The mole fractions of the other components of this mixture at equilibrium at 15° C. were: (A stands for acetate) $X_{HA} = 0.148_0$, $X_{H_2O} = 0.482_5$, $X_{EtOH} = 0.143_8$, and $X_{EtA} = 0.213_8$. From the good agreement at all temperatures, the authors assumed that the resin does not affect Q in mixtures in contact with it in the absence of soluble acids.

RESULTS

The Q values, with initial and equilibrium compositions of the mixtures, are shown in Table I. In all but one case, Q decreased slightly with temperature increase. In experiment 3, Q was constant at 2.05 ± 0.06. However, the slight increase is just above the titration error limit. This mixture is unique in having the highest ethanol content.

Jones and Lapworth (*1*) reported Q from 4 to over 8 with HCl as catalyst. Trimble and Richardson (*5*) report Q from about 3 to 14 with $HClO_4$, and 3.45 as the Q extrapolated to zero catalyst.

A multiple linear regression analysis was made on a digital computer to seek correlation between Q and mole fractions at equilibrium for experiments 1 through 13 at 25° C. The following approximate relationship summarized these results.

$$Q = 4.13 + 10.8\, X_{HA}\, X_{H_2O} - 2.53\, X_{EtOH}/(1 - X_{EtA}) - 1.89 \times 10^{-4}/X_{EtOH}\, X_{EtA} - 2.13\, X_{EtOH}\, X_{H_2O}$$

It reproduces the Q values within a standard deviation of 0.1 unit of the Q values, and reflects the fact that Q is high for mixtures with high acetic acid and water content, and low for high ethanol and ester content.

LITERATURE CITED

(1) Jones, W.J., Lapworth, A., *J. Chem. Soc.* **99**, 1427 (1911).
(2) Kirk, R.E., Othmer, D.F., "Encyclopedia of Chemical Technology," Vol. 5, pp. 782, 788, Interscience, N. Y., 1950.
(3) Koskikallio, J., *Suomen Kemistilehti* **B35**, 62 (1962); *CA* **57**, 5336*a* (1962).
(4) Swietoslawski, W., *J. Phys. Chem.* **37**, 701 (1933).
(5) Trimble, H.M., Richardson, E.L., *J. Am. Chem. Soc.* **62**, 1018 (1940).
(6) Weissberger, A., Proskauer, E., "Organic Solvents," p. 150, Oxford, N. Y., 1935.

RECEIVED for review June 9, 1966. Accepted June 5, 1967. Preliminary work was performed by William A. Lambeth. This project was supported by a National Science Foundation Grant for Student Research Participation in the summer of 1965. The work of A.D. was submitted to the Chemistry Department of the University of the South in partial fulfillment of the requirements for the degree of B.A. with Honors in 1966.

Contact Angles of Mercury on Various Surfaces and the Effect of Temperature

A. H. ELLISON, R. B. KLEMM, and A. M. SCHWARTZ
Harris Research Laboratories, Division of Gillette Research, Inc., Washington, D. C. 20011

L. S. GRUBB and D. A. PETRASH
NASA Lewis Research Center, Cleveland, Ohio

The contact angle of mercury on six different materials was measured as a function of temperature over the range 25° to 150° C. The materials were stainless steel, nickel, tungsten, glass, fused quartz, and Teflon. The contact angles were very high on all the substrates, ranging at equilibrium from about 130° to 145° at 25° C. Although there were significant differences between the dynamic advancing and receding angles, equilibrium was rapidly achieved in all systems, and the residual hysteresis was negligible. The temperature coefficient of the contact angle was very small in all the systems and was positive. The largest increase occurred with Teflon and amounted to about 15° of angle over the 125° C. temperature range explored.

IN THE weightless environment prevailing in space vehicles the behavior of a liquid is determined largely by its capillary properties. A controlling parameter of capillary behavior is the contact angle of the liquid against the solid material which forms its container. Thus a precise knowledge of the contact angle is necessary in the design of tankage systems for the various liquids used in spacecraft. One liquid of interest, because of its potential use as the propellant in an ion engine, is mercury. The object of this work therefore, was to determine the contact angle of mercury against various materials which might be used in tankage over a temperature range that might exist in use. Thus, mercury contact angles against stainless steel, nickel, tungsten, borosilicate glass, quartz, and Teflon were determined at 25°, 50°, 75°, 100°, 125°, and 150° C. The possibility that certain of the data also qualify as fundamental will be considered in the discussion.

ENGINEERING DATA

Materials. Type 347 stainless steel was obtained from Peter A. Frasse and Co., Inc., Philadelphia, Pa. Nickel (electrolytic grade) was obtained from Whitehead Metals, Inc., Baltimore, Md. Tungsten surfaces were prepared by depositing essentially pure tungsten on metal supports to form a specular film; the tungsten was specified to have no more than 875 p.p.m. of impurities with no more than 200 p.p.m. of impurities from any one metal group. Pyrex brand chemical glass number 7740 and Teflon are widely available and were obtained from a local source. Fused quartz (99.99%) was obtained from the General Electric Co., Willoughby, Ohio.

The mercury used was triple distilled, or another designation thereof, instrument grade and was obtained from Fisher Scientific Co. It was judged to be relatively pure, since a sample of it placed in a Petri dish and left open to the laboratory atmosphere did not form a "scum" in approximately 30 minutes (*9*). When a drop of benzene was placed on this open surface in the Petri dish within 10 minutes, it spread rapidly showing, according to previous work (*3*), that it was relatively free of trace impurities. Also, a drop of water would slowly spread on a fresh surface of this mercury in the dry nitrogen atmosphere described below if applied within 2 minutes of the formation of the surface. This strongly suggests freedom of organic contamination of the surface, at least for the time indicated.

Solid Surface Preparation. Steel, nickel, and glass specimens were cut, ground flat, and polished to a specular finish. Silicon carbide papers of decreasing grit size were used in preparation for final polishing which was carried out on a Fisher polishing wheel using Buehler No. 1 and No. 3 polishing alumina dispersed on a Buehler micropore cloth. As indicated above, tungsten surfaces were specular films on metal supports and did not require further polishing. Quartz specimens were received from the supplier in a polished condition. Teflon surfaces were prepared by abrading specimens on No. 600 grit carborundum paper and were polished to a specular finish using a wheel covered with silk cloth. The silk cloth was kept wet with water during polishing but no abrasive was used. Once specular surfaces were obtained, further polishing was avoided because of the tendency of polishing grit to embed in the surfaces (*4*).

The polished specimens were given a cleaning before each use with an aqueous detergent (Tide) solution. The specimens were immersed in the solution and the surfaces gently brushed using a soft camel's hair brush. This was followed by a very thorough rinsing with hot tap water and finally with hot distilled water (*3, 15*). The specimens were then placed in clean covered glass dishes and stored for a few hours at most prior to use in the dry nitrogen atmosphere of the glove box described below. Tests showed that the metal and metal oxide samples were still hydrophilic when removed from their containers for mercury contact angle measurements.

Contact Angle Measurements. Contact angles were measured by direct observations on sessile drops using a contact angle goniometer. Measurements were made while the solid-mercury system was in a thermostatically controlled optical cell. The temperature was controlled by circulating silicone fluid through the cell from a constant-temperature bath. The bath was regulated so as to produce the desired temperature in the cell. A mercury thermometer was used to determine and monitor the temperature in the cell.

The contact-angle thermostatically controlled cell was placed in a controlled atmosphere glove box enclosure in order to provide an atmosphere of dry nitrogen for the solid-mercury systems. In preparation for the measurements, the enclosure was flushed with dry nitrogen until the atmosphere was at least 99.5% N_2. During measurements a recirculating system was put into operation which maintained this atmosphere. Analyses of the gas atmosphere within the enclosure were accomplished by gas chromatography using a 13X molecular sieve at a constant temperature of 28° C.

Contact angles were determined under advancing and receding conditions—that is, following a series of incremental additions of liquid to the drop under observation or correspondingly a series of incremental withdrawals of liquid from the drop under observation. With these solid-mercury systems, however, the advancing and receding angles were not stable. The angle observed immediately after adding a small amount of mercury to the drop decreased steadily to a lower constant value. Likewise, the angle observed immediately after withdrawing a small amount of mercury from the drop increased steadily to a higher constant value. The authors decided that all four angles should be reported—i.e., the maximum angle observed immediately following an incremental addition of mercury to a sessile drop in the course of several such additions, or the maximum advancing angle; the equilibrium advancing angle or the constant angle to which the maximum advancing angle falls; the minimum receding angle which corresponds to the maximum advancing angle; and the equilibrium receding angle or the constant angle to which the receding angle rises.

Even after prolonged contact of mercury drops with any of the solids, several hours at the maximum temperature of these experiments, the surfaces showed no sign of attack by the mercury. Thus, the decay or change of the initially observed advancing and receding angles to the equilibrium values which took place rather rapidly, usually within 10 to 30 seconds, was probably related to the inherent vibrations in the system.

RESULTS AND DISCUSSION

The results of contact angle measurements of mercury on six solid surfaces at the six temperatures are summarized in Table I. All of the angles are high and very little difference is observed between the angles on the "high energy" surfaces of tungsten, steel, nickel, quartz, and glass and the "low energy" surface of Teflon. The variation in contact angle with temperature is very small for all solid-mercury systems. The slope of the contact angle–temperature relation although small is positive with all solid-mercury systems.

For each solid-mercury-temperature combination the four angles were reported because any one might be important depending upon the application. The table shows that the equilibrium advancing and the equilibrium receding angles are the same and also just about at the arithmetic mean of the maximum advancing and minimum receding angles. To relate these data to other contact angle data in the literature, the maximum advancing angle should be used. This recommendation is based on the fact that the value for Teflon-mercury at 25° C. in the table (157° C.) checks well with the literature values of 150° (*8*) and 151.7° C. (*10*).

This then covers the engineering data. The remainder of the discussion will consider interpretations of these results from a fundamental point of view.

FUNDAMENTAL DATA

In order to assess the fundamental significance of these results, the condition of various mercury-solid systems with respect to contamination must be examined. The possibility

Table I. Contact Angles of Mercury on Polished Solid Substrates at Various Temperatures

Solid Surface	Temperature, ° C. 25	50	75	100	125	150
Tungsten						
Max. adv.	142	150	155	155	159	160
Equil. adv.	130	130	140	137	140	137
Equil. rec.	132	132	137	135	141	137
Min. rec.	121	110	120	119	123	124
Stainless steel						
Max. adv.	146	150	151	158	162	157
Equil. adv.	133	134	136	146	142	141
Equil. rec.	132	134	138	143	144	141
Min. rec.	124	121	120	130	132	130
Nickel						
Max. adv.	148	150	156	161	160	165
Equil. adv.	139	135	138	146	145	145
Equil. rec.	138	134	137	146	146	145
Min. rec.	123	116	124	129	133	130
Quartz						
Max. adv.	147	144	150	152	155	159
Equil. adv.	132	132	124	130	132	136
Equil. rec.	134	132	122	131	132	136
Min. rec.	115	122	110	122	118	114
Glass						
Max. adv.	147	147	152	156	154	159
Equil. adv.	133	132	132	136	139	140
Equil. rec.	134	130	131	137	137	140
Min. rec.	122	112	120	125	126	125
Teflon						
Max. adv.	157	162	166	169	175	178
Equil. adv.	134	135	137	142	146	147
Equil. rec.	132	132	134	145	145	146
Min. rec.	104	98	109	119	119	116

of attack of solid surfaces by mercury such that equilibrium is not obtained in the time period of the observation has been ruled out.

With respect to the condition of the various surfaces, the observations noted above that the mercury surface and the metal and metal oxide surfaces were hydrophilic during the time period of the contact angle observations eliminates organic contamination as an important factor. The metal surfaces are undoubtedly covered with an oxide layer. The hydrophilic property of the metals and metal oxides does not eliminate the possibility of there being inorganic residues from the Tide cleaner, but previous work (*2, 3, 15*) strongly suggests that thorough rinsing, as was practiced here, should reduce such materials to a low level. The use of Tide for cleaning Teflon surfaces is satisfactorily documented (*1–3*).

Apparently, therefore, although the prime purpose was to obtain engineering data, the results may have fundamental significance. The satisfactory agreement between the mercury-Teflon contact angle reported here and two literature values supports this view. If the work does have fundamental significance, then two facets of the data are of interest. One concerns the similar contact angles of mercury on the various surfaces and the other concerns the effect of temperature on these mercury-solid contact angles.

It is unexpected that the contact angles of mercury on the "high energy" surfaces of tungsten, stainless steel, nickel, quartz, and glass are only slightly different from the contact angle of mercury on the "low energy" surface of Teflon. The different critical surface tension (γ_c) of Teflon surfaces (18.5 ergs per sq. cm.) *vs.* the other high energy surfaces (hydrophilic, therefore $>$ 72 ergs per sq. cm.) using Zisman's concept (*16*), or the different dispersion force contribution to the surface free energy (γ_s^d) of Teflon surfaces (19.5 ergs per sq. cm.) *vs.* quartz (silica-78 ergs per sq. cm.) or stainless steel (Fe and Fe_2O_3, 107 ergs per sq. cm.) using Fowkes' concept (*6*), both predict different contact angles of mercury on Teflon *vs.* the other surfaces. The expected difference in mercury-solid contact angles is probably too great to be accounted for on the basis of deformation of the interfacial boundary (*12*). One "contaminant" that has not yet been considered is water. According to Fowkes (*7*), adsorbed water could reduce the γ_s^d values for the metals and oxides to about 20, a value close to that of Teflon. Although dry nitrogen was the atmosphere for these experiments, adsorbed water which is tenaciously held by oxides would probably be held on the surfaces. This, then, is the best explanation that can be offered for the contact angle results.

The effect of temperature on contact angle has been reported for a number of systems, including hexadecane on a fluoropolymer (*11*), water on silicone-treated glass (*13*), and polar liquids on polyethylene (*14*). In all of these studies, temperature had only a small, sometimes negligible, effect on the contact angle. This work then enables us to add to this series of systems mercury on Teflon and mercury on metal oxides as further examples of the slight or negligible effect of temperature on solid-liquid contact angle.

LITERATURE CITED

(1) Bernett, M.K., Zisman, W.A., *J. Phys. Chem.* **63**, 1241 (1959).
(2) Bowers, R.C., Clinton, W.C., Zisman, W.A., *J. Appl. Phys.* **24**, 1066 (1953).
(3) Bowers, R.C., Clinton, W.C., Zisman, W.A., *Mod. Plastics* **31**, 131 (1954).
(4) Doyle, W.P., Ellison, A.H., *Advan. Chem. Ser.* No. **43**, 268 (1964).
(5) Ellison, A.H., *J. Phys. Chem.* **66**, 1867 (1962).
(6) Fowkes, F.M., *Ind. Eng. Chem.* **56**, 40 (1964).
(7) Fowkes, F.M., "Intermolecular and Interatomic Forces at Interfaces," 13th Sagamore Army Materials Research Conference, Raquette Lake, N. Y., August 23–26, 1966.
(8) Fox, H.W., Zisman, W.A., *J. Colloid. Sci.* **5**, 514 (1950).
(9) Gordon, C.L., Wickers, E., *Ann. N. Y. Acad. Sci.* **65**, 369 (1957).
(10) Gray, V.R., *Nature* **209**, 608 (1966).
(11) Johnson, R.E., Jr., Dettre, R.H., *J. Colloid Sci.* **20**, 173 (1965).
(12) Lester, G.R., *Nature* **209**, 1126 (1966).
(13) Phillips, M.C., Riddiford, A.C., *Ibid.*, **205**, 1006 (1965).
(14) Schonhorn, H., *Ibid.*, **210**, 896 (1966).
(15) Shafrin, E.G., Zisman, W.A., *J. Phys. Chem.* **66**, 740 (1962).
(16) Zisman, W.A., *Advan. Chem. Ser.* No. **43**, 1 (1964).

RECEIVED for review August 24, 1966. Accepted May 17, 1967. Work supported by the NASA Lewis Research Center, Spacecraft Technology Division, Cleveland, Ohio.