | | | | |
| A....... | 0.7119 | 0.12524 | 0.1165 | 0.1104 | 0.7228 | 398.3 | ..... |
| | | | In Octyl Alcohol. | | | | |
| A....... | 0.8252 | 0.12524 | 0.1083 | 0.1016 | 0.7197 | 351.7 | ..... |
| | | | In Nitro-ethane. | | | | |
| A....... | 1.0528 | 0.14375 | 0.1338 | 0.1234 | 0.7084 | 378.2 | ..... |

TABLE III (*continued*).

| | Density. | Diam. tip, cm. | Drop weight. G. | Corrected drop wt. G. | $\left(\frac{v}{V^{1/2}}\right)$. | Surface tension dynes. | |
|---|---|---|---|---|---|---|---|
| In Nitrobenzene. | | | | | | | |
| A....... | 1.185 | 0.14375 | 0.1240 | 0.1131 | 0.7005 | 350.5 | ..... |
| In Carbon Disulfide. | | | | | | | |
| A....... | 1.262 | 0.12524 | 0.10538 | 0.09555 | 0.7178 | 339.3 | ..... |
| In Carbon Tetrachloride. | | | | | | | |
| A....... | 1.593 | 0.12524 | 0.1197 | 0.1054 | 0.7249 | 362.2 | ..... |
| In Chloroform. | | | | | | | |
| A....... | 1.485 | 0.12524 | 0.1163 | 0.1034 | 0.7233 | 356.6 | ..... |
| In Methylene Chloride. After standing over mercury for 4 weeks. | | | | | | | |
| A....... | 1.337 | 0.14375 | 0.1225 | 0.1104 | 0.7035 | 340.7 | ..... |
| In Ethylidene Chloride. | | | | | | | |
| A....... | 1.175 | 0.12524 | 0.1063 | 0.0971 | 0.7181 | 336.8 | ..... |
| In Ethylene Dibromide. | | | | | | | |
| A....... | 2.178 | 0.12524 | 0.1124 | 0.0934 | 0.7205 | 326.0 | ..... |
| In Acetylene Tetrabromide. Before being placed over mercury. | | | | | | | |
| A....... | 2.97 | 0.12524 | 0.1192 | 0.0931 | 0.7240 | 320.3 | ..... |
| After standing over mercury for 4 weeks. | | | | | | | |
| B....... | ...... | 0.14375 | 0.1229 | 0.0959 | 0.7038 | 293.3 | ..... |
| In Methyl Iodide distilled from silver foil. | | | | | | | |
| A....... | 2.2786 | 0.12524 | 0.1051 | 0.0874 | 0.7176 | 304.1 | ..... |
| After standing over mercury for 6 weeks. | | | | | | | |
| B....... | ...... | 0.14375 | 0.1026 | 0.0854 | 0.6933 | 266.6 | ..... |
| Distilled from Mercury. | | | | | | | |
| C....... | ...... | 0.14375 | 0.1149 | 0.0956 | 0.7000 | 296.4 | ..... |
| In Ethyl Iodide distilled from silver foil. | | | | | | | |
| A....... | 1.9375 | 0.12524 | 0.1089 | 0.0929 | 0.7192 | 321.7 | ..... |
| After standing over mercury for 6 weeks. | | | | | | | |
| B....... | ...... | 0.14375 | 0.1056 | 0.0905 | 0.6950 | 282.7 | ..... |
| Distilled over mercury. | | | | | | | |
| C....... | ...... | 0.14375 | 0.1180 | 0.1011 | 0.7103 | 312.9 | ..... |
| In Benzene. | | | | | | | |
| A....... | 0.8784 | 0.12524 | 0.1092 | 0.1021 | 0.7197 | 353.2 | ..... |
| In Hexane. | | | | | | | |
| A....... | 0.6630 | 0.12524 | 0.1133 | 0.1077 | 0.7220 | 371.53 | ..... |
| In Octane. | | | | | | | |
| A....... | 0.7022 | 0.12524 | 0.1092 | 0.1035 | 0.7201 | 357.9 | ..... |

It will be noted that when the interfacial tension of mercury was determined in acetylene tetrabromide, methyl iodide, or ethyl iodide, which had been standing for some weeks over mercury, the values were in all cases considerably lower than those obtained before such a treatment. This seemed to be due to the fact that these liquids acted slowly on mercury forming halides, which dissolved to some extent in the organic liquid and was adsorbed by the mercury surface. Similar results were obtained with fresh liquids on adding a mercury halide.

The above tables are summarized in Table IV, which gives in addition the values for the adhesional work.

TABLE IV.—THE SURFACE TENSION OF MERCURY AND ITS INTERFACIAL TENSION AND ADHESIONAL WORK IN DIFFERENT ORGANIC LIQUIDS AT 20°.([a])

| | Density. | Wt. Hg. in drop. G. | Tip. | *f*. | $\gamma$ liquid. | $\gamma$ interface. | $W_A$. |
|---|---|---|---|---|---|---|---|
| Air | ...... | 0.1359 | 1 | 0.7290 | ..... | 464.35 | ...... |
| Air | ...... | 0.1475 | 2 | ...... | ..... | 465.8 | ...... |
| Air | ...... | 0.1519 | 3 | ...... | ..... | 464.6 | ...... |
| Hexane | 0.6630 | 0.1092 | 1 | 0.7220 | 19.24 | 378.1 | 121.71 |
| Octane | 0.7022 | 0.1092 | 1 | 0.7201 | 21.52 | 374.6 | 131.0 |
| Nitro-ethane | 1.0528 | 0.1338 | 3 | 0.7084 | 32.52 | 378.2 | 139.2 |
| Ethyl Alcohol | 0.7893 | 0.1120 | 1 | 0.7214 | 21.7 | 364.38 | 142.3 |
| Ethyl Alcohol | 0.7893 | 0.1255 | 3 | 0.7049 | 21.7 | 364.00 | 142.7 |
| Carbon Tetrachloride | 1.593 | 0.1197 | 1 | 0.7247 | 26.95 | 362.2 | 149.75 |
| Chloroform | 1.485 | 0.1163 | 1 | 0.7233 | 26.51 | 356.6 | 154.91 |
| Benzene | 0.8789 | 0.1092 | 1 | 0.7197 | 28.9 | 362.8 | 150.3 |
| Octyl Alcohol | 0.8252 | 0.1083 | 1 | 0.7196 | 27.51 | 351.7 | 160.8 |
| Methylene Chloride | 1.337 | 0.1098 | 1 | 0.7199 | 26.52 | 340.7 | 170.82 |
| Methylene Chloride | 1.337 | 0.1225 | 5 | 0.7035 | 26.52 | 342.5 | 168.00 |
| Ethylidene Chloride | 1.175 | 0.1063 | 1 | 0.7181 | 25.71 | 336.8 | 173.91 |
| Nitro Benzene | 1.185 | 0.1240 | 3 | 0.7005 | 43.55 | 350.5 | 178.05 |
| Carbon Disulfide | 1.262 | 0.1054 | 1 | 0.7220 | 34.49 | 339.3 | 180.19 |
| Water | 0.9982 | 0.1179 | 1 | 0.7234 | 72.8 | 374.8 | 183.00 |
| Water | 0.9982 | 0.1317 | 3 | 0.7076 | 72.8 | 375.6 | 182.20 |
| Ethyl Iodide | 1.937 | 0.1089 | 1 | 0.7192 | 31.79 | 321.7 | 195.09 |
| Ethyl Iodide | 1.937 | 0.1056 | 3 | 0.6950 | 31.79 | 282.7 | 234.09 |
| Ethyl Iodide | 1.937 | 0.1180 | 3 | 0.7013 | 31.79 | 312.9 | 204.89 |
| Ethylene Bromide | 2.178 | 0.1124 | 1 | 0.7205 | 37.89 | 326.00 | 196.89 |
| Methyl Iodide | 2.278 | 0.1051 | 1 | 0.7176 | 30.39 | 304.1 | 211.29 |
| Methyl Iodide | 2.278 | 0.1026 | 3 | 0.6933 | 30.39 | 266.6 | 248.79 |
| Methyl Iodide | 2.278 | 0.1149 | 3 | 0.7000 | 30.39 | 296.4 | 219.99 |
| Acetylene Tetrabromide | 2.97 | 0.1192 | 1 | 0.7240 | 48.21 | 320.3 | 212.91 |
| Acetylene Tetrabromide | 2.97 | 0.1229 | 3 | 0.7038 | 48.21 | 293.3 | 229.91 |

([a]) When several values are given for one liquid, Table III should be consulted for an explanation of the apparent discrepancy.

The above table represents the preliminary results obtained. A more complete table and a discussion of the results, will be found in the paper which follows.

CHICAGO, ILL.