Chemical Reviews

THE SURFACE PROPERTIES OF MERCURY

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I. Introduction

Mercury, one of our most important elements, has been used in various forms for centuries. Many of its uses depend upon its surface properties, but the study of these has produced some of the greatest controversies in the field of surface chemistry. Burdon,[1] in his monograph on spreading phenomena, discussed some of the surface properties of mercury, but his

review was very limited, and he drew attention to the need for a more comprehensive and critical review of the subject. Thus, the purpose of this review is to examine as much of the pertinent literature as possible in order that some objective conclusions can be drawn.

A close study of the existing literature, in which a wide range of techniques are reported for the determination of the surface tension of mercury, reveals widely discordant results.[2-159] The reported values not only vary with the method

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of measurement employed but also between different workers using the same technique. The discrepancies between the data of different investigators far exceeds the possible errors and differences occasioned by the methods themselves.

Mercury can probably be obtained in purities much greater than any other element or compound. Indeed purification procedures are quite simple and extremely effective. Thus, the wide discordance in values for the surface tension cannot, in the majority of cases, be attributed to the presence of internal impurities. Mercury has a high surface tension value, and impurities would be expected to interact strongly at the surface. The presence of external impurities (*i.e.*, gas phase) may explain some of the low values, but it is unlikely that all values below about 520 dyn/cm are due to this factor alone. It is unreasonable to conclude that the highest values obtained for the surface tension are likely to be the most reliable.

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It is proposed to examine the reasons for the discrepancies in the surface tension values, and to indicate the factors governing the determination of an accurate value of the surface tension of mercury. The influence of adsorbed gases and vapors, impurities (both internal and external), surface age, and temperature on the surface tension of mercury, and the interfacial tension between mercury and water will be considered. In addition, the methods of purification of mercury, and the adoption of some criterion of purity, will be discussed.

A section dealing with spreading and wetting phenomena in systems involving mercury surfaces is included. The purpose of this is to show that mercury has an "ideal" high-energy surface and, as such, should prove to be a good choice for studies of surface phenomena.

II. Results of Literature Survey

Almost 200 values obtained for the surface tension of mercury, by a wide range of techniques, are given in Table I. The earliest value recorded was that of 563 dyn/cm measured by Morveau[2] in 1773. The most recent value is 484.6 dyn/cm measured by Schwaneke, et al.,[159] in 1970.[159a] Values quoted in standard reference books and surface chemistry texts range from 402 to 521 dyn/cm.[137,160-171] In two different texts pub-

Surface Tension (dyne/cm.)

Figure 1. Values recorded for the surface tension of mercury since 1805.

lished recently, values of 434.6[165] and 521 dyn/cm[137] are quoted. The most comprehensive text to date dealing with the surface properties of mercury is probably that of Semenchenko.[160] He lists about 30 independent determinations of the surface tension of mercury, but concludes that "it is extremely difficult to draw any definite conclusions…" from the values cited.

The results of Table I are presented in graphical form in Figure 1. Values obtained for the surface tension under vacuum are denoted by (×) to distinguish them from those obtained in air and other gases (·). The data can be analyzed by plotting a distribution curve for these values (Figure 2a). It is assumed that all the values are equally valid. This is obviously not the case but will serve for a preliminary examination of the data. A more complete analysis of the data, by individual method, will be given in section III.

The results of Figure 1 show that the range of values for the surface tension of mercury has varied little with time. This does not mean that the range of the majority of determinations has not narrowed, since this is evident from Figure 2. Although techniques of measurement have obviously improved during the last 30 years, very low and very high values are still being recorded.

The average of all the experimentally determined values is 466.3 dyn/cm, with one standard deviation being 33.0 dyn/cm. There are two distinct peaks in the distribution of these values, one occurring at about 435 dyn/cm and the other at about 475 dyn/cm (Figure 2a). This led Gmelin[170] to conclude that a mercury surface atom may have different states, one corresponding to a stable state with a low surface tension and the other to one with a high surface tension. Values recorded dur-

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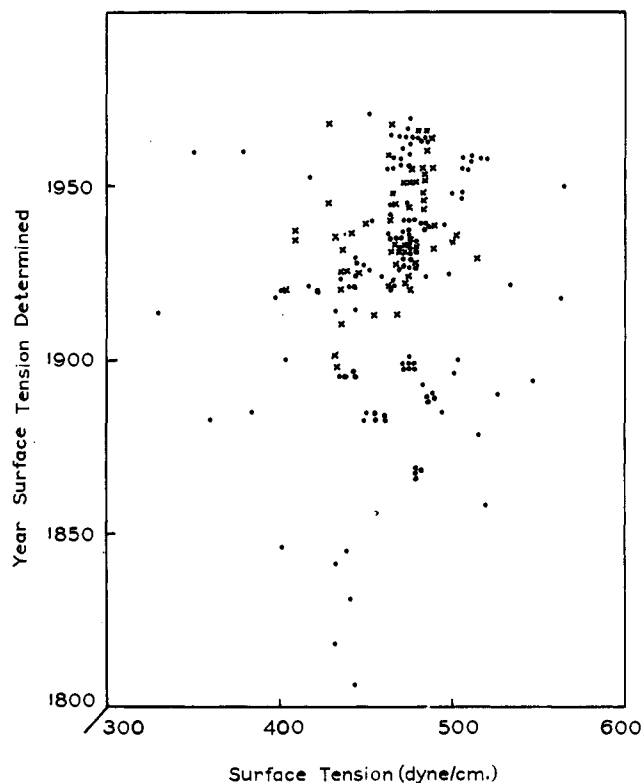
Table I

Values Recorded for the Surface Tension of Mercury

Year	Author (ref)	Method	Surface tension, dyn/cm	Temp,[a] °C	Conditions	Surface tension (25°), dyn/cm
1773	Morveau (2)	Plate detachment	563			562
1806	Laplace (3)	Shape of drop	443			442
1818	Gay-Lussac (4)	Capillary depression	434		Vacuum	432
1831	Poisson (5)	Sessile drop	442		Air	441
1841	Bravais and Martins (6)	Capillary depression	434		Air	433
1845	Laplace (7)	Sessile drop	440.5		Air	439.5
1846	Hagen (8)	Drop-weight	403		Vacuum	402
1857	Desains (9)	Sessile drop	457	20	Air	456
1858	Quincke (10)	Sessile drop	521	17.5	Air	519.5
1868	Quincke (11)	Drop-weight	398–560	20	Air	397–559
1869	Dupre (12)	Drop-weight	481		Vacuum	480
1869	Mensbrugghe (13)		482		Air	481
1878	Sondhauss (14)		491–541			490–540
1883	Bashforth and Adams (15)	Sessile drop	360	20	Air	359
1885	Worthington (16)	Sessile drop	493	20	Air	492
1885	Magie (17)	Curvature of a surface in a capillary	449	20	Air	448
1886	Lippman (18)	Sessile drop	470	20	Vacuum	469
1887	Sieg (19)	Capillary rise	456	20	Air	455
1887	Lenard (20)	Vibrating drop	461.9	20	Air	460.9
1889	Matthiessen (21)	Stationary waves on mercury surface	487	20	Air	486
1890	Piccard (22)	Vibrating drop	490	20	Air	489
1890	Smith (23)	Ripples on a mercury surface	529	12	Air	526.5
1890	Sentis (24)	Modified vertical plate technique	385	20	Air	384
1892	Cantor (25)	Maximum bubble pressure	452	20	Air	451
1893	Ramsey and Shields (26)	Capillary rise	479.7	40	Air	482.7
1894	Quincke (27)	Capillary rise	547	20	Air	546
1894	Verfasser (28)		445			444
1894	Meyer (29)	Capillary rise	439	18	Air	437.6
1895	Lohnstein (30)	Shape of drops	436.8			435.8
1897	Siedentopf (31)	Sessile drop	445	20	Air	443
			563	300	Hydrogen	508
1898	Meyer (32)	Vibrating jet	505	20	Air	504
1898	Stockle (33)	Sessile drop	435	15	Vacuum	433
			475	17	Dry air	473.6
			485	17	Moist air	483.6
			471	21	Hydrogen	470.2
			481	19	Carbon dioxide	479.8
			478	23	Oxygen	477.6
			479	16	Nitrogen	477.2
1900	Grunmach (34)	Capillary waves on mercury surface	491.2	18	Air	490.0
		Capillary waves on mercury surface (30 min old)	405	18	Air	403.8
1901	Watson (35)	Ripples on mercury surface	477.5–503.3	16	Air	475.7–501.5
1902	Kalahne (36)	Stationary waves on a mercury surface	432	18	Vacuum	430.6
1911	Schmidt (37)	Vibrating jet	435.5	17	Vacuum	434.0
1913	Cenac (38)	Drop-weight	437	0	Air	432
			460	0	Vacuum	455
1913	Lorenz and Liebmann (39)	Capillary depression	235	500	Hydrogen	330
1914	Hageman (40)	Vibrating jet	471.9	0	Vacuum	466.9
1914	Smith (41)	Capillary depression	447.5	15	Air	445.5
1916	Anderson and Bowen (42)	Capillary depression	400	16	Air	398.2
1917	Frenkel (43)	Calculation	472			472
1920	Harkins and Grafton (44)	Drop-weight	465	20	Air	464
1920	Palacois (45)	Maximum pressure in a drop	402	20	Vacuum	401
			402	20	Air	401
1920	Harkins and Ewing (46)	Drop-weight	476	20	Vacuum	475
1921	Popesco (47)	Sessile drop	436		Vacuum	435
1921	Hogness (48)	Maximum pressure in a drop	465	20	Vacuum	464
			465	20	Air	464
			465	20	Hydrogen	464
		Sessile drop	441	20	Air	440
1921	Richards and Boyer (49)	Sessile drop	441	30	Air	442
			432	30	Carbon dioxide	433

Table I (*Continued*)

Year	Author (ref)	Method	Surface tension, dyn/cm	Temp,[a] °C	Conditions	Surface tension (25°), dyn/cm
1922	Hartman (50)	Efflux of liquid jet	536	16	Air	534.2
1923	Iredale (51)	Drop-weight	472	18	Vacuum	470.6
1923	Glazebrook (52)	Capillary depression	436		Air	435
1924	Iredale (53)	Drop-weight	475	18	Vacuum	473.6
			460	18	Air	458.6
1925	Popesco (54)	Sessile drop	501	15	Air	499
			435	15	Vacuum	434
1925	Iredale (55)	Sessile drop	446	18	Vacuum	444.6
			445	18	Air	443.6
1926	Bircumshaw (56)	Maximum bubble pressure	470	19	Hydrogen	468.8
1926	Owen and Dufton (57)	Capillary rise	485	17	Air	483.6
		Hyperbola method	474	17	Air	472.6
1926	Sauerwald and Drath (58)	Maximum bubble pressure	453–480	19	Carbon dioxide	451.8–478.8
1927	Auerbach (59)	Oscillating jet	450		Air	449
1927	Michelli (60)	Drop-weight	471	25	Air	471
1927	Coffman and Parr (61)	Drop-weight	468	25	Vacuum	468
1927	Burdon and Oliphant (62)	Sessile drop	490		Air	489
1928	Bircumshaw (63)	Maximum drop pressure	480	20	Vacuum	479
1928	Brown (64)	Maximum bubble pressure	472	18	Nitrogen	470.6
			477	18	Nitrogen	475.6
			477	18	Air	475.6
1928	Oppenheimer (65)	Capillary depression	437	20	Vacuum	436
1929	Cook (66)	Sessile drop	515 ± 7[b]	31	Vacuum	513.8 ± 7
1929	Perucca (67)	Sessile drop	444		Air	443
1931	Bircumshaw (68)	Maximum bubble pressure	480	20	Hydrogen	479
1931	Cassel and Salditt (69)	Maximum pressure in a drop	459	50	Vacuum	464
1931	Kernaghan (70)	Sessile drop	438.4 ± 0.3	12.5	Vacuum	435.9 ± 0.3
1932	Bosworth (71)	Drop-weight	482	14	Air	479.8
1932	Burdon (72)[c]	Sessile drop	488	25	Vacuum	488
			480	25	Air	480
1933	Sauerwald and Schmidt (73)	Pendant-drop	470	20.5	Air	469
			470	20.5	Vacuum	469
1933	Binne (74)	Maximum pressure in a drop	469.2	20	Vacuum	468
1934	Loman and Zwikker (75)	Contact angles on various substrates	476 ± 1.6		Air	475 ± 1.6
1934	Bradley (76)	Sessile drop	500.3	16.5	Vacuum	498.6
1934	Brown (77)[d]	Sessile drop	472.9	25	Vacuum	472.9
			472.1–473.2	25	Air	472.6
		Drop-weight	471.5	25	Air	471.5
1934	Bircumshaw (81)	Maximum bubble pressure	483	20	Nitrogen	482
1935	Neugebauer (78)	Maximum pressure in a drop	473 ± 0.5	20	Vacuum	472 ± 0.5
1935	Lemarchand and Convers (79)	Drop-weight	481	17	Air	479.4
			434	17	Vacuum	432.4
1935	Satterley and Strachan (80)	Stationary wave on a vertical jet	563	20	Air	562
1935	Bond (82)	Ripples on surface	475.5 ± 2	20	Air	474.5 ± 2
1935	Kernaghan (83)	Sessile drop	476.5	20	Vacuum	475.5
			471.0	20	Hydrogen	470.0
			469.0	20	Nitrogen	468.0
			465.2	20	Carbon dioxide	464.2
1935	Semenchenko, et al. (84)	Maximum pressure in a drop	410	20	Vacuum	409
1936	Puls (85)	Moving sheet	475 ± 2	20	Air	474 ± 2
1936	Convers (86)	Drop-weight	442	20	Vacuum	441
1936	Bering and Pokrovski (87)	Maximum pressure in a drop	410	20	Vacuum	409
			465	20	Hydrogen	464
1937	Semenchenko (88)	Shape of drop	473	20	Air	472
1937	Klyachko (89)	Plate detachment	502	18	Vacuum	500.6
1938	Bosworth (90)	Maximum bubble pressure	484	20	Hydrogen	483
			484	20	Air	483
			479.2	20	Carbon dioxide	478.2
1939	Iyengar and Rao (91)	Drop-weight	473.9	23.2	Air	473.7
1939	Bosworth (92)	Drop-weight	483.7	20	Air	482.7
		Maximum bubble pressure	482.5	20	Air	481.5
1939	Bate (93)	Contact angle against glass	490	20	Vacuum	489
1939	Scardina (94)	Modified capillary rise	438.5	27		438.9

Table 1 (Continued)

Year	Author (ref)	Method	Surface tension, dyn/cm	Temp,[a] °C	Conditions	Surface tension (25°), dyn/cm
1939	Convers (95)	Drop-weight	450	20	Vacuum	449
			494	20	Air	493
1940	Dunken (96)	Drop-weight	472–477	18 ± 2	Air	470.6–475.6
			480	18 ± 2	Air (free of carbon dioxide)	478.6
1940	Lyalikov (97)		454			453
1941	Didenko and Pokrovski (98)	Maximum pressure in a drop	464.4	20	Vacuum	463.4
1942	McDougal and Ockrent (99)	Contact angles on tilting plate	478 ± 15		Air	478 ± 15
1943	Dorfman (100)	Calculation	500–650			500–650
1945	Samoylowich (101–105)	Calculation	644			643
1945	Kistemaker (106)	Curvature of a surface in a capillary	430 ± 5	18	Undried air	428.6 ± 5
1945	Kemball (107)	Sessile drop	484.2 ± 1.5	25	Vacuum	484 ± 1.5
			479.0 ± 1.5	50	Vacuum	484 ± 1.5
1946	Kemball and Rideal (108)	Sessile drop	484.2	25	Vacuum	484.2
1946	Breger and Zhukhovitskii (109–111)	Calculation	1550			1550
1946	Astakov, Penin, and Dobkina (112)	Drop-weight	465			464
1947	Pugachevich (113)	Maximum pressure in a drop	465–470	20–25	Vacuum	465–470
1947	Pugachevich and Konstantynov (114)	Maximum pressure in a drop	465–470	20–25	Vacuum	465–470
1948	Jura (115)	Calculation	500	20	Air	499
1948	Greenway (116)	Maximum bubble pressure	508	20	Hydrogen	507
			508	20	Nitrogen	507
1949	Pekrovsky (117)	Maximum pressure in a drop	532	300	Hydrogen	477
1950	Popel (118)	Sessile drop	423	20	Air	421
1950	Kunin and Klyachko (119)	Plate detachment	565		Nitrogen	564
1951	Foryst (120)	Maximum bubble pressure	494	20	Hydrogen	493
			489	20	Nitrogen	488
			487	20	Carbon dioxide	486
1951	Law (121)	Sessile drop	495	25	Vacuum	495
1951	Kunin (122)	Calculation	796.8			795.8
1951	Pugachevich and Timofeevicheva (123)	Maximum pressure in a drop	470.0	20	Vacuum	469.0
1951	Pugachevich (124)	Maximum pressure in a drop	465.2–468.0	21	Vacuum	464.4–467.2
1953	Ziesing (125)	Sessile drop	484.9 ± 1.8	25	Vacuum	484.9 ± 1.8
1953	Zadumkin (126)	Calculation	465	20		464
1953	Karpachev, Smirnov, and Volchenkova (127)	Sessile drop	484.3 ± 1.5	16.5	Vacuum	482.6 ± 1.5
			477.4 ± 1.5	30	Vacuum	478.4 ± 1.5
1953	Bering and Ioileva (128)	Maximum pressure in a drop	484 ± 0.8	20	Vacuum	483.4 ± 0.8
1953	Stratton (129)	Calculation	390		Air	389
1954	Taylor (130)		465			465
1954	Smithsonian Physical Tables (131)		513	0	Air	507.5
			588	−40	Air	565
1956	Hansen and Stage (132)	Pendant drop	461 ± 2	30	Vacuum	462 ± 2
1957	Gordon and Wichers (133)		480	0		475
1958	Bikerman (134–137)	Hysteresis of wetting	466	22	Air	465.4
			510–521	24	Air	510–521
			504–533	7	Air	507.6–536.6
1958	Ferroni and Gabrielli (138)	Torsion balance	508.1 ± 0.5	18	Nitrogen	506.9 ± 0.5
1959	Ziv and Shestakov (139)	Sessile drop	480	20	Air	479
			530	300	Hydrogen	475
1959	Pugachevich and Timofeevicheva (140)	Maximum pressure in a drop	462.3 ± 0.7	22	Vacuum	461.7 ± 0.7
1960	Bobyk (141)	Maximum bubble pressure	350.5 ± 4	21	Nitrogen	349.7 ± 4
			363.0 ± 4	100	Nitrogen	379.0 ± 4
1960	Fesenko and Eremenko (142)	Maximum bubble pressure	475	20	Hydrogen	474
			475	20	Helium	474
1960	Monma and Suto (143)	Sessile drop	472	20	Air	471
1961	Nicholas Joyner, Tessem, and Olson (144)	Sessile drop	483.5 ± 1.0	25	Vacuum	483.5 ± 1.0
1961	Mayer (145)	Calculation	404	354		476.2
1961	Smolders and Duyvis (146)	Sessile drop	434.6	25	Hydrogen	434.6
1962	Staicopolus (147)	Calculation	478.0 ± 8	25	Air	478.0 ± 8
1962	Ellison (148)		475	26	Nitrogen	475.2

Table I (Continued)

Year	Author (ref)	Method	Surface tension, dyn/cm	Temp,[a] °C	Conditions	Surface tension (25°), dyn/cm
1962	Timofeevicheva and Lazarev (149)	Maximum bubble pressure	430 ± 2.6	22	Air	429.4 ± 2.6
		Maximum pressure in a drop	465 ± 2.6	22	Air	464.4 ± 2.6
1963	Timofeevicheva, Valetov, and Anurov (150)	Maximum pressure in a drop	465		Vacuum	464
1963	Olsen and Johnson (151)	Sessile drop	485.1	25	Vacuum	485.1
1964	Roberts (152)	Sessile drop	485.4	25	Vacuum	485.4
1966	Wilkinson (153)	Drop-weight	476 ± 2	25	Air	476 ± 2
1966	Fowkes (154)	Calculation	484 ± 7		Air	484 ± 7
1966	Parvatikar (155)	Calculation	472.3–534		Air	472.3–534
1967	Smith (156)	Wilhelmy plate	480.0 ± 0.9	25	Vacuum	480.0 ± 0.9
			480.0 ± 0.9	25	Helium	480.0 ± 0.9
1968	Lee (157)	Maximum bubble pressure	464.8	23	Air	464.4
			464.8	23	Argon	464.4
1968	Melik-Gaikazyan, Voronchikhina, and Zakharova (158)	Pendant drop	484.6 ± 1.3	25	Vacuum	484.6 ± 1.3
1970	Schwaneke, Falke, and Miller (159)	Maximum bubble pressure	481.4 ± 2	25	Helium Hydrogen Nitrogen Argon	481.4 ± 2

[a] Where temperatures were not recorded, the ambient room temperature was taken as 20°. All values have been adjusted to 25° by taking the value for the temperature coefficient of the surface tension as −0.20 dyn/(cm °C). [b] A check of the calculation made by Cook[66] shows that the value at 31° should be 492.8 dyn/cm, and not 515 dyn/cm as given. [c] Although Burdon[72] consistently obtained values between 470 and 480 dyn/cm, *in vacuo* and air, he quotes the highest value recorded (488 dyn/cm). His reasons for this, namely, that the highest value is likely to be the actual one, are not considered justified. [d] A check of the calculation by Brown[77] shows that the value at 25° should be 475.6 dyn/cm, and not 472.1 dyn/cm as given.

ing the last 30 years still show the presence of two peaks. The one at 435 dyn/cm, however, is much reduced.

In Figure 2b, values recorded *in vacuo* have been plotted separately from those in air and other gases. The values *in vacuo* show the presence of two distinct peaks of similar magnitude, these again occurring at 435 and 475 dyn/cm. For values in air and various gases two peaks are evident, but the one at 445 dyn/cm is much smaller than that at 475 dyn/cm. It is therefore apparent that the presence of the lower peaks in Figure 2a is mainly due to the values obtained *in vacuo*.

The number of values in excess of 480 dyn/cm drops off rapidly, such that only 10% of the total number of values lie above 495 dyn/cm. This sharp decrease indicates that the surface tension of mercury is probably lower than 500 dyn/cm. The lower limit is of the order 420 dyn/cm.

III. Analysis of Experimental Techniques

About 70% of all the determinations are due to just five methods, namely, sessile drop (26%), drop-weight (15%), capillary rise or depression (12%), maximum bubble pressure (10%), and maximum pressure in a drop (10%). The range of surface tension values determined by these methods has varied greatly. For example, the sessile drop technique has provided the biggest range (360–560 dyn/cm), while the drop-weight method has yielded values in a much smaller range (402–490 dyn/cm).

A. SESSILE DROP METHOD

1. Theory

Quincke[10] derived a formula relating the surface tension, γ, of a liquid to the dimensions of a large sessile drop, *i.e.*

$$\gamma = h^2\rho g/2 \tag{1}$$

where h is the height of the apex of the drop above the maximum cross-sectional area, ρ the density of the liquid, and g the acceleration due to gravity. Worthington[16] introduced two terms to account for (i) the curvature of the drop acting at right angles to the horizontal plane and (ii) the curvature at the vertex of the drop. Thus, the complete equation becomes

$$\gamma = \frac{h^2\rho g}{2} - \gamma \int_0^h \frac{\sin\phi}{x}\, dz + \frac{2\gamma h}{b} \tag{2}$$

where x is the horizontal radius of a given section above the maximum cross-sectional diameter and z the distance between the apex and this horizontal section. ϕ is the angle of inclination of the normal to the axis, measured on the side of the vertex—the normal acting at the drop surface, distance x from the axis. The radius of curvature at the apex is denoted by b.

The value of the integral in eq 2 was determined, to a first approximation, by Laplace[7] and Mathieu[172] to be

$$\frac{4\alpha}{3L}\left(1 - \frac{1}{2\sqrt{2}}\right) \tag{3}$$

where L is the maximum radius of the drop (at $\phi = 90°$), and α is defined as

$$\alpha = (\gamma/\rho g)^{1/2} \tag{4}$$

Thus, upon insertion of the value of the integral into eq 2 and rearranging

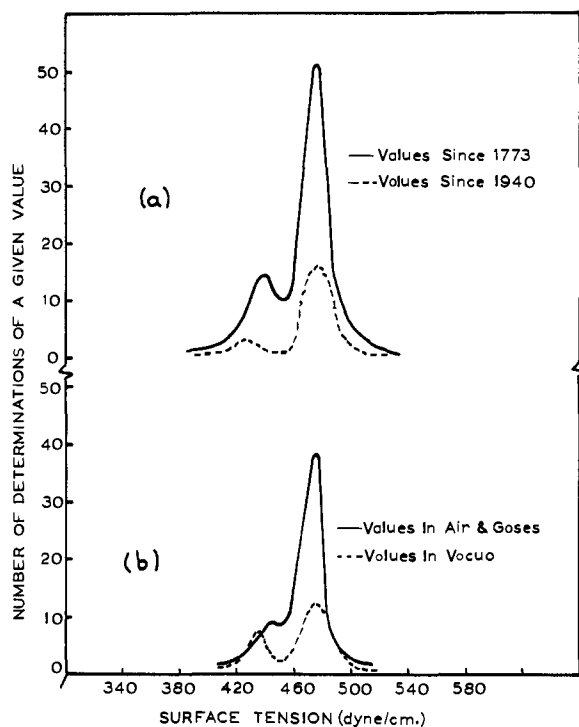(172) M. E. Mathieu, "Theorie de la Capillarite," Gauthier-Villars, Paris, 1883. p 137.

Figure 2. Statistical distribution of surface tension values for mercury.

$$\gamma = \frac{h^2\rho g}{2} \frac{1}{\left(1 - \frac{2h}{b} + \frac{0.8617\alpha}{L}\right)} \tag{5}$$

The term α can be replaced with the measured quantity h by means of the approximate relationship of eq 1 and 4. Further, the term involving b can be neglected[7] for drops greater than 4 cm in diameter since it becomes negligibly small. Thus, for large sessile drops eq 5 reduces to

$$\gamma = \frac{h^2\rho g}{2} \frac{1.641L}{1.641L + h} \tag{6}$$

If a value for γ is required to 0.1% or better, the complete value of the integral given in eq 2 should be employed. This is given by[172]

$$\int_0^h \frac{\sin\phi\,dz}{x} = \frac{4\alpha}{3} \frac{1 - \cos^3\phi/2}{x} + \frac{4\alpha}{3}\int 1 - \cos^3\phi/2\ dz \tag{7}$$

The error involved in the use of eq 6 varies with drop size. For example, Ziesing[125] has shown that for a 5-cm drop of mercury the error is 0.23%. Although some recent workers[152] have just added 1 dyn/cm to a value calculated by means of eq 6, it is clear that accurate values cannot be obtained unless recourse is made to eq 2.

All workers except Quincke,[10] Popesco,[47] Richards and Boyer,[49] and Iredale[55] have used the Worthington equation in the calculation of the surface tension of mercury. Worthington's value is based on Quincke's results. Although Richards and Boyer, and Iredale, used the Quincke formula, their drop size (1.5-cm diameter) was such that the Quincke equation

gives correct values for the surface tension.[72,173] Popesco's value, however, should be reduced to 410 dyn/cm.

2. Experimental Difficulties

a. Use of Nonoptical Flat for Observation Window

Kemball[107,108] found that, for a window where the faces are nonparallel by only 0.38°, the error involved in the measurement of h could produce an error as large as 28 dyn/cm in the calculated surface tension. Optical glass windows offered by technical firms usually have an angle between the faces of $\pm 0.0833°$; this would introduce an error of ± 7 dyn/cm. Since it is difficult to obtain a window in an apparatus which has no angle between the faces, it is important that a correction be made for the measured value of h.

b. Location of the Vertex of the Drop

The location of the vertex of a drop of mercury is a matter of some difficulty because of the high coefficient of reflectivity of the mercury surface. Poor location of the vertex of the drop would involve an error in the value of h, and, since this value occurs as a square in the final equation, a large error in the calculated surface tension would occur.

Various methods have been used by workers to define the top of the drop. Burdon[174] does not recommend the use of diffuse lighting since the true summit of the drop cannot be precisely located. Ziesing[125] has shown that the use of parallel light introduced an error in h of 0.001 cm (± 3.8 dyn/cm in γ) due to the presence of "diffraction bands." These bands did not originate from the true summit of the drop but from some vertical plane either on the near side or the far side of the summit.

Cook[66] located the apex of a mercury drop by using a background which was ruled with alternate black and white lines. This was placed such that the lines were inclined at about 30° from the vertical. The angle formed between the parts of the lines visible above the mercury and their reflections was sharply marked. Cook found that the apex could be located by this method to within ± 0.001 cm. The telescope must be focused on the card and not the drop, and there is thus a considerable horizontal distance between the points, the vertical separation of which must be measured. This increases any error due to inaccurate leveling, and if the aperture is small, it is not easy to see reflections from a horizontal surface using a truly horizontal telescope.

The pointer reflection method has been used by Kemball[107] to determine the position of the apex of a large sessile drop. The tungsten pointer was controlled externally by a magnet and came down about 2–3 mm from the center of the drop. He showed that for a drop 5 cm in diameter there was negligible difference in height between a point as far as 5 mm from the center of the drop and the vertex itself.

c. Location of the Maximum Diameter of the Drop

The maximum diameter of the drop can be located with great precision by astigmatic reflection of a small source of light in the curved surface.[49] An error in L of less than 0.05% will be incurred for a large drop.

(173) H. S. Gibson, *Proc. Roy. Soc., Ser. A,* **56,** 51 (1932).
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d. Alteration of the Height of the Measuring Instrument during Movement

The height of a 5-cm diameter drop is approximately 0.280 cm, but the horizontal distance between the maximum diameter and the maximum height of the drop may be 2 cm or more. If the instrument is of sufficiently long focus to require no horizontal movement between the settings, there might still be an error unless absolute horizontality of the optical axis is maintained. If the instrument itself has to be moved between settings of these points, then there is a consequent risk of altering the height of the instrument during movement.

B. DROP-WEIGHT METHOD

1. Theory

The approximate relation between the weight of a drop of liquid (volume, v) falling from an orifice (radius, r) and the surface tension of the liquid (γ) was first observed by Tate[175] in 1864. The theory of the method was later considered by Rayleigh,[176] Lohnstein,[177] Kohlrausch,[178] and Ollivier,[179] but that the method is now capable of giving accurate results is due to the work of Harkins and his two associates, Humphrey[180] and Brown.[181] Harkins and Brown did a complete analysis of the corrections which needed to be applied to give results corresponding with the capillary rise method.

The original equation developed by Tate for the mass of a drop (m) falling from a dropping tip of radius r is given by

$$\gamma = mg/2\pi r \tag{8}$$

The equations which are presently used in conjunction with the empirically determined correction factors are

$$\gamma = \frac{mg}{2\pi r f(r/a)} = \frac{mg}{2\pi r \psi(r/v^{1/3})} \tag{9}$$

The tables of $\psi(r/v^{1/3})$ correction factors are normally employed since the $f(r/a)$ correction factors involve a series of approximations to determine γ.

The Lohnstein correction factors [$f(r/a)$] were derived theoretically and are based on the ratio r/a, where a is the capillary constant, being defined as

$$a = (2\gamma/\rho g)^{1/2} \tag{10}$$

Values of r/a and $r/v^{1/3}$ are related by means of eq 11, which has been discussed by Lunn[182] and can be simply derived from eq 9 and 10.

$$\frac{r}{a} = \left[\pi \left(\frac{r}{v^{1/3}} \right)^3 \psi \left(\frac{r}{v^{1/3}} \right) \right]^{1/2} \tag{11}$$

It can be seen from Figure 3 that the Lohnstein correction factors are incorrect for $r/v^{1/3}$ values greater than 0.40.

Harkins and Brown's correction factors are applicable in the range $0.72080 \geq \psi(r/v^{1/3})$ [$=f(r/a)$] ≥ 0.5357, but where

possible dropping tips should be chosen such that the correction factor is in the range 0.6000–0.6250.[183] Harkins and Brown did not determine values for correction factors greater than 0.72080. Values of 1.0000, 0.9240, 0.8050, and 0.7410, which are given in some recent texts,[165,166] are attributable to Lohnstein. Recent work by Wilkinson[184] (Figure 3) indicates that these may be in error.

It can be seen from Figure 3 that errors as great as 40% can be expected unless the Harkins and Brown correction factors are employed. Harkins[163] suggests that, using his tables, an ultimate accuracy of 0.02% can be claimed for drops falling from the outside diameter of a dropping tip. For drops emerging from the inside diameter, i.e., nonwetting, the accuracy will not be as good, but should be better than 1%.

Coffman and Parr[61] reported that the surface tension of mercury, calculated by means of eq 9, varied with the size of the dropping tip. The surface tension decreased from 506 to 450 dyn/cm as the dropping tip radius was increased from 0.75 to 2.3 mm. These findings cannot be excepted since they are uncorroborated by any other worker. For example, Brown, Harkins, and Ewing, Wilkinson, Dunken, Lemarchand, and Convers, and Iredale all obtained values between 470 and 480 dyn/cm, and the dropping tips used varied from 1.2 to 2.5 mm.

a. Applicability of Correction Tables to Liquids of High Density

Harkins and Brown's correction factors were determined for liquids of surface tensions between 26.6 and 72.8 dyn/cm, and densities of 0.8787 to 2.178 g/cm³. Harkins and Grafton,[44] and later Harkins and Ewing,[46] proceeded to use the correction tables for the determination of the surface tension of mercury, density 13.59 g/cm³. Since that time a great deal of use has been made of the drop-weight method for the determination of surface tensions of liquid metals.[185-190]

Although the applicability of the correction tables to liquids of low densities (<2.2 g/cm³) is now firmly established, the extension of the tables to liquids of much greater densities may be questionable.[62,182] At the present time the accuracy with which many of the surface tensions of liquid metals is known is rather poor, and thus any differences in surface tensions determined by the drop-weight method, and other techniques, may not be large enough to be apparent.

Dunken[96,191-193] measured the weights of drops of mercury falling from small capillaries (0.009–0.084-cm radius) that were immersed in various organic liquids. His theoretical calculations of the mercury–organic liquid interfacial tensions

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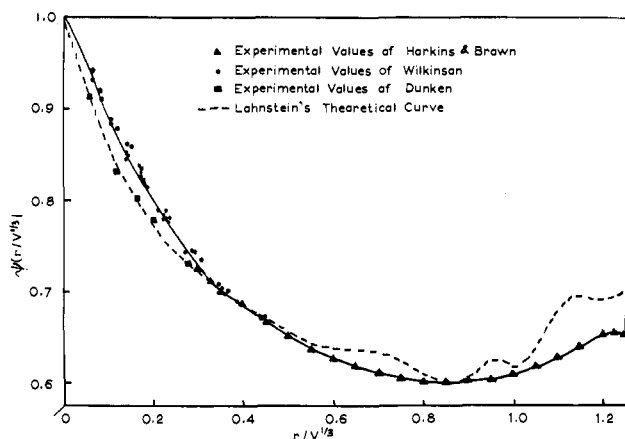(193) I. Fredenhagen, Dissertation, Halle, 1942.

Figure 3. Drop-weight correction factors for use in the calculation of surface and interfacial tensions.

agreed well with those of Harkins and coworkers, who had used the Harkins and Brown correction tables. Dunken therefore concluded that Harkins and Brown's correction tables must be applicable to liquid mercury.

Calculation of $r/v^{1/3}$ and $\psi(r/v^{1/3})$ values using Dunken's experimental data shows that the majority of results lay in the range $1.000 \geq \psi(r/v^{1/3}) \geq 0.700$, i.e., outside the range of the Harkins and Brown correction factors (Figure 3). Dunken's results are in agreement with Lohnstein's theoretical values, but in disagreement with the values of Wilkinson.[184] Wilkinson's values, however, are based on liquids with densities within the range used by Harkins and Brown.

Further work is in progress in these laboratories[193a] to settle the questionable validity of the Harkins and Brown's drop-weight correction factors to liquids of high density.

2. Experimental Difficulties

a. Process of Drop Detachment

For the determination of an accurate surface tension value, the drop should be formed as slowly as possible. Alternately, the method described by Harkins and Alexander[194] can be used. In this method approximately 90–95% of the final volume of the drop (found by practice) is formed in 0.5–1 min, the last fraction of the drop being formed very slowly (1–2 min). Although rigid control can be maintained on the rate of formation of a drop up to 99% of its final volume, when "breakaway" of the drop commences,[195] no further control is possible.

For "nonwetting" liquids which come from the inside bore of the orifice, stretching of the "necks" during detachment may lead to incorrect values for the cross-sectional areas of the tube. This is caused by the downward forces pulling the liquid from the sharp (and measured) edge of the orifice; i.e., the actual position at which the liquid is in contact with the bore of the orifice is displaced from the true edge of the orifice. Displacement of the liquid from the sharp edge of the orifice

may allow an external phase, i.e., wetting phase to penetrate up the bore of the orifice.[196] Thus, the mode of detachment may be different from that for a "wetting" liquid.[62] The actual cross-sectional area from which the drop breaks away will not be the measured cross-sectional area of the orifice edge. It will in fact lie part-way up the bore of the tube. If the mode of detachment of "non-wetting" and wetting drops are the same, then the true cross-sectional area will be at the position where the liquid is still in contact with the bore of the tube; i.e., if the tube is of constant bore no discrepancy in the calculated surface tension will occur. If, however, this is not the case then the value of r used in eq 9 will be incorrect. Since values of surface tensions of nonwetting liquids compare favorably with those obtained by other methods, it is probable that if any error of the type discussed is introduced, it is of small magnitude.

b. Noncircularity of the Orifice

To produce an orifice in glass which is completely circular and free from chipping is difficult. Harkins and Brown have suggested a method which "gave tips of excellent quality, such that various diameters of the same tip rarely differed from each other by 0.1%; furthermore the edges of the better tips had no flaws prominent enough to be visible under a magnification of 10 diameters." Some firms[197,198] specialize in grinding high-precision constant-bore tubing to give tips of excellent quality.

Before use the dropping tip has to be aligned such that the plane of the tip is in a horizontal plane. If the dropping tip is ground such that the end is at right angles to the body, then it can be aligned in a horizontal plane by use of a plumb line. The orifice is aligned in two vertical planes, mutually at right angles to each other. Gans and Harkins[199] showed that the variation in the angle of inclination of the tip of 5°, for water drops in air, only made an error of 0.3% in the drop-weight. Similar, small errors were found by Wilkinson[153] for mercury drops. Although, for angles of inclination up to 5° to the vertical little effect is produced on the calculated surface tension, it is suggested that in all cases extreme care is taken with the alignment of the orifice.

C. CAPILLARY RISE METHOD

The capillary rise method is probably one of the most accurate of all methods for the determination of surface tensions.[188,200] However, for accurate results, it is essential that the liquid completely wet the wall of the capillary (contact angle, 0°) so that there is no uncertainty with regard to the contact angle. This point is of particularly great interest when it is considered that θ can vary depending on whether the liquid is advanced or receded along the capillary wall. This phenomenon is referred to as contact angle hysteresis.[201]

Unfortunately there is no agreement on what the contact

(193a) Center for Surface and Coating Research, Lehigh University, Bethlehem, Pa. 18015.

(194) W. D. Harkins and A. E. Alexander, "Physical Methods of Organic Chemistry," 3rd ed, A. Weissburger, Ed., Interscience, New York, N. Y., 1959.

(195) H. E. Edgerton, E. A. Hauser, and W. B. Tucker, J. Phys. Chem., 41, 1017 (1937).

(196) A. Couper and D. J. Priest, Proc. Congr. Surface Activity, 3rd, Cologne, 2, 170 (1960).

(197) Burrough's Wellcome and Co., Ltd., Enston Road, London N.W.1. England.

(198) Wilmad Glass Co., Buena, N. J., U. S. A.

(199) D. M. Gans and W. D. Harkins, J. Amer. Chem. Soc., 52, 2289 (1930).

(200) T. W. Richards and E. K. Carver, ibid., 43, 827 (1921).

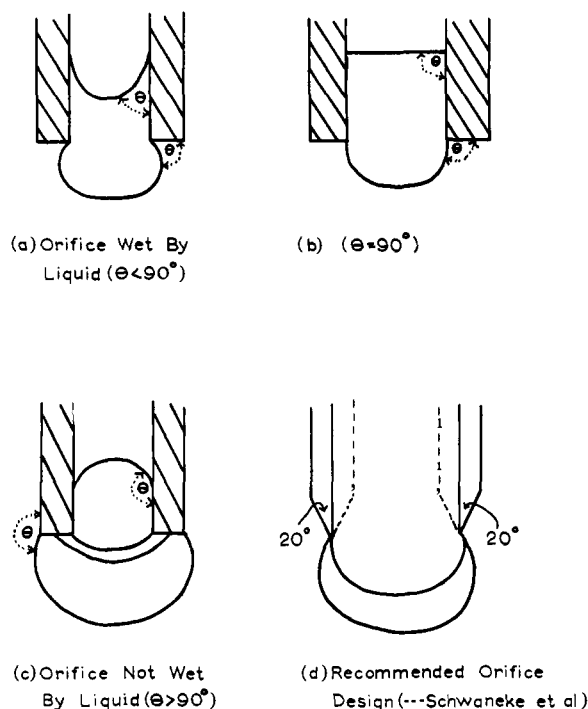(201) R. H. Dettre and R. D. Johnson, Advan. Chem. Ser., No. 43, 1964.

(a) Orifice Wet By Liquid ($\theta < 90°$)

(b) ($\theta = 90°$)

(c) Orifice Not Wet By Liquid ($\theta > 90°$)

(d) Recommended Orifice Design (---Schwaneke et al)

Figure 4. Bubble profiles on wetting and nonwetting tips and the preferred shapes of tips to be used in the maximum bubble pressure method.
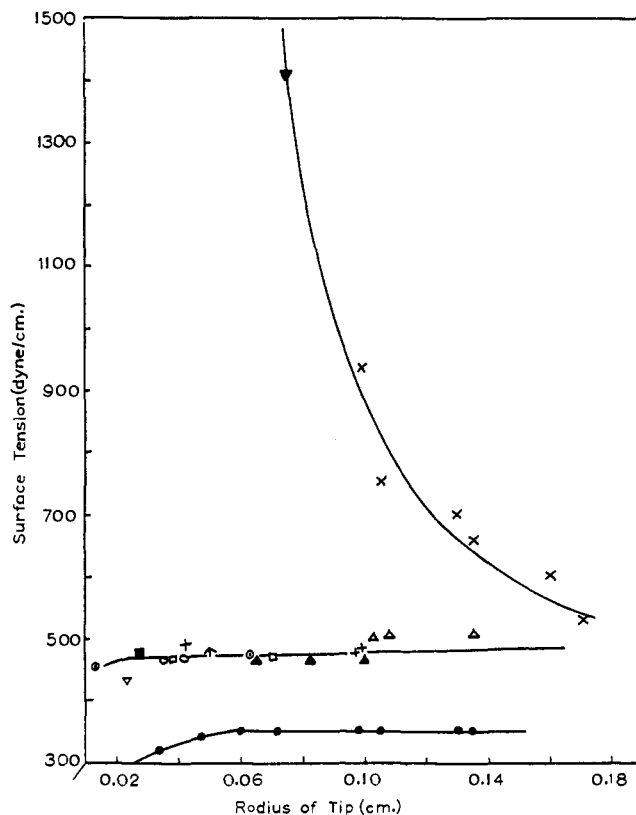

Figure 5. Surface tension values recorded by the maximum bubble pressure method using different size orifices. Symbol for inner radius, symbol for outer radius, tip, author, respectively: ●, ×, glass, Bobyk; ▼, ▽, glass, Pugachevich and Timofeevicheva; ○, □, glass and platinum, Brown; .., △, silica and stainless steel, Greenway; .., ▲, stainless steel, Lee; ■, +, amalgamated copper, Bosworth; ..,↑, glass, Bircumshaw; ..,⊙,.., Sauerwald and Drath.

angle of pure mercury is on glass or quartz.[43,75,93,99,202-205] Reported values for θ have varied from 90[93] to 150°.[42] This large variation in θ is in accord with the very large range of surface tensions measured by this technique, i.e., 330–546 dyn/cm.

D. MAXIMUM BUBBLE PRESSURE METHOD

The maximum bubble pressure method was first suggested by Simon[206] in 1851, and was subsequently developed by Jaeger.[207] Cantor[25] appears to have been the first to produce an account of the theory and to show how it could be used accurately. Sugden[208] considered the method in detail and made use of the Bashforth and Adams' tables to calculate correction factors. A recent critical analysis of the maximum bubble pressure method has been given by Pugachevich.[209]

The method does not depend on the contact angle for wetting liquids (contact angles <90°); see Figure 4. However, for nonwetting liquids, such as mercury on glass, the position of the gas–mercury–solid interface at maximum bubble pressure may lie between the inner and outer diameters of the jet. This particular problem has been very pronounced in the reported measurements on mercury and led Cantor to conclude that

the "ideal" jet should have internal and external diameters which are very close to each other. Unfortunately this type of jet is almost impossible to make in practice.

A jet of the type depicted in Figure 4d may be suitable for liquids whose contact angles against the material of the jet are greater than 90°. The end of the jet is machined to produce an angle at the tip of about 20°. This angle has been decided upon since the maximum contact angles recorded for mercury on most solids are of the order 150–155°.[202] It will be seen that, for jets of this type, liquids of contact angles between 90 and 155° will have stable positions at the sharp edge of the jet.

Most of the early workers using this technique recorded values for the surface tension of mercury calculated from both the internal and external diameters of the jets and decided which of the diameters gave the correct value for the surface tension by comparison with the then accepted values for mercury. The results of some of these workers are given in Figure 5. It is seen that very good agreement was obtained by different workers using different jets, values for the surface tension lying in the range 432–507 dyn/cm.

The surface tension of mercury should not vary with the diameter of the jet. This fact is well demonstrated by all workers, except Bobyk;[141] see Figure 5. The excessively high values obtained with the outside diameter are unreasonable, and it is certain that the bubble did not extend to the outer diameter of the jet at its maximum bubble pressure. This conclusion is confirmed by Timofeevicheva and Lazarev[149] who purposely

(202) A. H. Ellison, R. B. Klemm, A. M. Schwartz, I. S. Grubb, and D. A. Petrash, *J. Chem. Eng. Data*, **12**, 607 (1967).

(203) G. D. Yarnold, *Proc. Phys. Soc. (London)*, **50**, 540 (1938); **58**, 120 (1946).

(204) K. C. D. Hickman, *J. Opt. Soc. Amer.*, **19**, 190 (1929).

(205) W. Cawood and H. S. Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

(206) M. Simon, *Ann. Chim. Phys.*, **32**, 5 (1851).

(207) F. M. Jaeger, *Z. Anorg. Allg. Chem.*, **100**, 1 (1917).

(208) S. Sugden, *J. Chem. Soc.*, 858 (1922); 27 (1924).

(209) P. P. Pugachevich, "Surface Phenomena in Metallurgical Processes," A. I. Belyaev, Ed., translated by Consultants Bureau, New York, 1965, p 152.

employed a thick-walled jet and obtained an excessively high value of 1418 dyn/cm based on the outside diameter. The relatively constant value of about 350 dyn/cm obtained for the internal radius by Bobyk could be accounted for by considering that the gas-mercury-glass interface did not coincide with the internal diameter of the jet, i.e., $r > r_{int}$. Another possibility is that the value was real but low because of the presence of impurities.

Several workers have noted that the position at break-away of the bubble depends strongly on the treatment given the jet. Bircumshaw[56] gave an apparent value of 673 dyn/cm for the surface tension of mercury using polished silica tubes and assuming bubble break-away occurred at the outside diameter of the jet. After he had frosted the tubes the value fell to 481 dyn/cm. Similar observations were recorded by Greenway[116] and Brown.[64] These findings are understandable when it is considered that surface treatment of a solid surface can have a profound effect on the contact angle,[201] and thus the position of the gas-mercury-solid interface. Bosworth[71] considered this problem and showed that for amalgamated copper jets, where the contact angle was close to zero, only one type of bubble was obtained, i.e., from the inner diameter of the jet.

From the above discussion it is apparent that a knowledge of what value of r is to be taken is of paramount importance. To date many workers have used jets of appreciable thickness and have calculated the surface tension from the radius that gives the most likely value, the assumption being made that the bubble is either at the internal diameter or at the external diameter. Although this assumption may be valid in many instances, it can be a source of error. It is well known that mercury has a tendency under certain conditions to "stick" to glass.[64,210] This could lead to erroneous values for the true magnitude of r to be used in the calculation of γ.

E. MAXIMUM PRESSURE IN A DROP METHOD

This technique is analogous to the maximum bubble pressure method. It involves the measurement of the force required to force a liquid, whose surface tension is to be measured, through a capillary jet. The theory, which is the same as that for the maximum bubble pressure method, was developed by Cantor,[25] and later corrected by Feustel[211] and Verschaffelt.[212]

The method, unlike that of the maximum bubble pressure method, can be used to determine values for the surface tension in vacuo. For nonwetting liquids, such as mercury, the liquid attains its maximum drop shape while at the internal diameter of the capillary jet (see Figure 4). For wetting liquids the difficulty as to where the drop lies at the position of maximum drop pressure will become a problem. Timofeevicheva and Lazarev[149] concluded that the surface tensions of wetting liquids should be determined by the maximum bubble pressure method, and those of nonwetting liquids by the maximum pressure in a drop technique, the internal capillary radius being used in the calculations.

F. OTHER METHODS

Several workers[132,158] have used the pendant drop technique to determine the surface tension of mercury. This technique,

which was developed by Andreas, Hauser, and Tucker,[213] depends on several measurements on a hanging drop. Tables are now available for the accurate determination of surface tensions from these dimensions.[213-217] The usual procedure is to take photographs, and then make measurements directly from the photographic plate. Errors in any of the three measurements required results in a large error in the calculated surface tension since the measurement used in the calculation is less than unity and is squared. As in the case of the sessile drop, measurements are very difficult owing to the high reflectivity of the mercury surface, making the detection of the surface difficult.

The hyperbola method,[57] tilting plate,[99] curvature of a surface in a capillary,[18,107] contact angle against glass,[93] and modified vertical plate techniques[2,24,89,134-138,156] have been applied to the measurement of the surface tension of mercury. Since all these depend to some extent on the knowledge of the contact angle, the reported values may be dubious.

Various dynamic methods, such as studies of the wave forms of vertical jets[37,40,50,59,80] and ripples on a horizontal surface,[23,36,82] have been applied to the measurement of the surface tension of mercury. Values recorded have been in the range 434-534.2 dyn/cm. Many of these workers also used the technique to measure the surface tensions of other pure liquids, obtaining values which agreed well with accepted standards. The wide variation in the results for mercury may be due to the difficulties in measurements on the wave forms (refer to section detailing experimental difficulties in measurements on sessile drops).

G. CONCLUSIONS

The theoretical and experimental aspects of the five major methods used to measure the surface tension of mercury have been examined. Complete theoretical analyses of all these methods had been firmly established by the late 1800's and therefore the wide divergence between the vast majority of results cannot be accounted for on this basis.

The sessile drop, drop-weight, maximum bubble pressure, maximum pressure in a drop, and capillary rise techniques are all capable of measuring surface tensions to an accuracy of about 0.1%. The capillary rise-depression technique is not considered reliable for mercury, however, because of the lack of certainty of the contact angle, a problem which can also lead to erroneous results in the maximum bubble pressure method. The sessile drop method (and pendant drop) is probably one of the most popular methods but is wrought by many experimental difficulties, and unless great care is taken errors as large as 2-3% can be expected. The drop-weight and maximum pressure in a drop methods do not involve any great experimental difficulties and have also produced the most consistent range of values for the surface tension of mercury.

Although the range of surface tension values recorded has narrowed during the last 3 decades, it is still exceptionally large (Table II). The type of distribution of these values is given in Figure 2. The average of all these values is 469.7 ±

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(211) R. Feustel, Drud. Ann., 16, 6 (1905).
(212) I. E. Verschaffelt, Verh. Kon. Acad. Wetensch. Amsterdam, 27, 208 (1908).

(213) J. M. Andreas, E. A. Hauser, and W. B. Tucker, J. Phys. Chem., 42, 1001 (1938).
(214) D. O. Niederhauser and F. E. Bartell, Report of Progress—Fundamental Research on Occurrence and Recovery of Petroleum, 1948-1949, American Petroleum Institute, Baltimore, Md., 1950, p 114.
(215) S. Fordham, Proc. Roy. Soc., Ser. A, 194, 1(1948).
(216) O. S. Mills, Brit. J. Appl. Phys., 4, 247 (1953).
(217) C. E. Stauffer, J. Phys. Chem., 69, 1933 (1965).

Table II

Range of Surface Tensions (dyn/cm) Obtained by Different Methods

Method	Year theory estab-lished	Range of values	Values since 1940		
			Range of values	Av value	Std dev
Sessile drop	1885	359–508	421–495	474.4	20.6
Drop-weight	1919	432.4–493	464–478.6	472.8	5.5
Capillary rise	Pre-1880	330–546			
Maximum bubble pressure	1892	349.7–507	349.7–507	465.1	42.2
Maximum pressure in a drop	1892	401–483.4	461.7–483.4	469.0	6.5
Miscellaneous		384–564	428.6–564	485.5	36.3

34.3 dyn/cm, a value very little different from that of 466.3 ± 33.0 dyn/cm as the average of all the values in Table I. On this basis there is no justification for eliminating values simply because they were obtained 30, 40, or more years ago.

It has been possible to eliminate some of the values recorded for the surface tension of mercury, but in some cases this is not possible. For example, the exceptionally low value of 359 dyn/cm due to Bashforth and Adams is difficult to account for since the use of their classic tables for the shapes of drops is beyond refute. Also, the recent work of Bobyk is difficult to explain, although in this case the location of the bubble at break-away may not have coincided with r_{int}. Thus, recourse must be made to the examination of other factors, such as impurities (both internal and external), to explain the discordance.

IV. Purification and Criteria of Purity of Mercury

A. PURITY OF MERCURY

Many hundreds of papers have been written dealing with the purification of mercury, and several excellent reviews have appeared.[133,218] The purification of mercury, and the adoption of some criteria of purity, however, is of obvious importance to the present review. Thus, in this section some of the more important aspects of the preparation of pure mercury will be dealt with. The section will also include updated references that have appeared after Soucek's review in 1964,[218] wherein Soucek claimed to have referred to 95% of all references pertinent to the purification of mercury.

All commercially successful methods of purification of mercury are dry processes and depend on the separation of the mercury in the vapor state from the crude ore (cinnabar). Virgin mercury that is produced in this manner at the mines usually has a bright, mirror-like surface and is clean except for traces of scum, or perhaps particles of rust, or other foreign matter from dirty containers. It is perhaps not generally realized that virgin mercury contains a smaller percentage of impurity at this stage than most other known compounds in their pure states. A typical summary of the purity of virgin mercury, as produced at an Italian source,[219] is given below.

"The technical quality of mercury metal is far higher than almost all other elements and the total impurities present rarely add up to more than from 2–5 part per million as non-volatile residue. These consist principally of small amounts of mercury sulphide and/or oxide film from the distillation at the mine and physical contamination of the type which might be anticipated from the use of iron flasks (*i.e.*, rust, dust etc.). Other elements are present in concentrations which appear to be 1 part per million individually, which makes it extremely difficult to specify what is present, even by spectrographic analysis, due to the limits of sensitivity of the methods available. There has been some evidence of traces of magnesium up to 1 part per million and possibly copper, but at concentrations probably below 0.5 part per million, and somewhat lesser concentrations of tin, zinc, silver and other metals."

The specifications regarding the purity of mercury differ widely, and very little with regards to comparative statements can be made.[220] The ACS specifications,[221] which are quoted by most suppliers of mercury,[222–224] usually require foreign metals present in less than 5 ppm (wt/wt). Other standard texts[225] require total impurity metals to be less than 10 ppm. Some suppliers[223] have available very high purity mercury[226] and produce spectrographic analyses for their samples. Spectrographic analyses, however, are usually routinely concerned with the presence of silver, copper, zinc, and gold, and it is usually stated that "values of <0.3 ppm of these materials are barely detectable and should not be interpreted quantitatively."[226]

The metals which are usually present with mercury in its virgin state are copper, silver, gold, zinc, tin, and occasionally magnesium. Zinc probably accounts for the bulk or the impurities (see Table III), while silver and gold are rarely encountered in quantities greater than 1–2 ppm.[227] Although the total amount of metal impurities in mercury in its virgin state probably varies from source to source, the quantity almost certainly is very much less than 0.01% by weight. Some of the solubilities (20–25°) reported for metals in mercury[228–236] are given in Table III.

Most of the grades of mercury available, such as "triple distilled," "chemically pure," "commercial," "polarographic," etc., describe methods of purification and not standards of purity.[237] Although all these may comply with the ACS, USP (United States Pharmacopeia), NF (National Formulary), or

(218) J. Soucek, *Chem. Listy*, 58, 1203 (1964).

(219) Information Supplied by Italian Source of Mercury Shipped to River Chemical Co., Nottingham, England.

(220) D. A. Goldsmith, American Laboratory, Dec 1969.

(221) "Reagent Chemicals," ACS Specifications, 1968, American Chemical Society, Washington, D. C.

(222) Fisher Scientific Co., Fair Lawn, N. J. 07410.

(223) Bethlehem Apparatus Co., Inc., Hellertown, Pa.

(224) J. T. Baker Chemical Co., Phillipsburg, N. J. 08865.

(225) J. Rosin, "Reagent Chemicals and Standards," 5th ed, Van Nostrand, Princeton, N. J., 1967.

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(234) A. A. Sunier and C. B. Hess, *ibid.*, 50, 662 (1928).

(235) A. A. Sunier and C. M. White, *ibid.*, 52, 1842 (1930).

(236) H. A. Liebhafsky, *ibid.*, 71, 1468 (1949).

(237) D. F. Goldsmith Chemical and Metal Corp., Evanston, Ill. 60202.

Table III

Solubilities of Metals in Mercury

Metal	Solubility (% wt)	Ref	Metal	Solubility (% wt)	Ref
Antimony	2.9×10^{-5}	228	Lithium	0.09	228
Barium	0.33	228	Magnesium	0.24	228
Bismuth	1.4	228	Manganese	1.7×10^{-3}	229
Cadmium	4.92	228	Molybdenum	$<2 \times 10^{-5}$	218
Calcium	0.30	228	Nickel	$<2 \times 10^{-6}$	229
Cesium	4.34	228	Potassium	0.80	228
Chromium	4×10^{-7}	229	Rubidium	1.54	228
Colbalt	1×10^{-6}	229	Silver	0.042	228, 234
Copper	2×10^{-3}	230	Sodium	0.68	228
Gallium	1.3 (35°)	231	Thallium	42.8	228
Gold	0.13	228–236	Tin	0.62	228
Indium	27.0	232	Titanium	$<1 \times 10^{-5}$	230
Iron	1.5×10^{-6}	229	Tungsten	$<1 \times 10^{-5}$	230
Iron	1.5×10^{-8}	233	Vanadium	$<5 \times 10^{-5}$	230
Lead	1.3	228	Zinc	2.15	228

ADA (American Dental Association) specifications for having total foreign metals of less than 5 ppm, the actual differences in impurity content may in fact be small.[153] The problem is an analytical one, where reliable detection of impurities at, and below, 1 ppm becomes difficult.

It is the present unfortunate practice of most companies dealing in the purification of mercury to mix virgin mercury with mercury that is to be reclaimed.[237] Virgin mercury usually contains far less foreign metal impurities than mercury for reclamation and should be distilled separately to produce a "purer" distillate. The final decision as to purity required should be based on the total amount of impurities that can be tolerated, and not on any particular method of production.

Cherrier and Nalbantoglu[238] have recently analyzed samples of (i) "high-purity" mercury and (ii) mercury for reclamation, by means of spark source mass spectrometry (Table IV). It is

Table IV

Spectrographic Analyses of Mercury Samples

Impurities	Samples, ppm weight	
	(1) Industrial	(2) High purity
Bi	30	0.05
Cd	30	1
Ga	1.5	0.1
Zn	9	0.2
Cu	2.5	0.15
Fe	5–6	0.6
Mn	0.08	0.01
Ca	0.4	0.2
K	0.4	0.1
Cl	0.25	0.08
Al	0.4	0.1
Na	0.8	0.1
Total	81.33	Total 2.69

of note that virgin mercury does not normally contain such high levels of bismuth and cadmium. Further, although the mercury to be reclaimed had a large amount of metal im-

purity, the total amount in the "high-purity" sample was still 2.7 ppm. Normal emission spectrography of the "high-purity" sample of Table IV would probably have yielded a *total* impurity level of much less than 2.7 ppm, since the limit of detection is about 1 ppm for each element.

B. PURIFICATION OF MERCURY

Two methods are commonly employed for the purification of mercury, and they are either used separately or in conjunction.

1. Chemical Oxidation of Impurities[239-253]

This technique relies on the fact that nearly all base metal impurities to be found in mercury lie above mercury in the electrochemical series. Thus, the base metal impurities can be removed by the use of oxidizing solutions such as nitric acid or acidified potassium permanganate. For the removal of tin, zinc, and lead the oxidation procedure can be done with 4 N caustic soda solution.

Several methods have been described for creating a large mercury–solution interfacial area.[138] The simplest method, however, for agitating the mercury in contact with the acid or alkali, is by drawing air through the mercury as it stands under the oxidizing solution.[133]

The lower limit of base metal impurity which can be achieved

(238) C. Cherrier and M. Nalbantoglu, *Anal. Chem.*, **39**. 1640 (1967).

(239) V. G. Artamonov, *Zavod. Lab.*, **31** (2), 254 (1965).
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(246) Ying-Check-Chiu, *Hua Hsueh Tung Pao*, (1) 49 (1965).
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(250) V. Grmela, *Chem. Zvesti*, 20, 615 (1966).
(251) N. Heim, Hungarian Patent 148,842 (1960).
(252) B. H. Johnson, *J. Clin. Pathol.*, **23**, 1186 (1953).
(253) J. Fleck, Swiss Patent 288,422 (1967).

Table V

Amounts of Metal Impurities in Mercury during Distillation

	Zn	Cd	Cu	Sb	Pb	Au	Bi	Al	Sn
						Concentration, ppm (wt/wt)			
Liquid phase	80	50	0.3	0.01	3	<0.01	<0.01	<0.2	<0.01
Vapor phase	<0.7	<0.06	<0.1	<0.02	<0.1	<0.01	<0.02	<0.002	<0.02

by the chemical oxidation method is not known, but is probably very much less than 1 ppm of mercury. Moore,[254] using this technique of chemical oxidation, completely eliminated the main impurities of copper, lead and bismuth, in a sample of mercury. Gordon and Wichers[133] found that treatment with nitric acid reduced zinc, copper, and cobalt in commercial grade mercury to levels less than 1 part in 10^{10}.

It is difficult to lay down hard and fast rules about treatment times with acid wash, but where possible the treatment time should last at least 60 min. Russell and Evans[255] have suggested that the stage when the impurity metal is reduced to below 1 part in 10^6 can be detected by the simple fact that relatively stable (5 to 15 sec) mercury bubbles can be formed as air is aspirated through mercury which is covered with distilled water. Both the author[153] and Muller[256] have also recorded this phenomenon.

Chemical oxidation methods will not eliminate the noble metals, and therefore this process should always be followed by distillation.

2. Distillation[257-259]

Because of the relatively high vapor pressure of mercury, as compared with those of other metals,[260] its separation from base metal impurities by distillation is very efficient.[261] Vanyukov and Shashurin[262] found that a single distillation of mercury virtually eliminated completely impurities of zinc, gold, and cadmium (see Table V). An indication of the efficiency of base metal removal is shown by the fact that the residue in the National Bureau of Standards mercury still after 8,000,000 g of mercury had been distilled contained 14 g of silver, 0.56 g of gold, and no detectable amount of base-metal oxides; these levels correspond to 1.7 ppm of silver, 0.07 ppm of gold, and the level of base-metal impurity being much less than 0.005 ppm; *i.e.*, the mercury being distilled was already quite pure.

Hulett and coworkers[263-266] showed that, on distilling amalgams *in vacuo*, certain metals tended to distil over with the mercury. They found that after three or four distillations of a mercury–zinc amalgam, zinc could always be detected in

the distillate, even when only a trace of zinc was in the mercury in the still (see Table V for zinc). However, on distilling mercury amalgams in a partial pressure of air (25 mm), no metal impurity was carried over into the distillate. The air was allowed to bubble through the distilling mercury (200°), preventing bumping.

Since at 200° the dissociation pressures of all the base-metal impurity oxides are less than the partial pressure of oxygen in the still (5 mm), then the metallic vapors are completely oxidized. The oxides collect on the distillate, or remain in the still, and are easily separated by filtration of the distillate through a pinhole filter paper.

Oxides of the noble metals silver, gold, and platinum do not form at 200° and a partial pressure of 5 mm of oxygen. However, since the vapor pressures of these metals are small at 200° (silver, 10^{-22} mm; gold, 10^{-10} mm; platinum, $<10^{-22}$ mm) then they would not be expected to distil over in large quantities. Hulett[265] found the following impurity levels in the distillate when saturated amalgams of silver, gold, and platinum were distilled (silver, <2 ppm; gold, <3 parts in 10^8; platinum, <7 parts in 10^8).

Most firms who specialize in the purification of mercury distil *in vacuo*. To obtain a purer distillate the Hulett-type still, as used by the U. S. Bureau of Standards, should be adopted.[133,153,218]

3. Other Methods

a. Arc Stills

The use of arc stills[267-270] is not recommended since it has been shown that arc distillation carries over more impurities than vacuum distillation. Cowsik[271] explained the difference in terms of sputtering rates.

b. Electrolytic Purifications

Several methods have been devised for the electrolysis of impurities from mercury.[272-277] In general these methods have no advantage over the chemical oxidation technique, or that of distillation, and are very little used. If large quantities of mercury are cleaned by the chemical oxidation technique, then

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Table VI

Removal of Metals from Mercury by Different Methods in Descending Order of Ease of Removal

Order in potential series[a]	Order of absorption of oxygen by amalgams[b]	Metals removed by KOH[c]	Order of removal by HNO₃[c]	Order in vacuum distillation[c]	Order in arc distillation[d]	Order in 1 N H₂SO₄[d]	Order in acid KMnO₄[e]
Na	Na	Sn	Mg	Au	Mg	Zn	Zn
Mg	Mg	Zn	Al	Pt	Al	Cd	Cd
Al	Zn	Pb	Cr	Ag	Ni	Tl	Mn
Mn	Cd		Mn	Cu	Cu	Cu	Tl
Zn	Pb		Cd	Sn	Sn	Fe	Sn
Cr	Sn		Ni	Pb	Pt	Co	Pb
Fe	Tl		Sn	Zn	Ag	Ni	Bi
Cd			Pb	Cd	Au		Cu
Tl			Cu				Cr
Co							Fe
Ni							Mo
Sn							Co
Pb							Hg
H							Ni
Cu							W
Hg							
Ag							
Pt							
Au							

[a] Reference 278. [b] Reference 279. [c] Reference 271. [d] Reference 280. [e] Reference 281.

the mercury which goes into solution can be recovered by electrolysis of the solution using two platinum electrodes.

4. Removal of Adsorbed Contaminants

Because of the high surface free energy of mercury, many materials adsorb positively at the surface. The consideration of these factors is of great importance and will be dealt with in detail in section IV. Any surface-adsorbed component can be simply removed by filtration of the mercury through a pinhole filter paper.

C. RECOMMENDED PURIFICATION PROCEDURE

Different methods of purification remove metal impurities preferentially in different orders[271,278-281] (Table VI). To obtain complete purification it is suggested that both chemical oxidation and distillation methods are employed. The following procedure can be adopted.

(1) Virgin mercury is initially filtered (pinhole filter paper) and then degreased (organic solvent), if necessary.

(2) The mercury is subjected to the chemical oxidation technique outlined above. The first washing is done with 4 N caustic soda solution, followed by 4 N nitric acid. In each case the process is continued until the solution becomes clear. Finally the mercury is washed in the same manner using distilled water.

(3) The mercury is dried and filtered into the reservoir of an air still.[265] The mercury is then distilled twice under a partial

pressure of about 5 mm of oxygen. This procedure should reduce the total amount of metal impurities to much less than 1 part per million of mercury.

D. STORAGE OF MERCURY

If the mercury has been carefully purified, it is important that it be stored in containers which will not be "leached" by the mercury; mercury has a tendency to dissolve metals from the container. Although, structurally, stoneware containers are superior to glass containers, they are difficult to clean, and it is almost impossible to determine their state of cleanliness. Obvious difficulties also occur with metal containers. It is suggested that mercury is best stored in clean, heavy-walled, Pyrex containers.

After prolonged storage of pure mercury in glass containers in air, a slight film will usually form and the mercury is found to "stick" to the region of the glass surface in which it has been in contact. Although the oxidation of mercury in air at room temperature has been shown to occur at an infinitesimally small rate,[282] it is probable that a very small amount of impurity, either from the mercury itself, the glass container, or the atmosphere, has acted as a catalyst speeding up the oxidation process. These films, however, can easily be removed by filtration through a pinhole filter paper, and are not significant unless they reappear again within several minutes.

E. CRITERION OF PURITY OF MERCURY

Many methods have been applied to the determination of the purity of mercury. Density measurements[283] and thermal conductivity methods[284] are not very accurate, and it is not pos-

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Table VII

Results of Analyses of Mercury Samples after Purification

Method of analysis	Sample[a]	Zn	Cd	Pb	Concentration found, ppm (wt/wt) — Mg	Cu	Ag	Al	Sn	Ni
Chemical	1	1					<1			
	2	1					<1			
	3	1					<1			
Spectrographic	1	0.05	0.05	0.05	0.05	0.004	0.003	0.51		0.04
	2	0.06	0.06	0.02	0.12	0.006	0.002	0.28		0.02
	3	0.06	0.05	0.01	0.06	0.007	0.003	0.04		0.02
Polarographic	1	0.0003		0.0005		0.005				
	2	0.0001		0.003		0.006				
	3	0.0010		0.005		0.005				

[a] Sample 1, purified by chemical oxidation; samples 2 and 3, purified by distillation.

sible to distinguish the nature of the impurities present. Chemical methods,[284-287] which usually relay on colorimetric techniques, are only routinely reliable to about 1 ppm. Where very pure mercury is available electromotive force measurements are capable of measurements to levels as low as 1 part impurity in 10^{10} parts of Hg[266, 287-289] but will not detect the nature of the impurities. Polarographic[290-292] and spectrographic methods[234, 238, 262, 285, 287, 293, 294] are probably the most commonly used for the determination of the nature and quantities of impurities in mercury. These methods are capable of detecting metal impurities in concentrations of less than 1 part in 10^6 parts of mercury.

Recent work[262] has shown that, when analytical techniques for the determination of base metal impurities in mercury are used to detect levels which are close to the limiting sensitivity of the method, erroneous results may be obtained. In Table VII the results of analyses on mercury samples by three different techniques are compared. Several important points appear. (i) The efficiency of removal of metal impurities is very similar for the chemical oxidation and distillation methods. (ii) There are several orders of magnitude difference in the quantities given by the different analytical methods. (iii) The total impurity level had been reduced to <1 ppm by each purification procedure. Thus, with regards to the purification of mercury, it is probably more pertinent to enquire what levels of impurities can be detected reliably, rather than how pure can mercury be prepared.

It has been known for a long time that most of the base metal impurities to be found in mercury alter both its appearance and its mobility.[295, 296] The terms "sickening,"

"deadening," and "tailing" of mercury on glass surfaces have been used to describe this effect. It is assumed that the base-metal impurity oxidizes at the mercury surface, thus forming a film which wets the glass surface. However, since amalgams of silver, gold, and platinum (<0.1% concentration), where oxides are not formed, also exhibit tailing, it is possible that the foreign metals act as catalysts in the oxidation of the mercury itself.[266] It is of note that tailing of mercury is not always synonymous with its appearance. For example, although noble metals do cause tailing, they do not appear to affect the surface reflectivity, even at concentrations as high as 1000 ppm.[297]

The first quantitative correlation between tailing and the impurity content was shown by Isaacs.[298] He prepared separate samples of mercury containing 10 ppm of copper, zinc, tin, lead, bismuth, cadmium, arsenic, and antimony and observed that the samples immediately lost the characteristic "mirror-like" appearance of mercury and a film formed on the surface. Later Wichers[297] reported that Schwab[299] had found a changed appearance in the surface of mercury for amalgams containing no more than 2 parts of impurity in 10 million of mercury. The limiting sensitivity per 100 million parts of mercury was given as 6 to 9 parts of zinc, 9 parts of copper, 18 parts of lead, 15 parts of tin, and 14 parts of antimony. Thus, the surface appearance of mercury can serve as a sensitive test for the presence of base metals as low as 1 part in 10 million of mercury, a limit much lower than can be detected by most analytical techniques.

Although several other useful criteria of the purity of mercury have been suggested,[254-256, 300] it is probable that the observation of the surface condition of mercury will remain the limiting method for the detection of impurities (not including Au, Ag, or Pt).

F. SELECTION OF GRADE OF MERCURY

Mercury is undoubtedly one of the few elements that can be prepared in exceptionally high states of purity. Indeed, the purification procedures involved are quite simple, and if required it is probable that mercury containing no more than 1 part total impurity in 1,000,000,000 of mercury can be prepared. However, depending on the use that mercury is to be

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put, and the environment in which it is to be used, there will be a certain maximum level of impurity that can be tolerated before a change in any given property occurs. Thus, prior to the purchase of mercury it is important that the prospective buyer should consider to what use the mercury is to be put.

The most important property that mercury should possess when it is to be used in measuring instruments is that it does not "tail" on the walls of its container. For instruments which are under vacuum or in the presence of an inert gas, e.g., thermometers and barometers, the cheaper grades of mercury will probably be found to be equally as satisfactory as the more expensive "purer" grades. In these instruments tailing will not occur since oxygen is precluded from the external phase.

For instruments where mercury is exposed to atmospheric conditions a pure grade should be employed. In this case it will be found that, under identical conditions, mercury containing a lower level of impurities will have less tendency to tail and form surface scum than a sample containing a higher impurity level. However, even the purest grades of mercury will eventually form surface scums in air. Examination of a Fortin barometer, for example, will reveal that, after very long periods of use, the mercury in the evacuated limb remains bright and does not tail, while that on the atmospheric side is dull and tails badly.

The process of scum formation is extremely complex, and depends on the natures and concentrations of the dissolved impurities and the nature of the containing vessel and the external phase. Obviously as the concentration of metallic impurities increases the time for scum formation, surface dulling and tailing decrease. However, no systematic study of the times taken for various properties to alter with given concentrations of impurities has been undertaken. Most base metal impurities have rapid and pronounced effects on the surface properties at concentrations of about 1 ppm, but the degree of effect below this level is impossible to predict.

The criterion of purity for surface work is very difficult to define since the usual method for determination of surface purity, namely, surface tension, cannot be used. Further, the levels of impurities in purified mercury are so low that it is almost impossible to identify and reliably determine their concentrations. The surface activites of different metals in mercury is not known (section V). However, if various metals are surface active, their effects at levels below 1 ppm (10^{-7} to 10^{-8} M) will be time dependent. Elliott and Wilkinson[301] have shown that the surface tensions of seven different grades of mercury[302] were the same and did not alter over periods of 5 min. Smith[303] has worked extensively with mercury surfaces and has reached the same conclusions.

Although it is probable that, in the majority of cases, little difference will be found between the surface properties of the different grades of mercury available commercially, it is recommended that mercury for surface work should be purified according to the procedure outlined above. If the mercury does not come into contact with soluble impurities it will only be necessary to remove the surface films by filtration before re-use.

V. Factors Affecting the Surface Tension

A. TIME

Some workers[33,37,48,54,56,62,66,72,76,120] found that the surface tension of mercury in vacuo and in various gases varied with time of exposure, the most extensive works being due to Popesco[47,54] Schmidt,[73] Foryst,[120] Stockle,[33] Bradley,[76] and Cook.[66] No agreement exists between these workers on either the magnitude or effects of various gases. Cook,[66] for example, found that the surface tension in hydrogen fell by 56 dyn/cm in 96 min, while Bradley[76] recorded a drop of less than 2 dyn/cm in 1 day. Popesco[47,54] found that the surface tension in air, oxygen, argon, hydrogen, and carbon dioxide fell at very different rates, but after 1 day they all reached the same value of 418 dyn/cm. Similar findings were recorded by Foryst[120] for hydrogen, nitrogen, and carbon dioxide. In almost all cases it was found that the surface tension decreased with time of exposure.

An interesting explanation of the slow decrease in the surface tension of mercury on exposure to various gases was proposed by Bancroft.[304] He considered mercury to be a partially polymerized liquid. The molecular modification which has the lowest surface tension will tend to be positively adsorbed at the surface, and equilibrium will be reached when a certain relation exists between the concentration of this modification in the surface layer and in the bulk liquid. The attainment of this equilibrium may take a definite time, and Bancroft suggests that it may be instantaneous when a mercury surface is formed in vacuo, but relatively slow in the presence of gases. Iredale[55] and Smits,[305] however, do not agree with this hypothesis and conclude that mercury behaves as a unary substance.

Herschkowitsch[306] proposed that slow variations in surface tension with time could be explained on the basis of the formation of adsorbed polymolecular layers on the mercury surface. This is not considered tenable in the light of existing knowledge.

The surface tensions of many pure liquids are known to be established within milliseconds of the formation of the surface.[307-309] The orientation times for molecules in the surface regions are of the order of milliseconds, and there is no reason to believe that orientation times for pure liquid metals will be higher.[290] These assumptions are based on the fact that the liquid is in contact with its own vapor, or with another phase which does not interact with the liquid surface layers.

No satisfactory explanations have been given for the slow variations in the surface tension of mercury in different gases with time. More recent works show that the surface tension remains constant,[72,77,125,144,153] in some cases for periods of weeks.[76] Further, it must be assumed that the majority of workers, who only recorded a single value, did not observe any time effects. If different constituent gases of the atmosphere adsorb positively on mercury to lower its surface free energy, it would be expected that this process would occur rapidly.[63] Slow variations in the surface tension of mercury are

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probably due to the gradual accumulation of impurities at the surface, these coming from the external phase or from the mercury itself (dissolved metals). Water vapor present in small amounts may act to alter the interaction of gases with mercury; these processes may take many minutes or hours to proceed to completion (see section V.D). Small amounts of base metal impurities in mercury may react with gases over long time periods, and may even catalyze the reaction of mercury atoms themselves (see section V.E).

B. TEMPERATURE DEPENDENCE

The variation in the surface tensions of pure liquid metals with temperature[160] can usually be expressed fairly accurately by a quadratic equation of the following type

$$\gamma = \gamma_{0^\circ} - AT \pm BT^2 \tag{12}$$

where γ is the surface tension at $T\,^\circ C$. γ_{0° is the surface tension at $0\,^\circ C$, and A and B are constants, with A usually being much larger than B.

The majority of workers have found a linear variation of the surface tension of mercury with temperature (ref 26, 38, 46, 56, 70, 72, 74, 90, 98, 107, 113, 121, 125, 127, 128, 156, 310–314). Values obtained for the temperature coefficient, A (assuming $B = 0$), are given in Table VIII. Experimentally determined values range from -0.17 to -0.3015 dyn/(cm $^\circ C$); calculated values lie in the range -0.16 to -0.54 dyn/(cm $^\circ C$). It is surprising that such good agreement is found between the experimental and theoretical values, since several of the calculated surface tensions are very high.[312] The average of all the values in Table VIII is -0.231 dyn/(cm $^\circ C$), with one standard deviation being 0.063 dyn/(cm $^\circ C$). The average of the experimental values is -0.224 dyn/(cm $^\circ C$), with one standard deviation being 0.032 dyn/(cm $^\circ C$).

Several authors have considered that quadratic fits of the type given by eq 12 better describe the variation in surface tension with temperature, especially over large temperature ranges. Hogness[48] found that for the range 20–354° the following was a good fit to the data.

$$\gamma = \gamma_{0^\circ} - 0.043(T + 39) - 0.000386(T + 39)^2 \tag{13}$$

Hageman[40] for the same temperature range found

$$\gamma = \gamma_{0^\circ} - 0.148T - 0.000344T^2 \tag{14}$$

More recently Schwaneke, Falke, and Miller[159] have found

$$\gamma = \gamma_{0^\circ} - 0.149T - 0.000284T^2 \tag{15}$$

and Lee[157] found

$$\gamma = \gamma_{0^\circ} - 0.161T - 0.0001815T^2 \tag{16}$$

Values recorded in Table VIII for Hogness, Hageman, Schwaneke, *et al.*, and Lee, have been determined by means of a best fit to a linear relationship. If a quadratic best describes the data, it would explain the increased values in the temperature coefficients, at higher temperature ranges, re-

corded by Bircumshaw,[56] Brown,[64] Pugachevich and Timofeevicheva,[140] and Lee.[157]

Bircumshaw,[63] Binne,[74] and Karpachev, *et al.*,[127] are the only workers to measure surface tensions below 0 °C. Binne and Karpachev, *et al.*, find a linear relationship down to -38 and $-25°$, respectively. The results of Bircumshaw are interesting, since he found that as the age of the mercury surface increased, the surface tension decreased, differences as large as 30 dyn/cm being recorded. This phenomenon could be attributed to the effect of impurities, a possibility mentioned by Bircumshaw. More importantly Bircumshaw found that the surface tension of mercury went through a maximum at about $-34°$. Although the maximum is weak and may lie within the experimental error, it was reproducible. A maximum has been reported for cadmium, good agreement being obtained by Greenway[116] (609 dyn/cm at 400°), Bircumshaw[315] (597 dyn/cm at 400°), and Hogness[48] (622 dyn/cm at 421°). This, however, was not confirmed by Matuyama.[316] Sauerwald and Drath[58] found that the surface tension of copper increased between 1131 and 1215°, a result confirmed by Klyachko.[89] Positive $d\gamma/dT$ values were initially recorded for copper and germanium by Ibraginov, Pokrovski, and Pugachevich,[317] and by Karashev, Zadumkin, and Kuhmo,[318] but a more careful purification of the metals was found to change the sign. It is doubtful whether the values of Bircumshaw for temperatures less than 20° can be considered as reliable. Certainly more careful work is required at low temperatures to clarify this point.

It is of note that the temperature coefficient does not depend on the nature of the external phase; *i.e.*, similar values were recorded *in vacuo*, air, hydrogen, nitrogen, helium, argon, and carbon dioxide. This is an indication that none of the component gases of dry air interact with mercury, even at elevated temperatures.

C. SURFACE TENSION UNDER VACUUM

Values obtained for the surface tension of mercury *in vacuo* have varied from 401 to 500.6 dyn/cm at 25°. There is an increase in the values reported, up to the mid 1940's (Figure 1); values increased from about 430 dyn/cm to about 470–485 dyn/cm (see Figure 2a). Definite innovations in vacuum technology were made in the 1930's and 1940's, when it was generally recognized[72,76,107] that liquid air (nitrogen) cold traps had to be incorporated in the apparatus to prevent stopcock grease and vacuum pump oil from diffusing back into the measuring chamber.

Vacuum pump oils and greases can have a measurable effect on the surface tension of mercury if they are allowed to reach the exposed surface. For an equilibrium situation, the number of gas molecules striking each square centimeter of surface per second is given by

$$Z = 0.23PN \left(\frac{3}{MRT}\right)^{1/2} \tag{17}$$

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Table VIII

Temperature Dependence of the Surface Tension of Mercury

Year	Author (ref)	Method	Temp range, °C	Temp coeff, dyn/(cm °C)	Surface tension (25°), dyn/cm	Conditions
1893	Ramsey and Shields (26)	Capillary rise	40–170	−0.233	482.7	Air
1913	Cenac (38)	Drop-weight	0–180	−0.228	455	Vacuum
1914	Hageman (40)	Vibrating jet	0–360	−0.17	466.9	Vacuum
1920	Harkins and Ewing (46)	Drop-weight	0–60	−0.22	475	Vacuum
1921	Hogness (48)	Maximum pressure in a drop	0–354	−0.20	464	Vacuum, air, and hydrogen
1926	Bircumshaw (56)	Maximum bubble pressure	0–220 / 220–350	−0.20 / −0.25	468.8	Hydrogen
1926	Sauerwald and Drath (58)	Maximum bubble pressure	19–201	−0.23	451.8–478.8	Carbon dioxide
1928	Bircumshaw (63)	Maximum bubble pressure	(−37)–20	−0.20	479	Hydrogen
1928	Brown (64)	Maximum bubble pressure	0–200 / 200–350	−0.224 / −0.265	475.6	Nitrogen, air
1931	Kernaghan (70)	Sessile drop	12.5–67	−0.3015	435.9	Vacuum
1932	Burdon (72)	Sessile drop	20–230	−0.23	488	Vacuum
1933	Binne (74)	Maximum pressure in a drop	(−38)–50	−0.18	468	Vacuum
1938	Bosworth (90)	Maximum bubble pressure	20–220	−0.21	483	Air, carbon dioxide, and hydrogen
1941	Didenko and Pokrovski (98)	Maximum pressure in a drop	24–290	−0.197	463.4	Vacuum
1941	Haul (310)	Calculation		−0.54		
1946	Kemball (107)	Sessile drop	25–75	−0.20	484	Vacuum
1946	Frenkel and Gubanov (311)			−0.22		
1947	Breger (312)	Calculation		−0.18	1550	
1947	Pugachevich (113)	Maximum pressure in a drop	24–353	−0.19	465–470	Vacuum
1948	Skapski (313)	Calculation		−0.16 to −0.26		
1951	Law (121)	Sessile drop	25–75	−0.23	495	Vacuum
1953	Karpachev, Smirnov, and Volchenkova (127)	Sessile drop	(−25)–0 / 0–30	−0.30 / −0.23	476.4	Vacuum
1953	Bering and Ioileva (128)	Sessile drop	15–96	−0.20	483.4	Vacuum
1953	Ziesing (125)	Sessile drop	20–220	−0.20 ±0.01	483.6	Vacuum
1959	Pugachevich and Timofee-vicheva (140)	Maximum pressure in a drop	22–200 / 200–350	−0.21 / −0.27	461.7	Vacuum
1963	Astakhov, Penin, and Dob-kina (314)			−0.22		
1967	Smith (156)	Wilhelmy plate	23–115	−0.231	480.0	Vacuum and helium
1968	Lee (157)	Maximum bubble pressure	20–200 / 200–350	−0.19 / −0.26	464.4	Air and argon
1970	Schwaneke, Falke, and Miller (159)	Maximum bubble pressure	20–300	−0.23 ± 0.02	481.6 ± 3	Helium, hydrogen nitrogen, and argon

where P is the pressure, N the Avogadro number, M the molecular weight of the material, R the gas constant, and T the temperature in °K. Utilizing a molecular weight of 400, then at 25°C

$$Z = 2.78 \times 10^{18}P \text{ molecules}/(\text{cm}^2 \text{ sec})$$

Thus, if Apiezon C pump oil is being used, and equilibrium is achieved at its pressure of 10^{-7} mm, monolayer coverage (assuming 100 Å^2/molecule) is achieved after approximately 5 min. This calculation is based on the fact that the coefficient of sorption is unity, and that the Apiezon C pump oil exerts a pressure of 10^{-7} mm. Nicholas, *et al.*,[144] showed that vacuum and diffusion pump oil reduced the surface tension of mercury to values ranging from 450 to 250 dyn/cm in extreme cases. Holland and Bateman[319] found that exposure of a glass substrate to the vapor pressure of silicone grease with a vapor pressure of 5×10^{-9} mm for 3–5 min dramatically reduced

the stability to peeling of vacuum deposited films. Kemball[107] found that the presence of Apiezon-L tap grease (vapor pressure 10^{-11} mm) in any part of the apparatus produced a drop of 20 to 25 dyn/cm in the surface tension of mercury over a period of several hours. When liquid air cold traps were inserted between this grease and the mercury surface, the surface tension remained constant for as long as 12 hr.

It is of note that Popesco,[47] Iredale,[55] and Stockle[33] found high values for the surface tension in many different gases, but when the apparatus was exhausted γ dropped to about 430 dyn/cm. On readmitting gases no recovery in the surface tension was noted. In this context Bikerman[135] found that octacosane was capable of reducing the surface tension of mercury by about 50 dyn/cm. Octacosane has a carbon chain (28 C) of similar length to pump oil and vacuum tap greases employed in vacuum systems.

Didenko and Pokrovski[98] found that during their initial experiments the surface tension increased as the temperature was raised; the value increased from 409 at 20° to 456 dyn/cm

(319) L. Holland and S. K. Bateman, *Brit. J. Appl. Phys.*, **11**, 382 (1960).

at 100°. The surface tension then decreased between 100 and 200° (440 dyn/cm). On cooling the surface tension decreased and passed through a maximum value of 460 dyn/cm at 100°, but at 20° the surface tension was 434 dyn/cm. This experiment shows the obvious presence of volatile components (probably water vapor) and the presence of an adsorption-desorption process taking place during the experiment. Semenchenko considers that the presence of residual organic vapors and greases may explain many of the earlier low values obtained by his collaborators.[84,87] Certainly the later Russian works[113,114,123,124,140,150] did not reflect these earlier low values.

It is possible to reduce the considerable range of surface tensions recorded for mercury by consideration of the results of spreading of pure water on clean mercury surfaces (section VII). Since spreading only occurs slowly, and the mercury-water (degassed) interfacial tension is 426 dyn/cm (section VI), then the surface tension of mercury must be less than the sum of the mercury-water and water-gas surface tensions, i.e., ≤ 498 dyn/cm (see section V.D). Also since oxygen and carbon dioxide do not reduce the mercury-water interfacial tension below about 375 dyn/cm, then a lower limit for the mercury surface tension will be 447 dyn/cm.

With reference to the data in Table I, for surface tensions below 447 dyn/cm, it is found that the average for these is 428.4 ± 15.3 dyn/cm (see Figure 2). This is the value that might be expected (see below) if water or grease is adsorbed on the mercury surface; both these contaminants are likely to be present in the apparatus unless extreme care to eliminate them has been taken. Water vapor and various organic compounds have about the same effect on the surface tension of mercury. It is therefore not surprising that one might conclude[170] that there appears to be two values for the surface tension of mercury, namely, 430 and 475 dyn/cm. The low value can now be adequately accounted for on the basis of adsorbed contaminants. Further, it should be noted that the last reliable value reported below 447 dyn/cm was in 1936;[87] values since then have varied from 461.7 to 489 dyn/cm.

An analysis of the values obtained in vacuo that lie between 447 and 498 dyn/cm gives 33 values with an average of 475.5 dyn/cm and one standard deviation being 9.2 dyn/cm. It is of note that this value is very similar to the average of all values given in Table I, namely, 466.3 dyn/cm. A more detailed analysis of results for each of the three main methods employed is given in Table IX.

Not included in Table IX are the results of Dupre,[12] Lippman,[18] Convers,[95] and Cenac.[38] The results of Dupre and Cenac are based on incorrect drop-weight relationships. Lippman's result for a sessile drop is dubious, and Conver's result reflects the presence of impurity in vacuo, since he obtained a value 34 dyn/cm higher in air.

Table IX

Analysis of Values Obtained in Vacuo (between 447 and 498 dyn/cm) for the Surface Tension of Mercury

Method	No. of values	Av value, dyn/cm	Std dev, dyn/cm
Maximum pressure in a drop	13	468.5	6.3
Sessile drop	11	483.5	5.9
Drop-weight	4	471.8	3.1
Miscellaneous	5	477.9	9.6

It is difficult to reduce the range of surface tensions given in Table IX. As far as can be determined, all the values are equally reliable. The differences are probably due to either poor experimental technique or to the influence of *external* impurities. It is not considered likely that the presence of foreign metal impurities in levels normally expected in pure mercury, i.e., <1 ppm, will have any effect on the surface tension within the time taken for the measurement (section V.E).

At the present time it is not possible to quote a unique value for the surface tension of mercury. However, it is possible to considerably reduce the range of values recorded, the surface tension of mercury being 475.5 ± 9.2 dyn/cm.

D. EFFECT OF GASES AND VAPORS

In the consideration of the effects of gases and vapors on the surface tension of mercury it is important to specify whether interaction occurs by physical adsorption (often termed van der Waals) forces alone, or whether chemical interactions (chemisorption) are involved. The attainment of physical adsorption equilibrium is usually rapid and reversible. Multilayer physical adsorption is possible, and at the saturated vapor pressure of the gas physical adsorption becomes continuous, with liquefaction. Chemisorption usually requires an activation energy and may be slow in reaching equilibrium. Only monomolecular chemisorbed layers are possible,[320] and desorption is usually very difficult, or impossible.

The forces bringing about physical adsorption may be conveniently classified as those associated with (a) dispersion effects, (b) short-range repulsive effects, (c) permanent dipole moments in the adsorbed molecule, and (d) polarization, i.e., distortion of the charge distribution within the adsorbed molecule. In this context we can consider that most of the usual gaseous components of the atmosphere (inert gases, H_2, N_2, CO_2, CO, H_2O, and O_2) will only interact with a mercury surface by physical adsorption processes. Oxygen reacts very slowly with mercury at room temperature to form mercury oxide; ozone reacts much more readily. Many organic vapors interact with mercury through physical adsorption although some react chemically. Chemisorption and compound formation can be expected for certain gases such as hydrogen sulfide, sulfur dioxide, hydrogen chloride, and nitrogen dioxide.

Mercury is used in many different types of instruments where its surface is exposed to conditions varying from complete high vacuum, inert gases, hydrogen and nitrogen, to laboratory air. One of the most important properties it should possess is that it does not "tail" (see section IV); "tailing" has been shown to be caused by minute traces of impurities. With few exceptions mercury is found to perform well under these varied conditions for periods of years and decades. Indeed, most of the literature dealing with the action of gases on mercury is old.

van Laar[321] found no reaction between mercury and hydrogen, even after many days of exposure. This finding was confirmed by Berthelot[322] who also observed no reaction with argon or helium. The absence of any effect by argon was confirmed by Stark.[323] Mattheissen and Vogt[324] found that no

(320) I. Langmuir, *J. Amer. Chem. Soc.*, **38**, 221 (1916).
(321) J. J. van Laar, *Chem. Weekbl.*, **5**, 388 (1908).
(322) M. Berthelot, *C. R. Acad. Sci.*, **124**, 113 (1897).
(323) J. Stark, *Phys. Z.*, **10**, 785 (1909).
(324) A. Mattheissen and C. Vogt, *Pogg. Ann.*, **116**, 371 (1862).

oxygen was adsorbed by mercury, nor was any chemical reaction observed during shaking with dry air or oxygen for long periods. Similar conclusions were reached by Christiansen,[325] Crafts,[326] Baker,[327] and Amagat.[328] The rate of oxidation of mercury is in fact immeasurably slow at room temperature, and only begins to proceed at a measurable rate at temperatures in excess of 250°.[329] However, in the presence of water vapor the rate of oxidation is increased enormously.[330,331] Traces of ozone also catalyze this reaction, and ozone itself attacks mercury quite readily.[332,333]

Mercury does react with many gases when the mercury and/or the gas is in an excited state. There are now known a large number of reactions between atoms and molecules which only occur when they are in excited electronic states. The number of reactions which may occur after a molecule has become electronically excited may be considerable, and the products formed may be stable or unstable. Excitation can be caused in different ways, the most common probably being photoelectric, radiation, and heat. Compound formation at elevated temperatures may explain the variance in surface tensions obtained for liquid metals at high temperatures in various gases.[318,334] For example, the surface tension of molten nickel at 1470° was found to be 1735 *in vacuo*, 1570 in hydrogen, and 1615 dyn/cm in helium.[335]

Manley[336] found that the electric charge produced by oscillating a column of mercury up and down a tube was sufficient to cause a feeble glow in the presence of a little gas. This was accompanied by chemical interaction. In this manner he managed to show that mercury oxide and nitride were formed. Hydride and helide formation was also suspected but chemical analyses were not carried out on them due to their instabilities.[337] Oxides, nitrides, helides, and hydrides have also been observed in discharge tubes[338-340] and during irradiation.[341-344] The chemical compositions of these compounds varies considerably and for detailed descriptions and references the reader is referred to Gmelin,[345] Noyes and Leighton,[346] and Laidler and Shuler.[347]

The photoelectric threshold wavelength of mercury is of the order 2735 Å.[348-350] When a mercury surface is irradiated with light having wavelengths less than this value, photoelectric excitation occurs, and mercury reacts more readily with various gases. For example, although for the reaction $Hg + \frac{1}{2}O_2 = HgO$, $\Delta F°_{298} = -13,808$ cal, the reaction is immeasurably slow[350,351] at ordinary temperatures. The reaction proceeds very rapidly, however, when the mercury surface is irradiated with light below the photoelectric threshold wavelength.[350]

Bradley[76] found that γ decreased slowly (1-2 dyn/cm) in the presence of hydrogen at low pressures (0.12 mm), but at higher pressures (>8 mm) γ remained constant over long time periods. He suggested that mercury atoms excited by light below the photoelectric threshold value can react with hydrogen[352]

$$Hg \xrightarrow[\lambda\ 2735\ \text{Å}]{\text{excitation}} Hg'$$

$$H_2 \xrightarrow[\lambda\ 2537\ \text{Å}]{\text{excitation}} 2H' \quad (\text{ref } 352)$$

$$Hg' + H_2 \longrightarrow HgH' + H$$

$$HgH' \longrightarrow HgH + h\nu$$

$$HgH \longrightarrow Hg + H$$
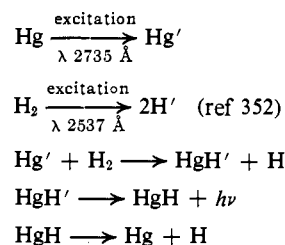
He proposed that at high hydrogen pressures the increased number of collisions with the mercury surface deactivates the Hg.

Excitation of the gas phase and/or the mercury surface could certainly lead to reaction between the surface mercury atoms and the gas molecules.[350,353,354] Oxygen, for example, begins to adsorb at a wavelength of about 2000 Å.[355] However, it must be realized that wavelengths <3000 Å are in the ultraviolet part of the spectrum and are only emitted by certain light sources. Furthermore, glass will not transmit wavelengths less than about 3000 Å, although quartz will transmit down to about 1800 Å.

Under normal conditions we can probably eliminate any chemical interactions between mercury and the usual atmospheric gases. Thus, any changes in surface properties must be due to physical adsorption processes of the pure gas or to spurious effects of trace impurities. Trace impurities in the gaseous phase can have a measurable effect depending on its concentration (or vapor pressure) and the vapor pressure of the gas under consideration. The influence of a given impurity gas exerting a vapor pressure P_i mm becomes more important as the total gas pressure, P, diminishes. From the gas diffusion theory, the time, t, required for a surface to adsorb M moles of gas is given by

$$T \simeq \left(\frac{M}{P_i}\right)^2 \left[\frac{(RT)^2}{\alpha}\right] P \tag{18}$$

where α ($= DP$) is a constant, R the gas constant, and T the temperature in °K. D is the diffusion coefficient of the im-

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Table X

Comparison of Surface Tension Values Recorded under Vacuum and in Various Gases

Author (ref)	Surface tension, dyn/cm	
	In vacuo	In gas
Meyer (32)		504 (air), 554 (H_2), 505 (O_2), 504 (N_2)
Stockle (33)	433	473.6 (air), 483.6 (moist air), 470.2 (H_2), 479.8 (CO_2), 477.6 (O_2), 477.2 (N_2)
Cenac (38)	432	455 (air)
Harkins, et al. (44, 46)	475	464 (air)
Palacois (45)	401	401 (air)
Popesco (47, 54)	434	517 (air), 510 (H_2), 525 (O_2), 540 (N_2)
Hogness (48)	464	464 (air), 464 (0–300 mm H_2)
Richards and Boyer (49)		442 (air), 433 (CO_2)
Iredale (51, 53)	473.6	458.6 (air)
Iredale (55)	444.6	443.6 (air)
Burdon and Oliphant (62)	490	490 (air)
Bircumshaw (56, 63, 68)	479	481 (H_2), 481 (moist H_2), 475 (O_2), 479 (air), 481 (CO_2)
Sauerwald and Drath (58)		451.8–478.8 (air, H_2, N_2, CO_2)
Brown (64)		475.6 (N_2, air)
Cook (66)	514 ± 7	500 (H_2, O_2, air)
Burdon (72)	480–488	480 (air, moist air)
Sauerwald and Schmidt (73)	469	469 (air)
Cassel and Neugebauer (376)	464	463 (Kr), 461.2 (Xe), 464 (Ar)
Bradley (76)	498.6	500.3 (H_2)
Brown (77)	472.9	472.6 (air, moist air)
Lemarchand and Convers (79)	432.4	479.4 (air)
Kernaghan (70, 83)	475.5 (435.9 obtained earlier)	470.0 (H_2), 468.0 (N_2), 464.2 (O_2)
Semenchenko (84, 88)	409	472 (air)
Binne (74)	468	468 (O_2, H_2)
Bering and Pokrovski (87)	409	464 (H_2)
Bosworth (90, 92)		483 (H_2), 483 (air), 478.2 (CO_2)
Convers (95)	449	493 (air)
Dunken (96)		475.6 (air), 478.6 (air free of CO_2)
Greenway (116)		507 (H_2), 507 (N_2)
Foryst (120)		493 (H_2), 488 (N_2), 486 (CO_2)
Law (121)	495.8	493.4 (H_2), 488.5 (O_2), 485.9 (CO_2)
Ziv and Shestakov (139)		479 (air), 475 (air)
Fesenko and Eremenko (142)		474 (H_2, He)
Nicholas, et al. (144)	483.5	483.3 (H_2), 483.1 (O_2), 484.2 (CO_2), 482.2 (He), 484.3 (CH_4)
Smith (156)	480.0	480.0 (H_2, He)
Lee (157)		464.4 (air, Ar)

Table XI

Desorption of Various Gases from a Mercury Surface on Collapse of the Surface

Expt	Gas	Gas pressure, mm	Time of exposure of surface to gas	Pressure increase on collapse of surface, mm × 10^4
a	CO_2	80	48 hr	4
b	CO_2	100	2 hr	8
c	CO_2	120	~5 min	1.5
d	CO_2	360	20 min	10
e	CO_2	500	10 min	5.5
f	CO_2	760	10 min	9.5
g	CO_2	760	2.5 hr	12.5
h	H_2	400	35 min	6.5
i	H_2	400	35 min	7.0
j	Air	450	5 min	5.5

$\alpha \simeq 7.6 \times 10^4$ mm cm²/sec. Thus, at 25° the time to form a monolayer is given by

$$T \simeq 10^{-8}(P/P_i{}^2) \tag{19}$$

If $P_i \simeq 10^{-4}$ mm and $P \simeq 760$ mm then T is 760 sec, but if $P \simeq 1$ mm T is only 1 sec.

If "long" term surface tension changes with time are neglected, then it is worthwhile comparing surface tension values recorded *in vacuo* and in various atmospheric gases (Table X). The values recorded in gases are the initial ones and, depending on the method of measurement, represent average ages of about 1 to 10 min. All values are at 25 °C. It is of note that, with few exceptions, the surface tensions in various gases are no lower than those *in vacuo*. Many authors measured surface tensions in various gases and found little change in value. Low values recorded *in vacuo* and corresponding high values in gases probably reflect the influence of organic contaminants.

1. Direct Measurement of the Adsorption of Gases by Mercury

Very little work on the direct measurement of adsorption of gases by mercury is in the literature. The obvious difficulty is in the formation of sufficiently large surface areas. Burdon[356] formed mercury surfaces of 60 cm² area in the presence of various gases. The gas was then pumped off after an interval (usually 5–10 min) and the mercury surface was then caused to collapse, the evolution of adsorbed gas being measured. The results obtained are given in Table XI.

Burdon used a molecular area of about 17.6 Å² for the carbon dioxide molecule, and, thus, for monomolecular coverage, collapse of 60 cm² of mercury surface should yield 34 × 10^{15} molecules, corresponding to a rise in pressure of 12 × 10^{-4} mm. It is of note that this was only achieved in one case, experiment g. In the case of physical adsorption, adsorption times are very rapid; in this respect it is difficult to comprehend the significance of results from experiments a and b and f and g. Furthermore, greater adsorption appears to be taking place at 360 mm of CO_2 than at 500 mm of CO_2, experiments d and e.

The results of experiment c are interesting and may indicate

purity gas. For monolayer coverage there are approximately 10^{15} adsorption sites/cm², so that $M \simeq 1.6 \times 10^{-9}$ mol. Also, since $D \simeq 0.1$ cm²/sec for gases at 760 mm and at 25 °C, then

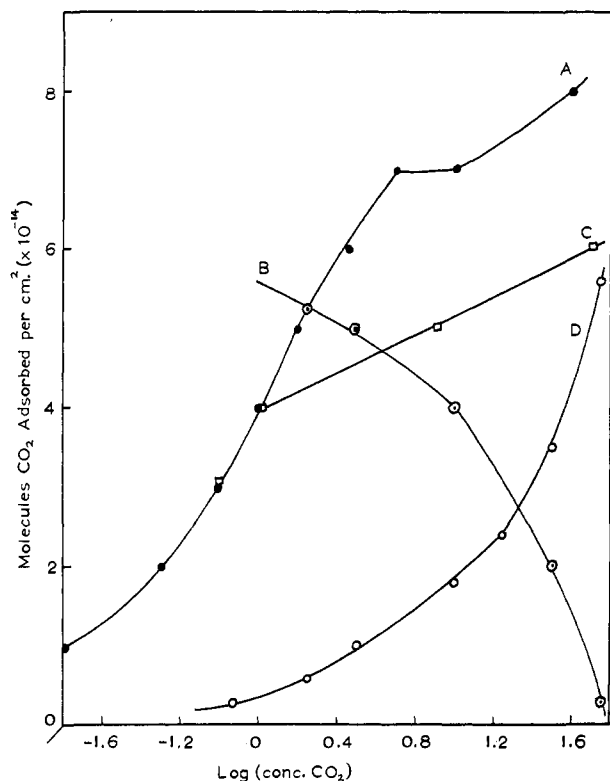(356) R. S. Burdon, *Proc. Phys. Soc., London*, **47**, 460 (1935).

Figure 6. Results obtained by Bosworth and Oliphant for the adsorption of carbon dioxide on mercury. Adsorption of CO_2 (A) from dry hydrogen (Oliphant); (B) in the presence of water vapor (Bosworth); (C) from dry air (Bosworth); (D) from moist air (1.2% water) (Bosworth).

that increases in pressure are not, in fact, due to desorption of gases from the mercury surface. This particular experiment was performed by initially forming the mercury surface *in vacuo* and then admitting the gas. After evacuation and collapse of the mercury surface the pressure increase was only 1.5×10^{-4} mm. Burdon explained this by assuming that less adsorption occurred at a surface initially formed *in vacuo* than at one formed in the presence of the gas. Other workers in the same laboratory as Burdon have ascribed to the idea that mercury atoms in a freshly formed surface *in vacuo* will speedily rearrange in such a way that the energy in the surface is a minimum.[62,71,72,357,358,359] However, when the surface is expanded in contact with a gas, a mercury atom which comes to the surface with an "active end" outward will possibly remain in such a condition for some time, as it is able to form a "compound" with a gas molecule which may have a life of several minutes.[357] These ideas are not tenable with modern thinking on reorientation times of molecules at interfaces.

An important aspect of the experiments carried out by Burdon is that the gas fills the adsorption chamber before the mercury is admitted. Admission of the mercury may entrap gas in the glass walls of the apparatus it is in contact with, and the gas is subsequently released when the mercury is drained away, thus causing in increase in pressure. The results of experiment c are a strong indication of this possibility.

Oliphant[357] presented experimental evidence which indicated that an expanding mercury surface selectively adsorbed carbon dioxide from a mixture of carbon dioxide with an excess of hydrogen or argon. Monomolecular coverage was achieved at about 2% carbon dioxide content. The results were obtained by allowing drops of mercury to fall down a column of the mixed gases. The mixed gases were fed into the center of the column (length 25 cm), and the gases exited at the top and bottom, where they were then fed into a Rayleigh gas refractometer to detect changes in carbon dioxide concentration (limit of detection: change of 0.001%). The mercury drops after falling through the column coalesced at the bottom, thus releasing any adsorbed gases. Since adsorption occurred within a fraction of a second and did not change between 16 mm pressure of CO_2 and 395 mm of CO_2, it is difficult to reconcile the findings with those reported by Burdon (Table XI).

Bosworth,[71] using the same apparatus as Oliphant, studied the adsorption of carbon dioxide, sulfur dioxide, and water vapor, and mixtures of these, on mercury. Some of his results are given in Figure 6 where the results for carbon dioxide can be compared with those of Oliphant. The very large lack of agreement in values for carbon dioxide concentrations greater than 1% was not explained by Bosworth. For a cross-sectional area of carbon dioxide of $\sim$20 Å^2, monomolecular coverage would correspond to 5.6×10^{14} molecules/cm^2. Although this is reached at about 2% level according to Oliphant, Bosworth's results indicate a composition of about 30%. The results obtained in moist air and carbon dioxide are very confusing, and Bosworth made no attempt to explain them.

The appropriate form of Gibbs adsorption equation[360] can be applied to determine the decrease in surface tension due to the adsorption of carbon dioxide according to Bosworth (Figure 6). Gibb's equation can be expressed in the form

$$\Gamma = -\frac{1}{RT}\frac{\partial\gamma}{\partial \ln P} \qquad (20)$$

where Γ is the surface excess concentration in mol/cm^2, R the molar gas constant, T the absolute temperature, γ the surface tension, and P the partial pressure due to the active gas. Equation 20 can be expressed in terms of molecular quantities as follows

$$n = -\frac{1}{KT}\frac{\partial\gamma}{\partial \ln P} \qquad (21)$$

where k is the Boltzmann gas constant and n the number of molecules adsorbed. The integral form of this equation can be expressed as

$$\Delta\gamma = 2.303kT\int n\mathrm{d}(\log P) \qquad (22)$$

where $\Delta\gamma$ is the decrease in surface tension produced by adsorption of the gas. The value of the integral in eq 22 can be obtained by determination of the area enclosed by the n vs. log concentration curve (Figure 6).

In the above manner Bosworth calculated $\Delta\gamma$ to be 116 dyn/cm for the adsorption of carbon dioxide. Thus, taking γ_{vac} for mercury of 475 dyn/cm, the value in carbon dioxide should be of the order 359 dyn/cm. No worker has obtained a value as low as this in carbon dioxide. Furthermore, Bos-

(357) M. L. Oliphant, *Phil. Mag.*, **6**, 422 (1928).
(358) R. S. Burdon, *Proc. Phys. Soc., London*, **38**, 148 (1926).
(359) M. L. Oliphant and R. S. Burdon, *Nature (London)*, **120**, 584 (1927).

(360) J. W. Gibbs, "The Scientific Papers of J. Willard Gibbs," Vol. 1, Dover Publications, New York, N. Y., 1961.

worth, 7 years later,[92] measured the surface tension of mercury in various concentrations of carbon dioxide (in dry air), by the drop-weight method, and found that the surface tension in pure dry carbon dioxide was of the order 478 dyn/cm. These conflicting findings throw serious doubt on the meaning and significance of the results of Bosworth, and also those of Oliphant.

2. Detection of Surface Changes by Means of Ellipsometric, Surface Potential, and Electron Diffraction Techniques

Ellipsometric techniques[361-364] have been applied to studies of the surface of mercury. The technique is an averaging one, and film thicknesses can correspond to a uniform film of the measured thickness, or to the average of much thicker "islands" on the surface. The technique is capable of detecting much lower surface coverages than monomolecular. For example, the presence of a 2-Å film, corresponding to less than monolayer coverage, is sufficient to cause significant changes in the measured optical constants of mercury.[364]

Sissingh and Haak[365] using an ellipsometric technique found that the reflective properties of a mercury surface *in vacuo* did not change with time, but on admission of dry air changes occurred over an 8-hr period. These adsorbed layers could not be removed by lengthy pumping procedures. The questionable presence of water vapor in the system was raised since in a later experiment, carried out in "dry air," ice crystals formed on the mercury surface on cooling below 0°. They calculated the thickness of the adsorbed layer as being 16 Å; similar values (17.4-27.3 Å) were obtained by Reeser[364] and Ellerbroek.[366] Herschkowitsch[306] found that different gases produced distinct changes in the optical properties of a clean mercury surface. When the gases were pumped off partial changes in the reverse direction occurred, a fact indicating that part of the change was due to physical adsorption, but part to chemical adsorption. Nitrogen does not have any effect on the optical properties of mercury,[367] but surface potentials appear to vary in nitrogen; Yamashita, Nagai, and Hirota[368] found that the surface potential in dry nitrogen only attained equilibrium after 20 min (−40 mV), whereas Ellison, Lyerly, and Otto[369] found that the surface potential varied from +25 mV initially to an equilibrium value of −150 mV after 6 min. Smith[156,303,370] has made many studies on the surface properties of mercury and has found no effects with time for hydrogen and helium on the ellipsometric or surface potential values.

Bailey, Fordham, and Tyson[371] studied the surface structure of mercury by means of electron diffraction. The patterns obtained under high vacuum did not entirely correspond to those expected for pure mercury; the surface appeared, in fact, to be covered with a very thin (~9 Å) layer of an "adventitious polycrystalline surface film." The nature of the surface film could not be ascertained, but it did not agree with the known structure of mercury oxide. Furthermore, they noticed that the film did not thicken on exposure to air, although the time of study in this respect was not recorded. They found that this surface film acted as an effective barrier against attack by many reagents; for example, gold evaporated onto the surface showed the characteristic pattern of gold in pronounced (1,1,1) orientation. Jenkins,[372] however, in a similar study found that the surface film corresponded to an oriented oxide layer, which could be removed by filtration, thus leaving only the halos of mercury itself. Recent low-energy diffraction experiments[373] under high vacuum (10⁻¹⁰ Torr) have shown that no changes in the surface properties of mercury occur within the time range 15 sec up to 15 min.

It is often difficult to interpret the findings of ellipsometric, surface potential, and electron diffraction results, in respect to surface tension changes, since these techniques are sensitive to adsorbed material on mercury at coverages much less than monomolecular. Changes in surface tension will not be recorded until monomolecular coverage is approached. Some of the early work is confusing, but the more recent results of Schilling and Webb[373] and Smith[303] show that the surface of pure mercury does not exhibit any spurious ageing effects and can be very well defined.

Where physical adsorption occurs on a mercury surface, the amount adsorbed is a function of the temperature and the relative vapor pressure of the gas only.[374] At room temperatures and pressures less than 1 atm, the relative pressures of all atmospheric gases (excluding water vapor) are exceedingly small. Certainly, they are less than the order 0.10 which is characteristic of the BET[375] requirement for monomolecular coverage. Thus, it would be expected that, where physical adsorption alone is occurring, no effects on the surface tension of mercury at room temperatures would occur. However, surface tension depressions in various gases have been recorded, and it is pertinent to consider these findings under the following headings.

3. Rare Gases (He, Ne, Ar, Kr, Xe, Rn)

Very little work has been attempted on the measurement of the surface pressures of the rare gases on mercury, and from normal considerations no effects are to be expected at room temperatures. Furthermore, several rare gases are commonly used gaseous "environments" since they do not appear to affect the reflective and "tailing" properties of mercury in various instruments. Smith[303] has worked extensively with helium atmospheres and has found that no changes in surface tension or ellipsometric or contact potentials occur, even

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(372) R. O. Jenkins, Ph.D. Thesis, London University, 1934.
(373) J. S. Schilling and M. B. Webb, *Phys. Rev. B*, **3** (2) 6, 1665 (1970).
(374) S. Brunauer, "The Adsorption of Gases and Vapors," Vol. 1, "Physical Adsorption," Princeton University Press, Princeton, N. J., 1943.
(375) S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, **60**, 309 (1938).

over long time periods. The careful work of Nicholas, Joyner, Tessem, and Olson confirms this.[144]

Cassel and Neugebauer,[376] Binne,[74] and Lee[157] have found argon to have no effect on the surface tension. Cassel and Neugebauer, and Binne, however, record smooth curves for the lowering of the surface tension of mercury by xenon and krypton. The temperatures are high (−18 to +20°) and the corresponding relative vapor pressures exceedingly low. The surface pressures recorded were very low (0.20–5.50 dyn/cm), except for several recorded in higher gas pressures of xenon (at −36° and 331 mm a value of 9.10 dyn/cm). It is certainly difficult to accept the claimed accuracy of the measurement of ±0.01%, especially since the majority of the most careful workers only claim under ideal conditions ±0.2%. The results are puzzling,[168] not to be expected, and cannot be accepted without further corroboration.

4. Nitrogen and Hydrogen

A close study of the data of Table X shows that nitrogen and hydrogen do not have any effect on the surface tension of mercury, as compared with the value *in vacuo*. Nitrogen and hydrogen atmospheres are commonly used where experiments dealing with spreading, wetting and adsorption at a mercury surface are concerned.[148,156,202,367–370,377–379] They are also widely used as the gaseous phase in the determinations of surface tensions of molten metals at elevated temperatures.[334] In this context Addison and Davies[380] found that the addition of mercury to liquid lithium profoundly reduced the reactivity of lithium with nitrogen. Temperatures as high as 300°, with 51.0 atom % lithium, were required before the formation of Li_3N occurred.

Bradley,[76] Cook,[66] and Law[121] reported that the surface tension of mercury in hydrogen was lower than the value *in vacuo*. Bradley's lowering of 1–2 dyn/cm in 1 day cannot, however, be considered as significant. Cook found that the surface tension dropped gradually with time, and that the adsorption which was occurring could not be reversed by pumping. Law also found that the adsorption isotherm could not be reproduced by pumping. He found that the surface tension decreased by 18 dyn/cm as the pressure was increased to 1.5 mm. However, at higher pressures the surface tension increased again. Similar results were found by Law for nitrogen.

Law suggests that the apparent inapplicability of the Gibb's equation (eq 20) can be explained if the change in electrical potential at the mercury surface is taken into account. The Gibbs equation is derived with the assumption that the electrical potential at the surface is constant. Law considers, however, that when molecules containing dipoles, or in which dipoles may be induced, are adsorbed, they will form an electrical double layer and the surface potential will change with the number of molecules present. The adsorption isotherm should still, however, be reversible. Since this was not the case the results obtained from this analysis may be dubious.

The surface tension of mercury in nitrogen and hydrogen

atmospheres is the same as that *in vacuo*, namely, 475.5 ± 9 dyn/cm.

5. Carbon Dioxide and Carbon Monoxide

Although the boiling point of carbon dioxide is much higher than those of other atmospheric gases, its saturation vapor pressure at room temperature is still extremely large. Thus, relative vapor pressures for pressures of less than 760 mm will be very small, certainly ≪0.1. In this case, and considering physical adsorption alone, the amounts adsorbed should be very small. The careful work of Nicholas, Joyner, Tessem, and Olsen[144] showed that no decrease occurred in the surface tension of mercury during an exposure of 24 hr at 760 mm. Similar conclusions were reached by Stockle,[33] Bircumshaw,[56,63.68] Sauerwald and Drath,[58] and Foryst.[120]

Law[121] reports a drop of about 2% in the surface tension value in the presence of 14.7 mm of carbon dioxide. In 1939 Bosworth[92] found a progressive fall in the surface tension of mercury in carbon dioxide as the percentage of carbon dioxide in dry air increased. The value fell from 482.7 dyn/cm at 0% to a low of 452 dyn/cm at 3% content, after which the value recovered until in pure carbon dioxide the surface tension was within 1% of the original value. These findings are contrary to the earlier works of Oliphant[357] and Burdon,[358] from the same laboratory, who concluded that roughly monomolecular coverage of a mercury surface by carbon dioxide occurred at about 2% content in the gaseous phase and did not alter at higher levels.

No satisfactory explanations have been proposed to explain the results of Law, and particularly those of Bosworth. The most recent work[144] indicates no effects in carbon dioxide. This finding is certainly what might be expected if adsorption is of a physical nature and obeys the BET equation.

To the author's knowledge Law is the only worker who studied the effect of carbon monoxide. He found small decreases in the surface tension, but the adsorbed layer could not be completely removed by pumping.

6. Oxygen and Ozone

Mercury is oxidized in the presence of oxygen, but the rate of oxidation at room temperature is infinitesimally slow.[329] Taylor and Hulett[282] studied the reaction between mercury and oxygen and found that measurable reaction rates did not occur until the temperature was above 300°. They found that when oxygen was passed over a clean mercury surface at 200° the surface remained bright, but did tend to "tail" after a period of several hours; this indicated the formation of an impurity at the mercury–container (glass)–oxygen intersection. The impurity was probably an oxide of some form and may have been derived from the container. Certainly the rate of oxidation is markedly affected by catalysts, which may be foreign metal oxides. However, for pure mercury, it is certain that the rate of oxidation at room temperature in dry conditions is so slow that no measurable effect on the surface tension will be measurable for many weeks or probably months under ideal conditions.

Ozone reacts more readily with mercury, but under normal conditions the rate of formation of the oxide is very slow. Hodgson[381] found only trace amounts of oxide had been formed after bubbling oxygen (7% O_3) through mercury for

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50 hr at 25°. Callear, Patrick, and Robb[382] studied the reaction of mercury with oxygen by photometric and thermal methods, and they concluded that mercury oxide was formed mainly by reaction with ozone. The ozone was produced by reaction of excited oxygen (O_2^*) with normal oxygen molecules as follows.

$$Hg6(^3P_1) + O_2 \longrightarrow O_2^* + Hg6(^1S_0)$$

$$O_2 + O_2^* \longrightarrow O_3 + O$$

$$O_3 + Hg \longrightarrow HgO + O_2$$
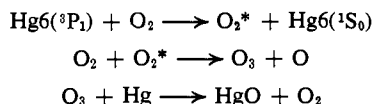
This mechanism of oxidation *via* O_3 is confirmed by the work of Dickinson and Sherril[383] and Noyes,[384] although Darwent[343] considers that oxidation proceeds *via* the normal oxygen molecule.

The surface tension of mercury, under normal conditions, is not affected by oxygen or ozone over short time intervals.

7. Surface Tension of Mercury in Air

Detailed discussions have been given for the reasons for the wide discordance in values reported for the surface tension of mercury *in vacuo*. With measurements in gases the effects of tap greases (unless in contact with the mercury) and low vapor pressure organic materials will be minimal. However, care must be taken to ensure the gases are free from reactive vapors and water vapor. Small amounts of surface-active contaminants usually found in laboratory air can over long periods of time lower the surface tension of mercury to below 400 dyn/cm, and in extreme cases to values below 300 dyn/cm.[144]

The influence of various gases which constitute the atmosphere has been discussed. It was concluded that very little, if any, effect was noticed for any of the gases at room temperatures. The influence of water vapor is discussed below.

There is a great deal of evidence (Tables I and X) in support of the fact that the surface tension of mercury in dry air is the same as that *in vacuo*. Long-term surface ageing effects observed in dry air are almost certainly due to the gradual accumulation of impurities at the surface.

Metal oxides on the mercury surface will not affect the surface tension unless they are surface-active. To the author's knowledge no systematic study has been made of the surface activities of metal oxides at mercury surfaces.

An analysis of the values recorded in dry air and various gases (Table I), between 447 and 498 dyn/cm, results in an average of 475.5 dyn/cm with one standard deviation being 10.1 dyn/cm. This value is the same as that recorded *in vacuo* (p 595).

8. Water Vapor

The results obtained for the variation in the surface tension of mercury with pressure of water vapor vary considerably (Figure 7). Differences cannot be explained simply on the basis of impure samples of mercury, and reference to Table I shows that most of the workers recorded surface tension values which were in good agreement with each other. Surface pressure measurements have varied from 24 dyn/cm at a partial pressure of water of 0.00042 mm[127] to no effect until the saturation
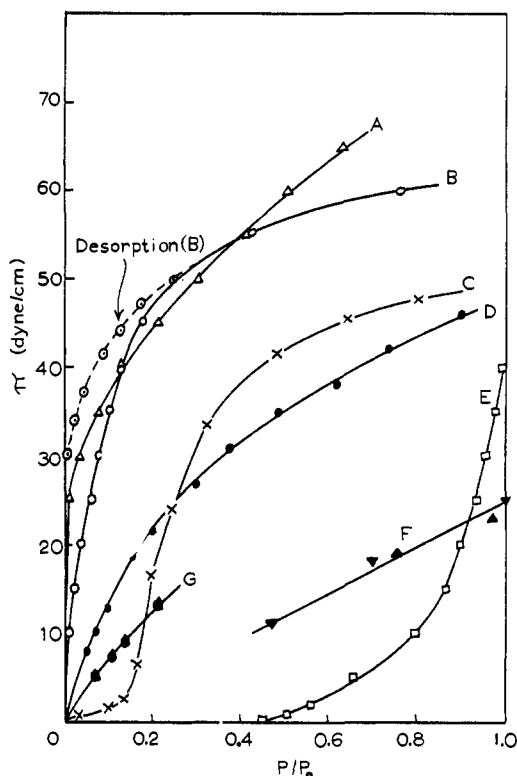
Figure 7. Adsorption isotherms for water on mercury: (A) Karpachev, Smirnov, and Volchenkova, and also Roberts, 25°; (B) Law, 25°; (C) Nicholas, Joyner, Tessem, and Olson, 25°; (D) Kemball, 25°; (E) Bering and Ioileva, 25°; (F) Iredale, 20.5°; (G) Kemball, 50°.

vapor pressure is reached.[53,72,77,385] Further, there is a difference in effect of water vapor according to whether it acts alone or in the presence of other gases. The greatest variation has been with measurements made in the absence of other gases.

(i) *Measurements Made in Air.* Most workers have found that the surface tension of mercury in air is not greatly affected by water vapor until the saturation value is reached.[53,72,77,385] At the saturation value the surface tension falls rapidly to that expected for mercury covered with a condensed film of water, *i.e.*, to the interfacial tension value for mercury–water (refer to section VI). The apparent "blocking" of the adsorption of water vapor by the presence of air led Iredale[53] to conclude that the presence of air may raise the pressure of the water vapor necessary to form a saturated adsorbed film.

Burdon[72] found that the surface tension was the same *in vacuo*, dry air, and initially in air that had been bubbled through distilled water. The surface tension in the moist air only fell by 6 dyn/cm in 30 min. Increasing the relative vapor pressure accelerated the rate of fall, γ falling 30 dyn/cm in the same time. Finally, after leaving water in the apparatus for 1 day, the surface tension fell from 480 to 430 dyn/cm during 30 min. On pumping out to a moderate vacuum the surface tension recovered to 482 dyn/cm, but this dropped at about the same rate as was observed in moist air. Burdon had shown by these experiments that the adsorption was reversible; *i.e.*, physical adsorption was occurring.

Burdon and Oliphant[62] carried out some interesting experi-

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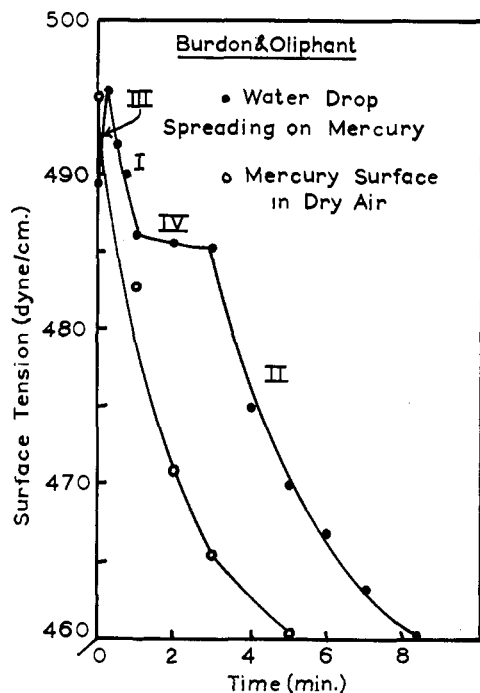
Figure 8. Variation in the surface tension of mercury with time.

ments on the variation in the surface tension of mercury with time of exposure to (1) dry air and (2) initially dry air, but with a droplet of water spreading over the mercury surface. The experiment was accomplished by using a very large pool of mercury and measuring the surface tension *via* the Worthington equation for large sessile drops. The fall in surface tension in dry air (Figure 8) must be attributed to the gradual accumulation of impurity at the surface. It is of note, however, that the presence of the droplet of water did not affect the rate at which the surface tension of the mercury fell; *cf.* sections I and II with the results in dry air. Thus, water vapor, which must have been present in the chamber, did not have any influence on the mercury–air surface tension. The initial increase in γ (section III) and the portion where γ remained constant for about 3 min (section IV) are unexplained.

Bartell, Case, and Brown[385] and Brown[77] found the surface tension of mercury in air saturated with water vapor was 447 dyn/cm. Brown found that this initial value fell rapidly to 430 dyn/cm and lower in the course of 30 min, and continued to fall on longer standing. These slow decreases in the surface tension are explicable on the basis of chemical interactions at the mercury–water interface (section VI).

Gibbs[360] predicted that the surface tension of mercury measured in contact with saturated water vapor should be equal to the interfacial tension of mercury against bulk liquid water plus the surface tension of liquid water in contact with its own vapor. Since the interfacial tension of air-saturated bulk water against mercury is about 375 dyn/cm (section VI) and the surface tension of water is 72 dyn/cm, the surface tension of mercury in saturated water vapor should be 447 dyn/cm. This value agrees with the measured values of Bartell, Case and Brown, and Brown. However, if this is the case, the surface tension of mercury measured in saturated water vapor in the *absence* of air or gases should be 498 dyn/cm, since 426 dyn/cm is the value for the interfacial tension between mercury and *degassed* water. This is impossible since the surface tension

of mercury itself is less than 498 dyn/cm. Thus, it seems that in saturated water vapor what is actually measured, using the normal methods of measurement, is the mercury–water (bulk) interfacial tension.

Iredale[53] recorded a value in saturated water vapor (in air) of 368 dyn/cm; the surface tension varied only slightly from 472 dyn/cm with relative pressures of water less than unity (Figure 7). Iredale also measured values of 447 dyn/cm at 26° in saturated water vapor, and he remarked that values between 368 and 447 dyn/cm could be obtained under identical conditions. He concluded that the value of 447 dyn/cm corresponded to a mercury surface completely covered with a close-packed monomolecular layer of water molecules, the lower value of 368 dyn/cm corresponding to the interfacial tension between mercury and a condensed phase of water (containing dissolved laboratory air; see section VI). This does not imply that Gibbs analysis is incorrect, but rather a composite mercury–water–air surface tension cannot be measured by the drop-weight or sessile drop techniques.

Kemball found that water had little inclination to form a second layer on mercury and only a monolayer was formed at high values of P/P_0. The *surface tension* of the mercury covered with a monolayer of water was found to be 438 dyn/cm, similar to the values recorded by Bartell, Case and Brown, Brown, and Iredale. At saturation condensation occurs, resulting in the lower *interfacial tension* value of 427 dyn/cm.

The only reported direct measurement of the adsorption of water vapor by mercury is due to Bosworth.[71] He found that, at a relative vapor pressure equal to 0.60, the number of water molecules adsorbed from air was $5 \times 10^{14}/cm^2$. Taking a value of 12.5 Å^2 for the area occupied by a water molecule,[386] then 8×10^{14} molecules/cm^2 would be required to form a monolayer. Thus, according to Bosworth only 60% of the surface of mercury is covered at a relative vapor pressure of 0.60.

Although mercury oxidizes at an infinitesimally slow rate in dry oxygen at room temperature, the reaction takes place at a much more rapid rate in moist air. Smith[303] attempted to follow this reaction but found that the reaction rates were completely irreproducible. He concluded that the rate of reaction was related to the (unreproducible) small fraction of a monolayer of contamination that acted as nucleating centers for the reaction. Oxidation will probably proceed most rapidly at mercury oxide sites, and islands of oxide will gradually build up with time. These "islands" may act as sites for preferential adsorption of water vapor, and the effect of water vapor on the bare mercury surface itself could be reduced. This process could explain the discordance in the observations recorded and the irreversibility reported for adsorption of water vapor in the absence of air.[121]

(ii) *Measurements in the Absence of Air*. Measurements of water adsorption in the absence of air have provided the greatest discordance of values. Most workers found that water vapor was reversibly adsorbed, indicating physical adsorption. This is substantiated by the values of 6847 and 7700 cal/mol obtained by Kemball[107] and Law[121] for the free-energy change occurring on adsorption. Karpachev, Smirnov, and Volchenkova[127] recorded a value for the heat of adsorption of 6000 cal/mol.

The entropy of adsorption was large ($\Delta S = -36$ cal/deg

(386) A. L. McClellan and H. F. Harnsberger, *J. Colloid Interface Sci.*, 23, 577 (1967).

mol), and Kemball considered that this could only be explained on the basis of the association of water molecules on the mercury surface, forming clusters of molecules.

Water adsorbs on mercury forming a primary gaseous film which obeys the Volmer[387] equation

$$\pi(A - b) = kT \tag{23}$$

where π is the surface pressure ($\gamma - \gamma_{\text{film}}$), A the area occupied per adsorbed molecule, b a constant termed the co-area, k the Boltzmann constant, and T the temperature in °K. The co-area in the Volmer equation can be identified with the cross-sectional area of the adsorbed molecule. A combination of the Volmer and Gibbs equations yields

$$\ln P = \ln \pi + \frac{b\pi}{kT} + C \tag{24}$$

where P is the gas pressure and C a constant.

The free energy of adsorption can be calculated by means of

$$-\Delta G = RT \ln P_2/P_1 \tag{25}$$

where P_1 and P_2 refer to the bulk and surface phases, respectively. Transforming the surface excess, Γ, into suitable units and taking the thickness of the surface layer to be 6.0 Å, it is possible to combine eq 25 with the Gibb's adsorption equation (eq 20) to yield

$$-\Delta G = RT \ln 12,500 \frac{\partial \pi}{\partial P} \tag{26}$$

This equation is applicable to the region of the isotherm where the adsorbed film is ideal, i.e., as $\partial \pi/\partial P \to 0$. From eq 24

$$\frac{\partial P}{\partial \pi} = \left(\frac{b\pi}{kT} + 1\right)e^{(b\pi/kT) + C} \tag{27}$$

and, therefore, as $\pi \to 0$, $\partial P/\partial \pi = e^C$ or $\partial \pi/\partial P = e^{-C}$. Thus, ΔG can be calculated from eq 26 via a knowledge of the intercept, C, on the Gibbs–Volmer plot (Figure 9).

A plot of $\ln P/\pi$ vs. π for Kemball's results is shown in Figure 9; it was linear up to values of $P/P_0 = 0.9$. The co-area of 12.3 Å² given by the Volmer equation agrees very well with the accepted value for the effective cross-sectional area of a water molecule, i.e., 12.5 Å². Since the $\ln P/\pi$ vs. π plot was linear up to $P/P_0 = 0.9$, then the adsorbed water film remained monomolecular up to the saturation value. This is probably to be expected for adsorption on a perfectly smooth homogeneous surface. The usual deviations in the adsorption isotherms for solids is due to either capillary condensation or clustering on isolated reactive sites.

It is of note that sections of the curves for the results of Law, Karpachev, et al., and Roberts are of similar slope to the Kemball plot. However, departures from linearity over other sections of the curves are not explained.

Karpachev, Smirnov, and Volchenkova's values for the surface excess, Γ, at different temperatures are inexplicably high, giving values of 6.9, 8.3, and 10.4 Å² per molecule at relative pressures of 0.189, 0.0714, and 0.0314, respectively. These are lower than the excepted cross-sectional area of 12.5 Å² for the water molecule.

Law's adsorption isotherm was not completely reversible, indicating that some chemisorption had occurred. This is a possibility if traces of oxygen were present, whereby mercury

oxide formation and propagation could occur. The presence of trace amounts of oxygen or carbon dioxide could lead to numerous surface reactions and wide variations in surface tension measurements.

Cassel and Salditt[69] found that water vapor at 50° had no effect on the surface tension of mercury for pressures up to the saturation value. Their measurements with normal alcohols also reflected much smaller surface tension changes than recorded by Kemball (Figure 12). However, their results for benzene and n-heptane agreed fairly well with those of Kemball (Figures 10 and 14). Since the surface tension in vacuo (459 dyn/cm at 50°) is rather low, it is possible that their mercury surfaces were contaminated with some form of nonpolar contaminant, and polar vapors could not displace this.

There is certainly a great need for the most careful examination of the adsorption of water vapor on mercury. The present wide discordance is probably due to either the presence of trace impurities or to the fact that complex and time-variable surface reactions (such as oxidation) are occurring.

9. Reactive Gases

Mercury is attacked by hydrogen chloride, hydrogen sulfide, sulfur dioxide, nitrous oxide, and the halogens. However, at room temperatures the rate of attack in dry air is very slow, but in the presence of trace amounts of water vapor the reactions are greatly accelerated.[327] No systematic study has been made of the influence of reactive gases on the surface tension of mercury. Compound formation usually results,[388] and this manifests itself as a surface scum, producing tailing. Difficulties of this type are commonly observed when mercury manometers are used for measurements in reactive gas atmospheres.

10. Organic Vapors

Many gases are reversibly adsorbed by mercury, while some are irreversibly adsorbed. In reversible adsorption physical adsorption is occurring, while in irreversible adsorption surface chemical reactions are usually occurring.

(i) Reversible Adsorption. Mercury is an ideal surface to study the adsorption of vapors since it is completely homogeneous and molecularly "smooth." The surface free energy is high, and according to Fowkes[389] the dispersion force contribution to the surface tension is about ten times higher than the corresponding value for water. It would therefore be expected that long-chain organic compounds would be adsorbed at low surface coverages in a fully extended "flat" configuration. As further "packing" on the surface occurs, lateral interactions may involve the unrolling of the molecules to some extent, to form an end-on adsorbed state. At higher relative pressures adsorption of a second or third layer probably occurs.

Studies have been made of the adsorption of alkanes, alcohols, fatty acids, and certain aromatic compounds. The results are given in Figures 10–14 as plots of surface pressure, π (defined as the difference between the surface tension in vacuo (or air) and in the gas), against the relative vapor pressure, P/P_0, where P is the actual pressure of the gas and P_0 is its

(387) M. Volmer, Z. Phys. Chem., **115**, 253 (1925).

(388) C. A. Jackobson, "Encyclopaedia of Chemical Reactions," Vol. IV, Reinhold, New York, N. Y., 1951.

(389) F. M. Fowkes, "Chemistry and Physics of Interfaces," American Chemical Society, Washington, D. C., 1965.
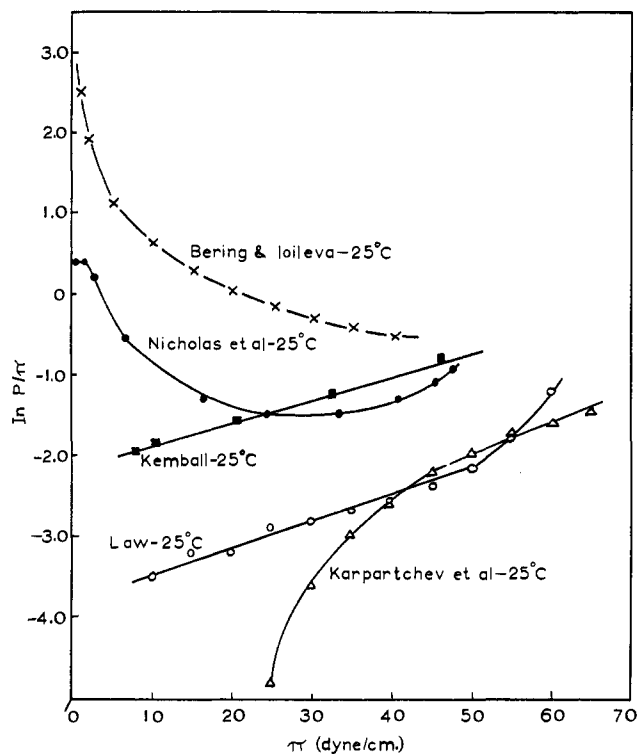
Figure 9. Gibbs-Volmer plots (eq 24) for the adsorption of water on mercury.
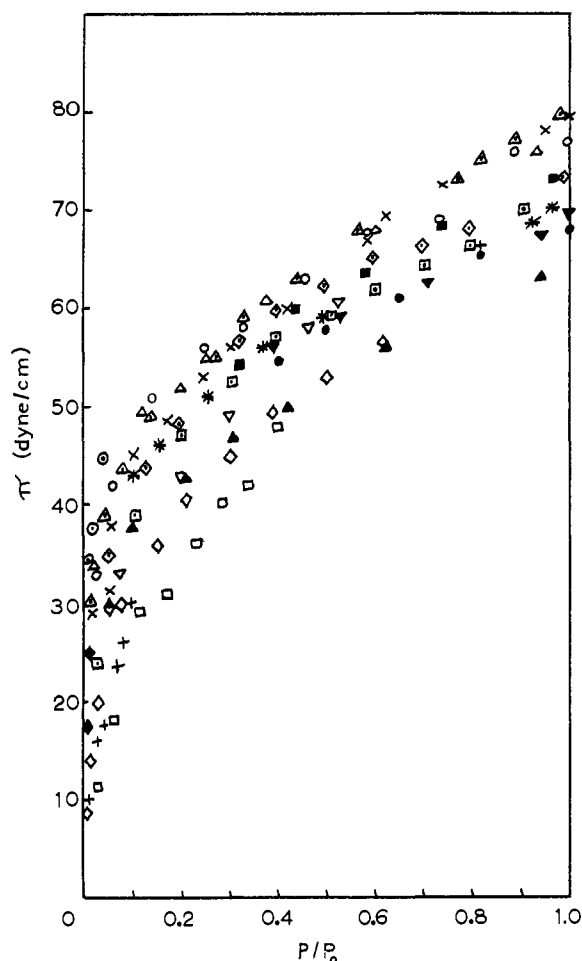

Figure 10. Adsorption isotherms for the normal alkanes (C_3-C_8) on mercury. Symbol, alkane, and author(s), respectively: ◆, propane, Nicholas, Joyner, Tessem, and Olson; +, propane, Smith; □, butane, Smith; ⊡, pentane, Smith; ▽, pentane, Roberts; ⊙, neopentane, Roberts; △, 2,2,4-trimethylpentane, Roberts; ×, hexane, Roberts; ●, hexane, Michelli; ■, heptane, Michelli; O, heptane, Roberts; *, heptane, Kemball; ▲, heptane, Hansen and Stage; ◇, heptane, Cassel and Salditt; ◈, heptane, Bering and Ioileva; ◬, octane, Kemball; ▼, octane, Michelli.

saturation pressure at that particular temperature.[390] The adsorption isotherms were generally reversible, as expected for physical adsorption phenomena. Occasionally irreversible adsorption occurred, indicating the presence of impurity that was not removed by evacuation.

All the alkanes (Figure 10) gave rise to almost identical surface pressures at the same relative pressures. The carbon chain lengths ranged from C_3 to C_8. It is of note that considerable agreement was obtained between different workers. For heptane in particular, the differences in π reported by different workers, for a given value of P/P_0, were always 'less than the differences in their values reported for the surface tensions in vacuo.

Kemball's adsorption isotherms for normal alcohols were much higher than those of Cassel and Salditt, and also of Hansen and Stage for ethyl alcohol. Kemball suggested that, since Cassel and Salditt recorded a low value for the surface tension in vacuo (459 dyn/cm at 50°), the surface may be contaminated with some nonpolar contaminant. This nonpolar contaminant would not be displaced by polar material (see p 603) but would be by nonpolar material. This is a distinct possibility since both Cassel and Salditt, and Hansen and Stage, did record adsorption isotherms for n-heptane which were in good agreement with those of Kemball. Furthermore, there is good agreement between Kemball and Cassel and Salditt on the adsorption of benzene at 50° (Figure 14).

The adsorbed films of organic vapors were generally gaseous and obeyed the Volmer equation (eq 23) over large pressure ranges. In many cases the Volmer equation was obeyed up to almost saturation pressures. Some of the data of Figures 10-

14 are plotted as $\ln P/\pi$ vs. π in Figures 15 and 16 to illustrate the good degrees of fit for the states of these adsorbed films to the combined Volmer-Gibbs equation (eq 24). A number of phase changes occurred on completion of the first monolayers; examples of this phenomenon are at $\pi = 53$ dyn/cm for Kemball's results for toluene, and at $\pi = 43$ dyn/cm for Hansen and Stage's results for ethyl alcohol. The phase change in some cases corresponded to the changeover from "flat" to "vertical" orientation, and in others to the two-dimensional condensation on the adsorption of a second layer.

Kemball found that the Langmuir adsorption equation[391] did not provide as good a fit to the experimental data as the Volmer equation. Tedoradze[392] has considered the Frumkin[393] and Parsons'[394] modifications of the basic Langmuir equation. However, the basic Volmer equation best describes the state of the adsorbed phase while it is in a gaseous state.

(390) T. E. Jordan, "Vapor Pressures of Organic Compounds, "Interscience, New York, N. Y., 1954.

(391) I. Langmuir, J. Amer. Chem. Soc., 40, 1361 (1918).
(392) G. A. Tedoradze, Dokl. Akad. Nauk. SSSR, 155, 1423 (1964).
(393) A. N. Frumkin, Tr. Khim. Inst. L. Karpova, 4, 56 (1925).
(394) R. Parsons, J. Electroanal Chem., 7, 136 (1964).
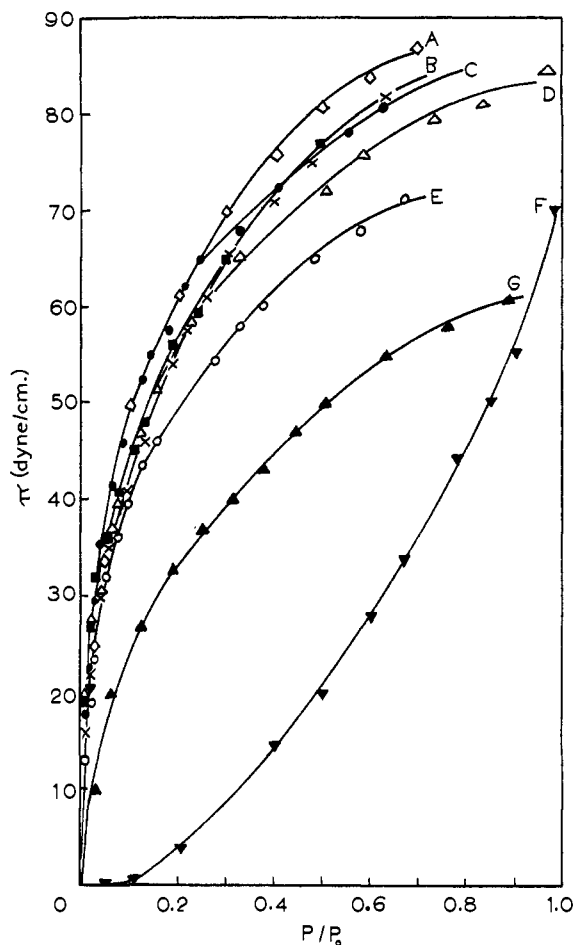
Figure 11. Adsorption isotherms for the normal alcohols (C₁-C₆) on mercury: (A) Kemball, hexyl alcohol, 25°; (B) Kemball, butyl alcohol (■) and ethyl alcohol (×), 25°; (C) Kemball, methyl alcohol, 25°; (D) Kemball, pentyl alcohol, 25°; (E) Kemball, propyl alcohol, 25°; (F) Bering and Ioileva, methyl alcohol, 25°; (G) Hansen and Stage, ethyl alcohol, 30°.

Table XII

Co-areas and Free Energy Changes for Molecules Adsorbed on Mercury

Substance	Free energy change, ΔG, cal/(g mol)	Co-area, Å^2 (temp, °C, investigator)
n-Pentane	−6,844	29.1 (25° Roberts), 32 (25°, Smith), 19.8 (25°, Micheli)
n-Hexane	−8,344	31.7 (25°, Roberts), 23.2 (25° Micheli)
n-Heptane	−8,817 ± 8	33.7 (25°, Roberts), 32.1 (25°, Kemball), 25.5 (25°, Micheli)
n-Octane	−9,963	35.7 (25°, Roberts), 27.5 (25°, Micheli)
2,2,4-Trimethyl-pentane	−9,113	34.6 (25°, Roberts)
Neopentane		34.7 (20°, Roberts)
Benzene	−8,513 ± 15	33.7 (25°, Kemball), 20.5 (25°, Micheli), 22 (26°, Iredale)
Toluene	−9,625 ± 8	36.2 (25°, Kemball)
Methyl alcohol	−7,879 ± 22	31.3 (25°, Kemball)
Ethyl alcohol	−8,057 ± 11	22.9 (25°, Kemball), 29 (26°, Iredale)
n-Propyl alcohol	−8,445 ± 12	19.1 (25°, Kemball)
n-Butyl alcohol	−9,817 ± 10	28.1 (25°, Kemball)
n-Amyl alcohol	−10,506 ± 23	35.2 (25°, Kemball)
n-Hexyl alcohol	−11,231 ± 15	42.8 (25°, Kemball)
Acetone	−6,150 ± 10	18.8 (25°, Kemball)
Methyl acetate		27.5 (26°, Iredale)
Propyl chloride		40 (26°, Iredale)
Ethyl bromide		40 (26°, Iredale)
Methyl iodide		13 (26°, Iredale)

The gradient of the $\ln P/\pi$ vs. π plot is b/kT, and therefore the co-area of the adsorbed molecule can be calculated. Values determined in this fashion are given in Table XII. Also given in this table are the calculated free energy changes that accompanied adsorption. They lie within the range of values expected for processes of physical adsorption. The values of b have been calculated from the first sections of the $\ln P/\pi$ vs. π plots. Values given by Iredale and Micheli have been determined from the Gibbs' plot, i.e., γ vs. $\ln P$. The co-areas are larger than the corresponding cross-sectional areas of the fully erect molecules. The area occupied by a CH_2 group is of the order 7 Å^2, which, for octane, should lead to a value of 56 Å^2 for the area occupied by the fully extended form; however, the co-area is only 35.7 Å^2. Thus, it appears that at close packing the carbon chain is not fully erect but kinked; in the case of octane five CH_2 groups will be on the mercury surface while three are erect. As the carbon chain grows longer the co-area will also increase accordingly. This is demonstrated by the plots of π vs. A (area per molecule) in Figure 17.

Phase changes in the adsorbed states of molecules at mercury surfaces can sometimes be detected by surface potential or ellipsometry measurements. These measurements, however, cannot be correlated directly with surface tensions. A typical set of results determined by Smith for stearic acid on mercury is given in Figure 18. For comparison, the π vs. A curve for stearic acid on water is also given.

Kemball was able to correlate the surface phase change that occurred with toluene on mercury at a surface pressure of 53 dyn/cm (Figure 16) to the reorientation of the molecule from a "flat" adsorbed state to one that is fully erect. He found that the surface potential remained constant up to 53 dyn/cm; it then fell by 0.05 V and remained constant up to a surface pressure at 65 dyn/cm. The calculated co-area for the second section of the $\ln P/\pi$ vs. π plot for toluene is 23.5 Å^2, which agrees well with the cross-sectional area of 24 Å^2 given by Adam[168] for an aromatic amine or phenol on a water surface. The phase change that occurred at 53 dyn/cm for benzene is believed to correspond to the same phenomenon of reorientation.

Schwartz, Ellison, Klemm and Otto[378] have demonstrated that contact angles of liquids on films deposited on a mercury surface can provide information with regard to phase changes occurring in the adsorbed phase. The technique has been applied successfully to various long-chain fatty acids and alcohols; examples of the changes recorded are given in Figure 19. A large amount of other work dealing with the equations of state of nonvolatile compounds adsorbed on the surface of mercury is dealt with by Smith.[303]

In many cases the Volmer equation describing the formation of the first monolayer region is found to persist until fairly high surface pressures are reached. The phase changes observed in the $\ln P/\pi$ vs. π and π vs. A plots can be due to phase changes in the first monolayer, or to the formation of a
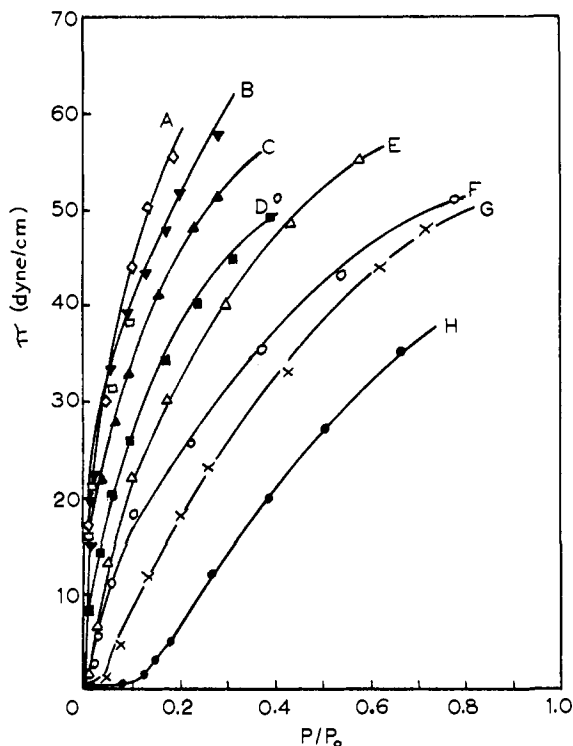
Figure 12. Adsorption isotherms for the normal alcohols (C_1-C_5) on mercury at 50°: (A) Kemball, butyl alcohol; (B) Kemball, propyl alcohol (□) and ethyl alcohol (▼); (C) Kemball, methyl alcohol; (D) Cassel and Salditt, butyl alcohol; (E) Cassel and Salditt, allyl alcohol; (F) Cassel and Salditt, propyl alcohol; (G) Cassel and Salditt, ethyl alcohol; (H) Cassel and Salditt, methyl alcohol.

Figure 13. Adsorption isotherms for the normal fatty acids (C_0-C_5) on mercury.

second layer. If a second layer is adsorbed on the first layer, and it still obeys the Volmer equation, the two layers might be assumed to exert separate surface pressures.[107] If x is the fraction of the adsorbed material in the first layer and A the area per molecule, then the total surface pressure will be the sum of the individual surface pressures; i.e., $\pi = \pi_1 + \pi_2$. For the two layers

$$\pi_1\left(\frac{A}{x} - b\right) = kT \tag{28}$$

$$\pi_2\left[\left(\frac{A}{1-x}\right) - b\right] = kT \tag{29}$$

Therefore

$$\pi\left(A - \frac{b}{2}\right) = kT - (\pi_1 - \pi_2)b\left(\frac{1}{2} - x\right) \tag{30}$$

If the second layer only begins to form after the first is complete, then x approaches $^1/_2$ rapidly, and eq 30 reduces to

$$\pi(A - b/2) = kT \tag{31}$$

Kemball's results for acetone provided evidence for this type of relationship. The plot of $\ln P/\pi$ vs. π (Figure 15) showed three separate regions, and the values of b calculated from the slopes were 18.8 ± 0.3, 9.6 ± 0.2, and 6.5 ± 0.4 Å^2, indicating that the equations $(A - 18.8) = kT$, $(A - 9.6) = kT$, and $(A - 6.5) = kT$ were obeyed in these three regions. The values of b for the second and third regions are almost exactly one-half and one-third of the values for the primary film.

Zorin[395] has studied the thicknesses of benzene films on mercury at high relative vapor pressures (>0.93). He found that the thickness of the film increased from 10 Å (± 3 Å) at $P/P_0 = 0.93$ to 67 Å at saturation. However, he also found another stable thickness at saturation, with a value of 210 Å. He designated these α and β modifications and considered that they were two different film modifications, with the orientation of the benzene molecules being different in the two cases. Films of thickness greater than 210 Å had the structures of benzene in bulk.

(ii) *Irreversible Adsorption*. Kemball[107] studied the chemisorption of carbon tetrachloride, hexachloroethane, and chloroform on mercury, the reactions being followed by recording changes in surface potentials. The rate of reaction varied with the gas pressure and temperature, increasing with both pressure and temperature. Some of the results obtained at 25° are given in Figure 20. The kinetics indicated that the substances were dimerizing under the action of the mercury surface with negligible activation energy. This conclusion was reached since the gradients of the log (dV/dT) vs. log P plots were linear and the slopes were equal to 2. Thus, the initial reactions were of second order with respect to the pressures of the vapors and involved two molecules of the adsorbent.

The rates of reaction varied; for carbon tetrachloride, the initial rate of reaction at 0.10 mm, pressure corresponded to a reaction rate of 2.5×10^{11} chemisorbed units per cm^2 per

(395) Z. M. Zorin, "Research in Surface Forces," Vol. 2, B. V. Deryaguin, Ed., translated from Russian by P. P. Sutton, Consultants Bureau, New York, N. Y., 1966, p 134.
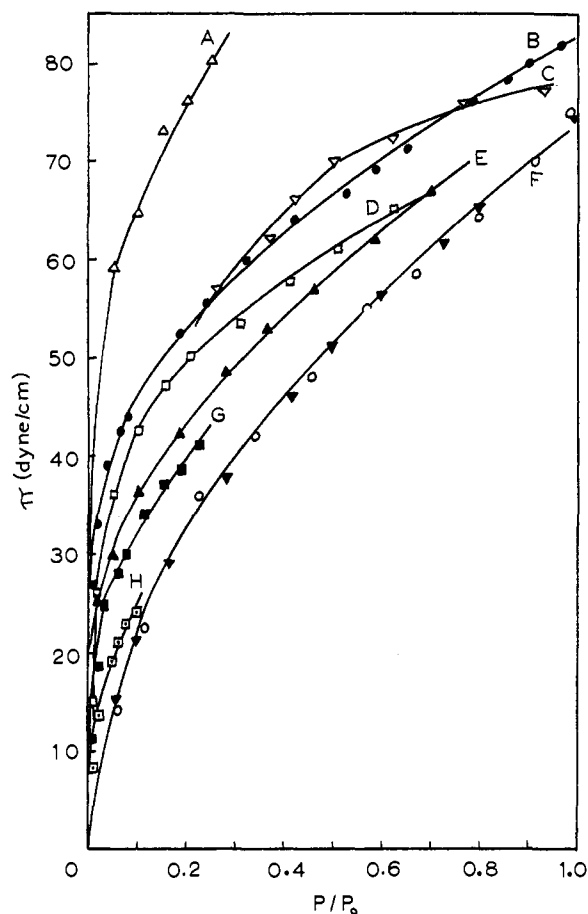
Figure 14. Adsorption isotherms for benzene, toluene, and acetone on mercury: (A) Michelli, benzene, 26°; (B) Kemball, toluene, 25°; (C) Iredale, benzene, 26°; (D) Kemball, benzene, 25°; (E) Cassel and Salditt, benzene 50°; (F) Kemball (O) and Bering and Ioileva (▼), acetone, 25°; (G) Kemball, benzene, 50°; (H) Kemball, benzene, 75°.
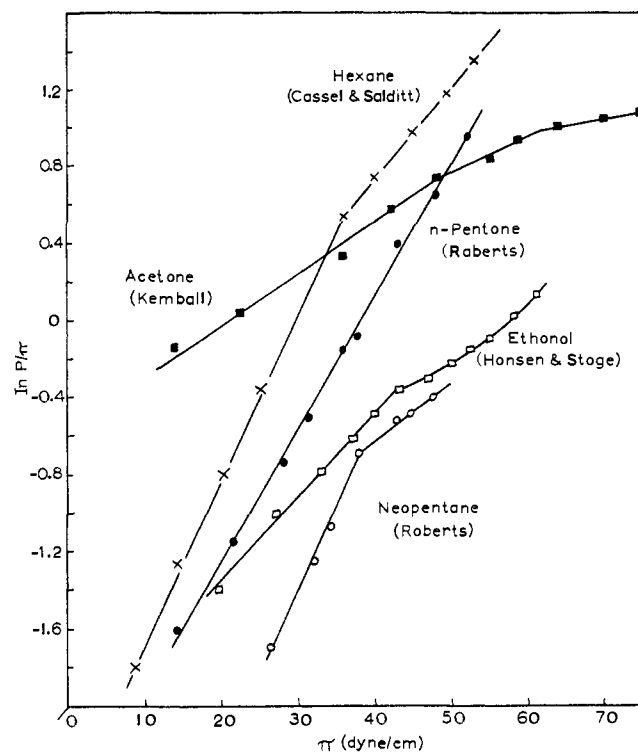

Figure 15. Gibbs–Volmer plots for the adsorption of hexane, pentane, neopentane, acetone, and ethanol on mercury.

Table XIII

Photochemical Reaction of Methyl Iodide with Mercury[a]

Light intensity	Irreversible surface pressure, π, dyn/cm		
	6.00 mm	17.4 mm	25.1 mm
11		4.4	15.4
23		8.0	22.3
52	3.7	13.7	31.1
100	6.7	18.7	38.2

[a] Illumination time 10 min.

sec. Assuming the chemisorbed unit occupied 50 Å², then about 15 min would be required for monolayer coverage to be achieved. It was postulated that the complex consisted of two physically adsorbed molecules loosely held together so that each retained its normal rotational and vibrational degrees of freedom. The complex would then have only two degrees of translational freedom, both in the plane of the mercury surface. The four lost translational degrees of freedom would be replaced by a rotation of the complex as a whole in the plane of the surface, and three vibrations, one between each molecule and the mercury, and one between the two molecules themselves. One of these three vibrational modes would, however, be adsorbed in the so-called reaction coordinate of the activated complex.

If the change in surface potential was proportional to the amount of chemisorbed species, then the graphs of π vs. $1/\Delta V$ might be similar to those of π vs. A. A plot of π vs. $1/\Delta V$ for carbon tetrachloride is given in Figure 21, where the irreversible surface pressures were measured after different periods of contact. This can be compared directly with the π vs. A plot obtained by Cassel.[396] Cassel calculated the area per molecule for carbon tetrachloride in a close-packed monomolecular

film to be about 32 Å², a value somewhat lower than that of the dimer ($\sim$50 Å²) proposed by Kemball.

Iredale studied the effect of methyl acetate, methyl iodide, ethyl bromide, and propyl chloride on the surface tension of mercury. In all cases the adsorption isotherms were not reversible, indicating chemisorption. Kemball, however, found that methyl iodide only reacted with mercury when the surface was irradiated with light of wavelengths less than 3600 Å, i.e., below the photoelectric threshold value for mercury. The photochemical reaction occurring was found to follow first-order kinetics, as expected. Further, the rate of reaction depended on the intensity of the light source (Table XIII), the rate being proportional to the square root of the intensity.

E. DISSOLVED METALS

Mercury has become quite popular in recent years for use as a heat transfer medium.[397] The wide range of the liquid state, the relatively high boiling point, and low specific heat value

(396) H. Cassel, *Trans. Faraday Soc.*, 28, 177 (1931).

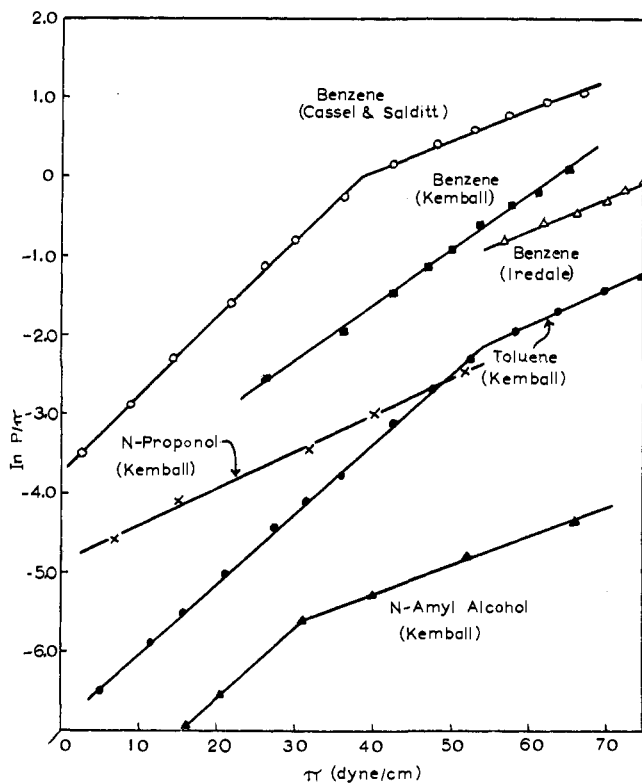(397) S. S. Kutateladze, "Liquid Metal Heat Transfer Media," Consultants Bureau, New York, N. Y., 1959.

Figure 16. Gibbs–Volmer plots for the adsorption of benzene, toluene, 1-propanol and n-amyl alcohol on mercury.

are obvious advantages over water. Mercury can be used in steel containers since the solubility of iron in mercury is very low (<1 ppm). Unfortunately mercury wets steel very poorly (contact angle $\sim$140°), and this has prompted studies of the surface tensions of amalgams to determine the abilities of different metal additives to increase wettability.

Several workers have measured the surface tensions of various amalgams *in vacuo*, but little agreement exists.[38,65,84,86,113,123,138,151,157] The results obtained for sodium and potassium amalgams are given in Figure 22. Some of the discordance may be explicable on the basis of contaminated mercury surfaces.[160] Schmidt,[37] Oppenheimer,[65] Convers,[86] and Semenchenko, Bering and Pokrovski,[84] all of whom recorded low values for the surface tension of pure mercury (refer Table I), found small depressions in the surface tension. Much larger changes were recorded by workers who recorded high values for the surface tension of pure mercury.[113,123,157] However, even where workers obtained good agreement on the surface tension of pure mercury, poor agreement was recorded for the effect of sodium and potassium (Figure 22).

Although the effects vary, it can be concluded that (i) metals of groups 1a and 2a are surface active in that they reduce the surface tension of mercury,[38,65,84,86,113,123,157] (ii) metals of groups 1b and 2b are surface inactive,[38,84,86,138] and (iii) metals in groups 3 and higher are surface inactive.[38,84,151] Many of these findings are in agreement with Semenchenko's theory of generalized moments,[160] which predicts that Cs, Rb, Au, K, Ag, Na, Ca, Li, Ba, Bi, Pb, and Sr should be surface active, and Cu, Cd, Sn, Co, Zn, Mg, and Be should be surface inactive. There is still a great need for a thorough and systematic investigation of the effects of different metals on the surface tension of mercury.

Table XIV

Metal Complexes with Mercury

Lithium	Hg_3Li, Hg_2Li, $HgLi$, $HgLi_2$, $HgLi_3$, $HgLi_6$
Sodium	Hg_4Na, Hg_2Na, Hg_8Na_7, $HgNa$, Hg_2Na_3, $HgNa_3$
Potassium	$Hg_{12}K$, $Hg_{11}K$, $Hg_{10}K$, Hg_9K, Hg_8K, Hg_9K_2, Hg_4K, Hg_3K, Hg_2K, Hg_7K_3, HgK
Rubidium	$Hg_{11}Rb$, Hg_9Rb, Hg_6Rb, Hg_9Rb_2, $Hg_{18}Rb_5$, Hg_7Rb_2, Hg_2Rb, Hg_4Rb_3, Hg_8Rb_7
Cesium	$Hg_{20}Cs$, $Hg_{12}Cs$, $Hg_{10}Cs$, Hg_6Cs, Hg_4Cs, Hg_2Cs, Hg_4Cs_3, $HgCs$
Calcium	$Hg_{11}Ca$, Hg_5Ca, Hg_3Ca, Hg_4Ca_3, $HgCa$, Hg_2Ca_3
Strontium	$Hg_{11}Sr$, Hg_5Sr_2, $HgSr$
Barium	$Hg_{11}Ba$, $HgBa$
Zinc	$HgZn_3$
Cadmium	$HgCd_3$
Thallium	Hg_5Tl_2
Antimony	Hg_3Sb_2
Bismuth	$HgBi$, $HgBi_2$, $HgBi_3$, $HgBi_4$, $HgBi_5$, $Hg_{38}Bi$
Platinum	$HgPt$, Hg_2Pt, Hg_4Pt

The analysis of any surface tension data for amalgams is extremely complicated since most metals readily form complexes with mercury. Some of the complexes that have been claimed to exist are given in Table XIV. Apart from these complexes, polynary alloys of even greater complexity are known to exist. Any modified Gibbsonian treatment of the adsorption of metal impurities at a mercury surface must take into consideration the surface activity of the metal complex itself. Since the surface activity will vary with the nature of the complex, and possibly more than one modification will be present at any time, the theoretical considerations became exceedingly difficult. Although, at the present time, many theoretical treatments have been developed for describing the surface tensions of metals and alloys,[130,145,160,398,399] they yield results which in many cases agree only approximately with experimental findings.

One of the most difficult experimental problems is prevention of reaction of the dissolved metal with the external phase. Since the dissolved metals are present in the bulk in the atomic state, they are extremely reactive when they come into the surface layers. Even under vacuums of 10^{-6} to 10^{-7} mm sufficient residual gases may be present so that chemical reactions occur. This may result in the gradual "creaming" of impurities at the mercury surface, especially if traces of oxygen or water vapor are present whereby oxide formation will occur. These impurity metal oxide sites may catalyze the oxidation of mercury itself.

The gradual dulling of mercury surfaces when kept in air is undoubtedly due to the creaming of dissolved metals and the slow oxidation of mercury itself. These impurity metal oxides form a visible skin on the mercury surface. The time taken before visible effects are noticed depends not only on the purity of the mercury but also on the nature of the external phase. Elliott and Wilkinson[301] have shown that mercury saturated with metallic impurites ($\sim$4% level) had a surface tension in air of about 610 dyn/cm at a surface age of 5 sec, which only increased to 650 dyn/cm at 5 min. Metal oxide formation occurred extremely rapidly within seconds of formation of fresh surface. However, if a fresh mercury surface

(398) C. J. Leadbeater, Selected Government Reports, Vol. 9, "Powder Metallurgy," Her Majesty's Stationery Office, London, 1951.
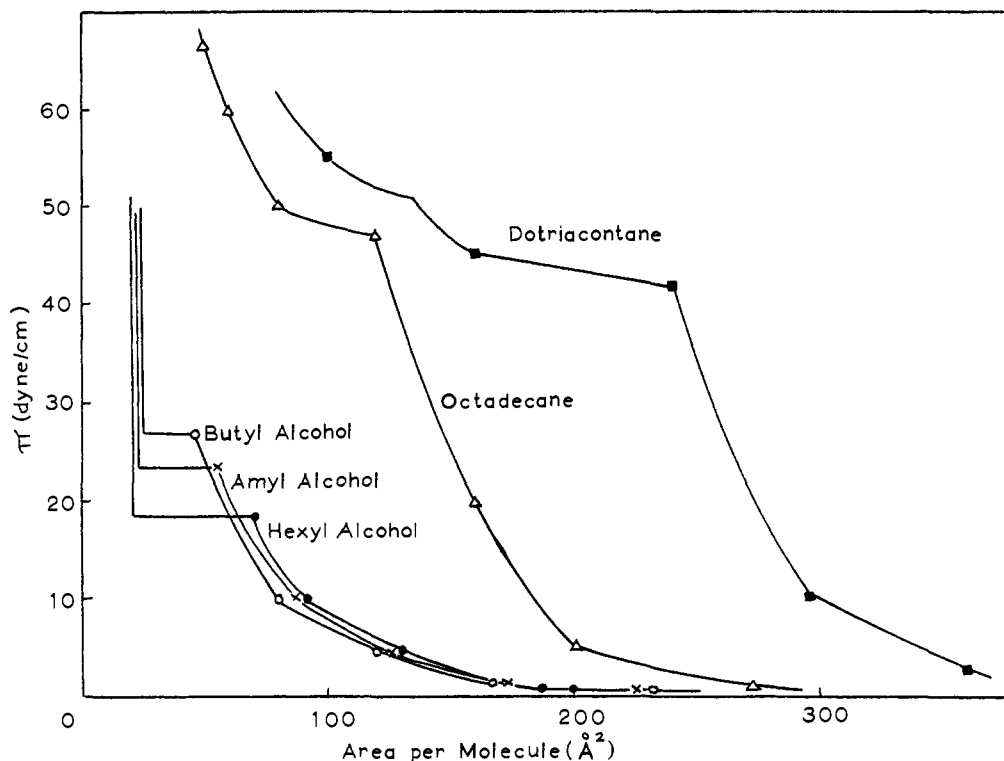(399) P. I. Gold, *Chem. Eng. News*, 192 (May 19, 1969).

Figure 17. Surface pressure *vs.* area per molecule for various molecules on a mercury surface.

was formed under high vacuum, the mercury surface remained bright and it did not "tail," even after several years of storage.[400]

Recent work has shown the existence of a relation between the photoelectric work function and the surface tension of a metal.[401-405] The work function of pure mercury is close to 4.52 V,[405] and small concentrations of certain impurity metals affect this drastically.

Lazarev and Malov[403,404] found a close resemblance between the surface tension *vs.* concentration and work function *vs.* concentration plots (Figure 23) for potassium amalgams. A very similar work function *vs.* concentration plot for potassium amalgams was reported by Turner.[405] The photoelectric current levels off at about the same concentration where the surface tension becomes constant. Lazarev and Malov have extended the studies to sodium and cesium, and Turner to sodium, thallium, cadmium, and indium amalgams. The surface tension data are from the work of Pugachevich and Timofeevicheva.[123]

Cesium, sodium, and potassium seem to be quite surface active, whereas thallium is only slightly surface active, and indium is not surface active at all. These findings are in accord with the surface tension measurements for thallium and indium amalgams made by Olsen and Johnson.[151] They found

that the surface excess for thallium was only 1.78×10^{-10} mol/cm², whereas the expected value for a close-packed monolayer would be about 12×10^{-10} mol/cm². The observed increase in surface tension at the eutectic composition of about 0.095% composition probably corresponded to the formation of a complex which was less surface active.

Malov and Lazarev[404] have shown that for sodium and cesium amalgams there is a linear relationship between the work function and the surface tension, the relationship covering practically the entire range of concentrations studied. For dilute amalgams of sodium, potassium, and cesium which are in the liquid state at 25°, the following empirically derived relation is satisfied

$$\phi = 3.56 \times 10^{-3} R_0{}^2 \gamma^3 \sqrt{R_0/R_g} \qquad (32)$$

where ϕ is the work function, R_0 and R_g are the atomic radii of mercury and the alkali metal, respectively, γ is the surface tension, and 3.56×10^{-3} is the experimentally determined coefficient.

Malov and Lazarev also found that there was a linear relationship between the work function and the surface tensions of polynary amalgams. This was demonstrated for the mercury–cadmium–potassium and mercury–cadmium–cesium systems.[406,407]

The correlations between the work functions of amalgams, and alloys, and their surface tensions, may aid substantially in the understanding of changes occurring in the surface layers of these complex systems.

(400) H. E. Bent, *J. Phys. Chem.*, **37**, 431 (1933).

(401) L. L. Kunin, *Sb. Tr. Tsentr. Nauchn.-Issled. Inst. Chern. Met.*, No. 40, 67 (1965); *Chem. Abstr.*, **65**, 1901a (1966).

(402) S. N. Zadumkin and V. G. Yegiyev, *Fiz. Metal. Metalloved.*, **22**, 121 (1966).

(403) V. B. Lazarev and Yu. I. Malov, *Dokl. Akad. Nauk*, **161**, 875 (1956); **164**, 846 (1965).

(404) Yu. I. Malov and V. B. Lazarev, *Fiz. Metal. Metalloved.*, **26**, 940 (1968).

(405) G. Turner, *Phil. Mag.*, **21**, 257 (1970).

(406) V. B. Lazarev and Yu. I. Malov, *Fiz. Khim. Obrab. Mater.*, **4**, 141 (1967).

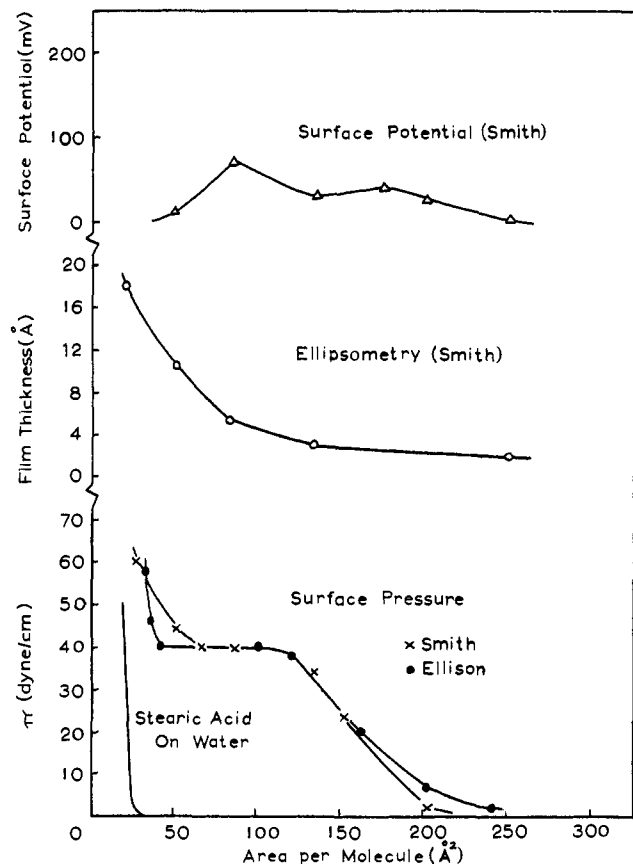(407) P. P. Pugachevich and V. B. Lazarev, *Dokl. Akad. Nauk SSSR*, **113**, 127 (1957); **117**, 445 (1957).

Figure 18. Variation in surface potential, film thickness, and surface pressure as the area per molecule for stearic acid on mercury is varied.
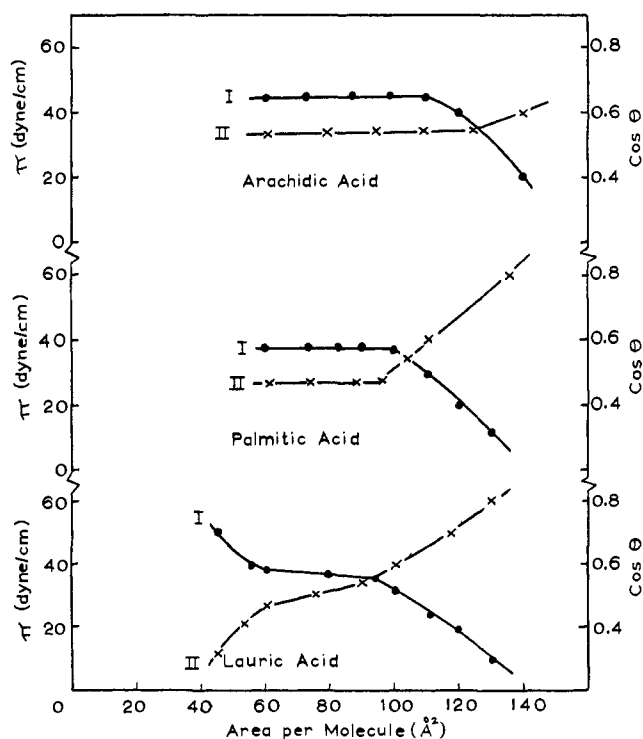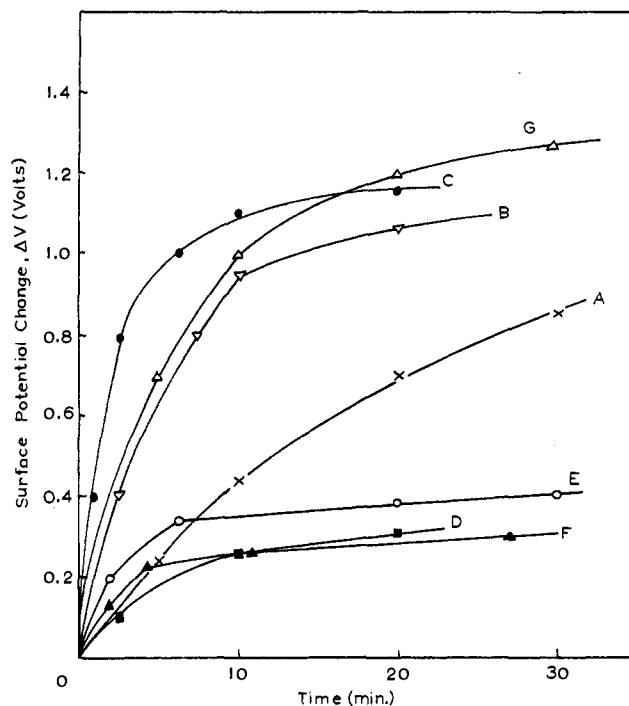

Figure 20. Changes in surface potential with time due to the chemisorption of carbon tetrachloride, hexachlorethane, and chloroform on mercury (25°): (A) 0.074 mm of carbon tetrachloride, (B) 0.123 mm of carbon tetrachloride, (C) 0.210 mm of carbon tetrachloride, (D) 0.022 mm of hexachloroethane, (E) 0.077 mm of hexachloroethane, (F) 2.08 mm chloroform, (G) 0.123 mm of carbon tetrachloride (at 50°).

F. ELECTRICAL CHARGE

With measurements *in vacuo* care must be taken that electrical charge does not build-up on the mercury surface, since this can lead to a variation in surface tension. Auerbach[59] found that the surface tension decreased from 450 to 394 dyn/cm as the potential was increased to 25,000 V[408] (see Table XV).

Table XV

Effect of Electrical Charge on the Surface Tension of Mercury

Potential, V	0	5000	10,000	15,000	20,000	25,000
Surface tension, dyn/cm	450	441	432	416	405	394

Ziesing[125] found that the distillation of mercury in a silica apparatus produced sufficient electrical charge to depress the value of γ by as much as 6 dyn/cm. He used a small dental X-ray plant to restore the original, earth, potential.

VI. Mercury–Water Interfacial Tension

A great deal of work has been done with mercury in the field of electrocapillarity. In this work a charge is imparted to the mercury by means of an applied potential, and the interfacial tension between the mercury and various solutions is measured. For detailed texts of this type of work the reader is re-

Figure 19. Variation in surface pressure (I) and contact angle of water (II) as the area per molecule for various long-chain fatty acids on mercury is varied.

(408) M. Steenbeck, *Wiss. Venoff. Siemens-Konzern,* **8** (3), 94 (1930).
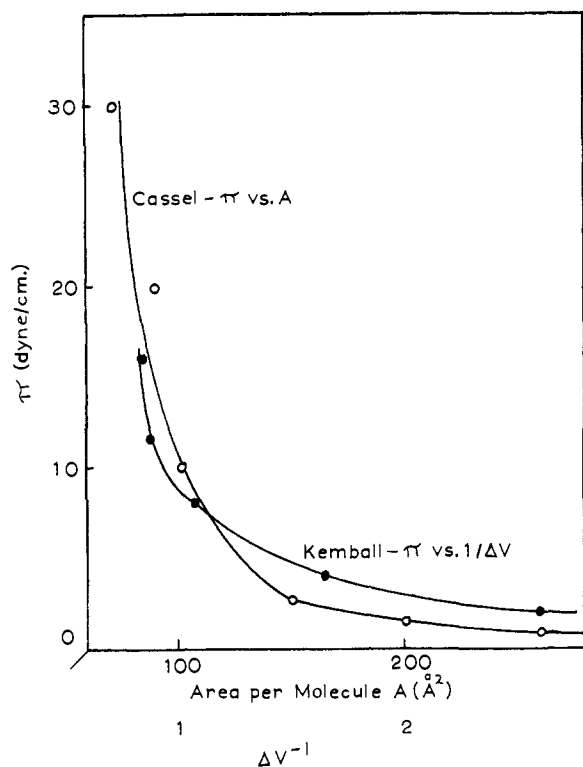
Figure 21. Variation in surface pressure of carbon tetrachloride on mercury as functions of area per molecule and reciprocal of the surface potential.
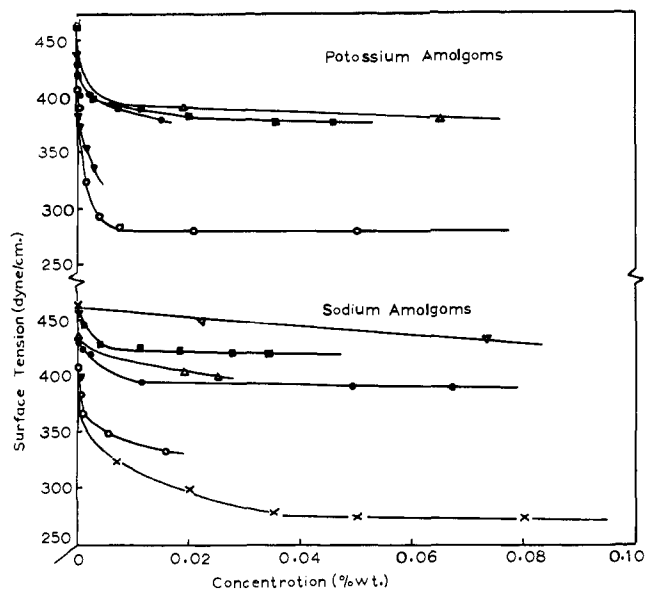

Figure 22. The effect of sodium and potassium on the surface tension of mercury. Sodium: ●, Schmidt; ×, Lee; △, Oppenheimer; ▽, Pugachevich; ○, Semenchenko, Bering, and Pokrovski; ■, Pugachevich and Timofeevicheva; ▼, Convers. Potassium: ●, Schmidt; ■, Pugachevich and Timofeevicheva; ▼, Convers; ○, Semenchenko, Bering, and Pokrovski; ●, Pugachevich.

ferred to ref 409. This section deals with the mercury–water interfacial tension where no charge is applied to the mercury. Any charge which develops on the mercury thus arises from an interaction between the mercury and the contiguous liquid.

Most of the common methods that have been used for the determination of the surface tension of mercury have been applied to the measurement of the mercury–water interfacial tension. Values obtained (ref 16, 35, 44, 64, 146, 150, 153, 191, 196, 213, 385, 389, 410–422) have varied between 362 dyn/cm at 16°[35] to 428 dyn/cm at 25°;[419] see Table XVI. Where possible the conditions under which the measurements were made have been given; where degassed water was not specified it is probable that the water contained dissolved laboratory air. A temperature coefficient of −0.20 dyn/(cm °C) has been taken. In this context Butler's results are of interest since he found that the interfacial tension did not vary between 15.6 and 49°; no explanation for the invariance was given.

(409) "Electrical Phenomena at Interfaces," J. A. V. Butler, Ed., Methuen, London, 1951.
(410) W. C. Lewis, Z. Phys. Chem., 73, 129 (1910).
(411) V. Patrick, ibid., 86, 545 (1914).
(412) M. G. Gouy, Ann. Phys., 6, 3 (1916).
(413) K. E. Glidden, J. Amer. Chem. Soc., 57, 236 (1935).
(414) V. Sivertz, W. H. Taylor, and H. V. Tartour, ibid., 58, 782 (1936).
(415) D. C. Henry and J. Jackson, Nature (London), 142, 616 (1938).
(416) M. Potau, An. Real Soc. Espan. Fis. Quim., Ser. A., 44a, 445 (1948).
(417) G. F. Dusher, Ph.D. Thesis, University of Michigan, 1950.
(418) F. E. Bartell and F. E. Bjorkland, J. Phys. Chem., 56, 453 (1952).
(419) F. E. Bartell and R. J. Bard, ibid., 56, 532 (1952).
(420) D. O. Zeiliger, Tr. Penzensk. Sel'skokhoz. Inst., No. 22, 447 (1958).
(421) E. B. Butler, J. Phys. Chem., 67, 1419 (1963).
(422) R. Parsons and P. C. Symons, Trans. Faraday Soc., 64, 1077 (1968).
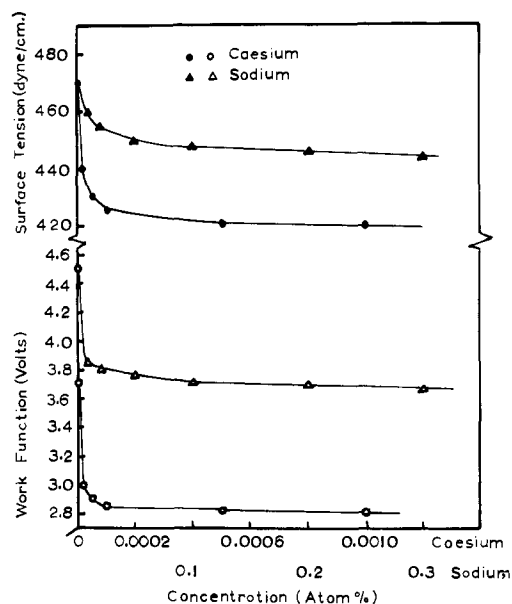
Figure 23. Plots of work function vs. concentration and surface tension vs. concentration for cesium and sodium amalgams.

Fowkes' calculated value of 425.6 ± 2 dyn/cm is based on the assumption that the predominant intermolecular forces between mercury and water are dispersion forces, where the dispersion force contribution to the surface free energy of water is 21.8 ± 0.7 dyn/cm and that of mercury, 198 ± 11 dyn/cm. The interfacial tension is then, according to Fowkes, given by

$$\gamma_{Hg/H_2O} = \gamma_{Hg} + \gamma_{H_2O} - 2\sqrt{21.8 \times 198} \qquad (33)$$

Table XVI

Mercury–Water Interfacial Tension

Year	Author (ref)	Method	Interfacial tension, dyn/cm	Temp, °C	Conditions	Interfacial tension (25°), dyn/cm
1885	Worthington (16)	Sessile drop	377	20		376
1901	Watson (35)	Ripples on surface	364–386	16		362–384
1910	Lewis (410)	Drop number	377	16		375.2
1914	Patrick (411)	Drop-weight	375	18		373.8
1916	Gouy (412)	Sessile drop	375	20		374
		calculation	426.7			425.7
1920	Harkins and Grafton (44)	Drop-weight	375	20		374
1933	Bartell, Case, and Brown (385)	Drop-weight	374.1	25	Water contained dissolved	374.1
		Capillary rise	375	25	laboratory air	375
1934	Brown (77)	Drop-weight	374.8	25		374.8
			374.2	25		374.2
1935	Glidden (413)	Drop-weight	374.4	20		373.4
1936	Sivertz, Taylor, and Tartour (414)	Capillary rise	374.8	25		374.8
1938	Henry and Jackson (415)	Sessile drop	426	20	Degassed water	425
		Capillary rise	427	20	Degassed water	426
			375	20	Water contained dissolved laboratory air	374
1938	Andreas, Hauser, and Tucker (213)	Pendant drop	369	25		369
1940	Dunken (191)	Drop-weight	374.4	20 ± 2		373.4
			385.1	18 ± 2		383.4
1948	Potau (416)	Drop-weight	364.5	27		364.9
1949	Dusher (417)	Pendant drop	377	25		377
1950	Bartell and Bjorkland (418)	Pendant drop	385	25	Water contained dissolved laboratory air	385
1952	Bartell and Bard (419)	Pendant drop	428	25	Degassed water	428
			390	25	Water contained dissolved laboratory air	390
1957	Couper and Priest (196)	Drop-weight	389.7 ± 1.5	25		389.7 ± 1.5
1958	Zeiliger (420)	Maximum pressure in a drop	375			374
1961	Smolders (146)	Sessile drop	378.5	25		378.5
1963	Butler (421)	Pendant drop	414.2 ± 2.3	15.6–49	Degassed water	414.2 ± 2.3
1963	Timofeevicheva, Valetov and Anurov (150)	Maximum pressure in a drop	370.0	20		369.0
1963	Fowkes (389)	Calculation	424.8	20		424
1966	Wilkinson (153)	Drop-weight	395.0 ± 2	25	Water contained dissolved laboratory air	395.0
1967	Parsons and Symons (422)	Drop weight	425 ± 4	25	Degassed water	25

Fowkes used a value for γ_{Hg} of 485 dyn/cm. Using instead a value of 475.5 dyn/cm, and recalculating the dispersion force contribution to the surface tension of mercury based on known mercury–organic liquid interfacial tensions, a value of 176 dyn/cm is obtained. If this value for the dispersion force contribution is used in eq 33, together with a value for γ_{Hg} of 475.5 dyn/cm, a value for γ_{Hg/H_2O} of 423 dyn/cm is obtained.

There is fairly widespread agreement for the value of about 375 dyn/cm for water containing dissolved laboratory air. The values in excess of 400 dyn/cm were for carefully degassed water. It is of note that workers who obtained high values in degassed water found lower values in water containing dissolved laboratory gases, namely, oxygen and carbon dioxide. There therefore appears to be a distinct difference between the interfacial tensions between mercury and carefully degassed water, and mercury and water containing dissolved atmospheric gases.

Gradual changes in the surface tensions of pure liquids or of the interfacial tensions between pairs of pure liquids are usually ascribed to the gradual accumulation of surface-active

impurities. In the case of a polarized interface, Gouy[412] described the effect of "active bodies" on the mercury–water interfacial tension. He considered that the time delay involved before an equilibrium interfacial tension was reached was due to the time required for the adsorbate species to diffuse to the interface, and he referred to the effect as "electrocapillary viscosity." Grahame, Larsen, and Poth[423] found that, with the most carefully prepared salt solutions, the mercury–solution interfacial tension, at certain potentials, gradually decreased with time. They considered the effect to be due to the adsorption of trace amounts of surface-active impurities.

Bjorkland[424] was probably the first to study the variation with time of the interfacial tensions between mercury and various liquids. He found that the interfacial tension between mercury and water containing dissolved laboratory air varied from an initial value of 385 dyn/cm to a low value of 366 dyn/

(423) D. C. Grahame, R. P. Larsen, and M. A. Poth, *J. Amer. Chem. Soc.*, 71, 2978 (1949).
(424) C. W. Bjorkland, Ph.D. Thesis, University of Michigan, 1950.

cm after 12 hr. The rapid initial drop in surface tension was followed by a more gradual decrease. Bjorkland proposed that the effect was due to the action of dissolved oxygen.

The interfacial tension between mercury and the external phase is not only determined by the nature of the external phase, but also by the charge on the mercury. The effect of charge is independent of the source of that charge.[425] Thus, charge can develop at the mercury–liquid interface in unpolarized systems if some component of the liquid interacts chemically with the mercury. The change of potential with immersion in water of a number of metals, including mercury, has been studied by Procopiu.[426] The presence of oxygen leads to an initial potential which is more "negative" than the "normal" value; i.e., the potential becomes more positive after the electrode has been immersed for some time. Thus, the presence of oxygen, and perhaps other dissolved gases, will affect the interfacial tension of mercury against water. The time lapse involved before equilibrium is achieved will undoubtedly depend on the concentration of the dissolved "active" gaseous component (see below).

Bartell and coworkers[418,419] found that the interfacial tension between mercury and pure water containing dissolved laboratory air fell with time (Figure 24). These results can be compared with the ones obtained for mercury against degassed water. The initial values correspond to surface ages of about 30 sec. In both cases the interfacial tension fell with time, but the initial and final equilibrium values were quite different. Bartell and Bard concluded that for the degassed water system the initial and reproducible value of 428 dyn/cm corresponded to the interfacial tension between pure mercury and pure water. The decrease in the interfacial tension in the degassed system was ascribed to the fact that all gases had not been completely removed and slow surface interactions were occurring. Inactive gases, such as nitrogen and hydrogen, do not affect the mercury–water interfacial tension (Figure 24), the slow ageing being attributed to small residual amounts of an "active" gas (probably oxygen).

There is close agreement on the value of about 426 dyn/cm reported by workers using carefully degassed water (Table XVI) and the value of 426.7 dyn/cm at 18° measured by Gouy as the interfacial tension between mercury and pure water at the potential of the electrocapillary maximum for that system. Mercury possesses zero charge at the potential of the electrocapillary maximum; therefore, the mercury–water interface on initial creation must have zero charge, and this value is of the order 426 dyn/cm.[427] Values lower than this must be due to the interaction of dissolved laboratory gases at the mercury–water interface.

A. EFFECT OF DISSOLVED OXYGEN

Bartell and Bard[419] found that the interfacial tension between mercury and oxygen-saturated water was 388.7 dyn/cm, a value almost identical with that of 390.9 dyn/cm for the interfacial tension between mercury and water containing air that was free of carbon dioxide.

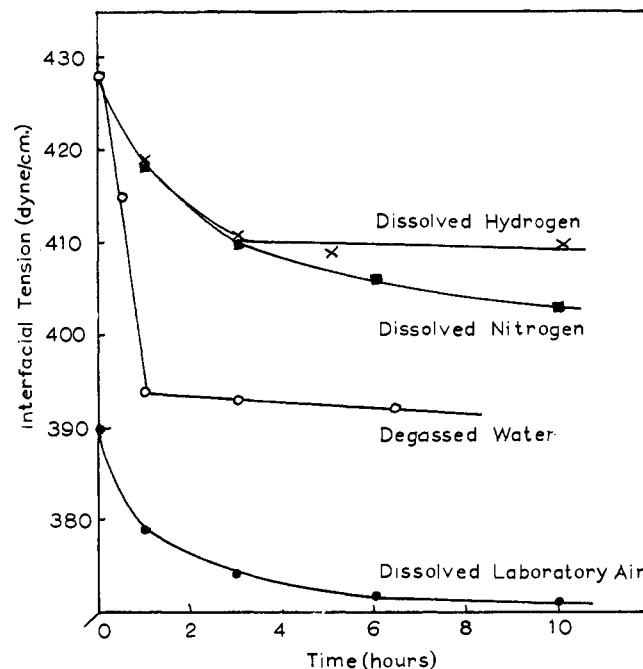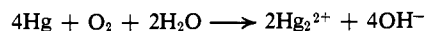The corrosion of mercury in water probably proceeds according to the reaction

Figure 24. Variation in the mercury–water interfacial tension with time due to the interaction of dissolved gases.

$$4Hg + O_2 + 2H_2O \longrightarrow 2Hg_2{}^{2+} + 4OH^-$$

Positive charge due to the excess of mercury ions builds up on the mercury surface and the tendency for mercury ions to go into solution increases. Mercury has little tendency to develop a protective oxide film in the presence of dissolve oxygen.[428] Thus, mercury ions go into solution and the potential of the mercury is determined by the equilibrium between mercury ions in the metal and in the solution.

The potential of a Hg|HgO|OH⁻ electrode is +0.51 V, at a pH of 7, relative to the hydrogen electrode. Craxford[429] considers that the corresponding interfacial tension at this potential should be about 392 dyn/cm. This value is in very good agreement with the experimentally determined value of Bartell and Bard.

According to Gatty and Spooner[425] the static potential for the Hg HgO|OH⁻ electrode is only reached after the concentration of mercury ions in solution is fixed by the precipitation of mercuric oxide, a process which takes many days. It is difficult to reconcile this suggestion with the experimental results of Bartell and Bard (Figure 24).

B. EFFECT OF DISSOLVED CARBON DIOXIDE

Figure 25 contains data given by Bartell and Bard for the effect of dissolved carbon dioxide on the interfacial tension between mercury and oxygen-saturated water. Oxygen-saturated water was used as the reference liquid since it yielded the most reproducible time variation curve (see Figure 24). No attempt was made to determine the effect of dissolved carbon dioxide on deoxygenated water since electrocapillary data[430] indicate that carbonate, bicarbonate, and hydronium

(425) O. Gatty and E. C. R. Spooner, "The Electrode Potential Behavior of Corroding Metals in Aqueous Solutions," Oxford University Press, London, 1938.
(426) V. Procopiu, *Ann. Sci. Univ. Jassy, Sect. I,* 27, 411 (1941).
(427) J. St. L. Philpot, *Phil. Mag.,* 13, 775 (1932).

(428) G. W. Akimov and G. B. Clark, *Trans. Faraday Soc.,* 43, 679 (1947).
(429) S. R. Craxford, *Phil. Mag.,* 16, 66 (1933).
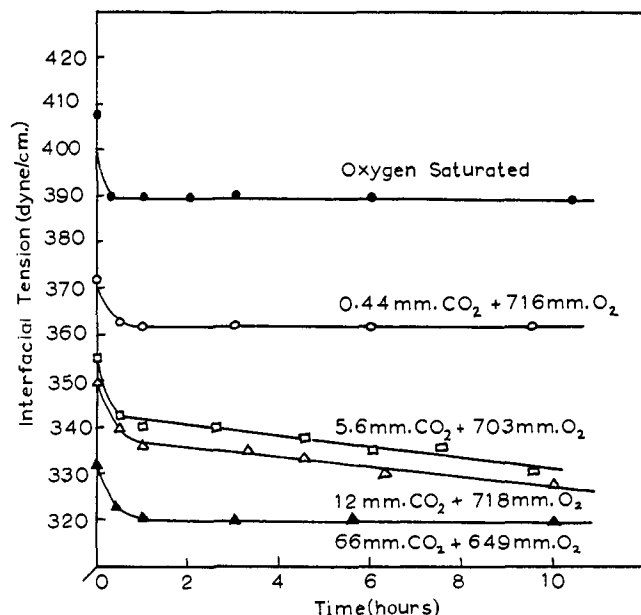(430) R. J. Bard, Ph.D. Thesis, University of Michigan, 1951.

Figure 25. Effect of carbon dioxide on the mercury–water (oxygen saturated) interfacial tension.

ions cause no appreciable depression of the electrocapillary maximum.

The attainment of equilibrium values for the interfacial tensions takes much longer than for the system containing oxygen alone. This is probably due to the time required for equilibrium to be established between carbonate and bicarbonate ions in the double layer and in the bulk solution. The adsorbed double layer contains a mixture of all anions in solution, the relative proportions of carboxyl, bicarbonate, and hydroxyl ions being determined by their specific adsorption tendencies and concentrations. As the carbonic acid concentration is varied, the pH of the solution changes, and the concentration of all anions changes.

The carbon dioxide concentrations corresponding to 0.44 mm and 66 mm pressures produce pH's of 5.6 and 4.4, respectively.[431] The potential of a Hg|HgO|OH⁻ electrode under these conditions would alter from +0.60 to +0.66 V. Thus, it appears that alteration in charge at the interface caused by changes in pH can account for the reductions in interfacial tensions for carbon dioxide containing systems.

C. CONCLUSION

The interfacial tension between mercury and *degassed* water at 25° is 426 ± 2 dyn/cm. Both oxygen and carbon dioxide lower the interfacial tension, the effects varying with time. Oxygen alone lowers the value to 389 dyn/cm, but carbon dioxide and oxygen together can reduce the interfacial tension to values as low as 320 dyn/cm, although at normal levels of carbon dioxide in the atmosphere a lower level of about 360 dyn/cm is found.

Laboratory air usually contains about 0.27 mm of carbon dioxide,[432] and water saturated with this amount of carbon dioxide should yield interfacial tensions of 375–380 dyn/cm

when the measurements are made at times less than 5 min. Many of the values given in Table XVI lie within this range and can be accounted for by the combined effects of oxygen and carbon dioxide, and the age of the interface when measurements were made.

D. EFFECT OF SURFACE-ACTIVE AGENTS

In studies of mercury–solution interfacial tensions as functions of the concentrations of the solutes a comparison between observed adsorption and that calculated by application of the Gibbs' adsorption equation can be made. Direct measurements are usually carried out by measuring concentration changes occurring in a column of solution through which a large number of drops of mercury have fallen.

It has been generally found that for many different types of solutes the Gibbs' adsorption equation applies to the mercury–solution interface.[410, 411, 413, 416, 433–437] Schofield[433] found quantitative agreement between the calculated and observed adsorption for various mercurous salts. Gibby and Argument[436] have reported the variation of the mercury–solution interfacial tension with concentration of various dyes in solution. Other workers have studied the effect of various fatty acids in hydrocarbons on the mercury–hydrocarbon interfacial tension[434, 435] and the interfacial tension between mercury and various binary organic liquid solutions of varying concentrations.[96]

VII. Spreading and Wetting Phenomena

If a liquid in the form of a drop is placed on the surface of another immiscible liquid or a solid it is found to make contact and spread. Depending on the relative values of the surface tensions acting at the edge of the drop the area of contact between the drop and the substrate increases, rapidly at first and then more slowly, until the free energy of the system is at a minimum. During this process the contact angle, *i.e.*, the angle formed between the drop and the substrate, varies; this is referred to as a dynamic contact angle. When the free energy of the system is at a minimum the drop may either have spread to a thin film, the contact angle being low or zero, or have spread to a limited area only. In this latter case what is termed a static (or equilibrium) contact angle is formed.

The type of spreading described is that of "self" spreading, where spreading is determined by the magnitudes of the surface and interfacial forces, and those of the viscous and frictional forces present in the system. In "forced" spreading a stress is applied to a system which is initially at equilibrium. For example, one of the interfaces may be propelled relative to the others, as in the case where a solid plate is pulled through a liquid–air interface. Although many examples of both self and forced spreading occur in practice, most studies have been confined to self spreading systems.

Most practical systems where spreading is occurring are never at equilibrium, but unfortunately little work has been done on the study of the kinetics of spreading processes. This

(431) H. T. Byke, *Science*, 75, 224 (1932).
(432) E. L. Quinn and C. L. Jones, "Carbon Dioxide," Reinhold, New York, N. Y., 1936.

(433) R. K. Schofield, *Phil. Mag.*, 1, 641 (1926).
(434) S. S. Bhatnegev and W. E. Garner, *J. Soc. Chem. Ind. London*, 39, 185 (1920).
(435) H. Dunken, I. Fredenhagen, and K. L. Wolf, *Kolloid-Z.*, 95, 186 (1941).
(436) C. W. Gibby and C. Argument, *J. Chem. Soc.*, 596 (1940).
(437) N. V. R. Iyengar and B. S. Rao, *Proc. Indian Acad. Sci., Sect. A*, 10, 20 (1939).

is probably due to the fact that the mathematical treatments involved are quite complex. A great deal of effort has thus been expended on the measurement of equilibrium contact angles. These are of value since they do provide information about surface energetics, surface roughness, and surface heterogeneity. The equilibrium contact angle was first linked with the surface and interfacial forces acting at the three-phase intersection by Young in 1805,[438] and can be expressed as

$$\gamma_{2/3} = \gamma_{1/2} + \gamma_{1/3} \cos \theta \qquad (34)$$

where $\gamma_{2/3}$, $\gamma_{1/2}$ and $\gamma_{1/3}$ are the interfacial forces acting (see Figure 26a). If phase 2 is fluid (Figure 26b), then, according to Neumann[439]

$$\gamma_{1/2} = \gamma_{1/3}{}^2 + \gamma_{2/3}{}^2 - 2\gamma_{1/3}\gamma_{2/3} \cos \psi \qquad (35)$$

which can also be written in the form

$$\frac{\gamma_{2/3}}{\sin \alpha} = \frac{\gamma_{1/3}}{\sin \beta} = \frac{\gamma_{1/2}}{\sin \phi} \qquad (36)$$

It is of particular note that $\gamma_{2/3}$ and $\gamma_{1/3}$ may not always be the same as the values recorded in the absence of the third phase; e.g., $\gamma_{2/3}$ could be lowered by material adsorbed from phase 1, and $\gamma_{1/3}$ by material from phase 2.

All pure liquids spread to some extent on another surface;[440,441] this is to be expected from thermodynamic considerations since the surface free energy at an interface between two phases is always less than the sum of the surface tensions of each phase with respect to another separate phase (e.g., air). Thus, a value of $\theta = 180$ means that phases 1 and 2 have not come into contact; a layer of phase 3 is trapped between the two phases. The larger the magnitude of the contact angle the less is the work of adhesion of phase 1 to phase 2. The work of adhesion, W_A, or the work required to pull apart 1 cm² of the interface (½), is given by Dupre[12] as

$$W_A = \gamma_{1/3} + \gamma_{2/3} - \gamma_{1/2} \qquad (37)$$

which can be written in the following form by means of Young's equation.

$$W_A = \gamma_{1/3}(1 + \cos \theta) \qquad (38)$$

The work of cohesion, W_C, is that work necessary to create inside a liquid an area of 2 cm², or more specifically to break apart a column of liquid 1 cm² in cross section in such a way as to give two surfaces, each 1 cm² in area, i.e.

$$W_C = 2\gamma_{1/3} \qquad (39)$$

From these definitions the contact angle becomes an important parameter, since it is some measure of the difference in the work of adhesion of a liquid for a substrate and its work of cohesion for itself.
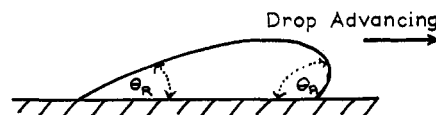
When $\theta = 0$, $W_A = W_C$; i.e., the forces of attraction of the substrate for the liquid are the same as those of molecules of the bulk liquid for itself. If $W_A > W_C$, then the measured contact angle is still zero. In these cases it is convenient to con-
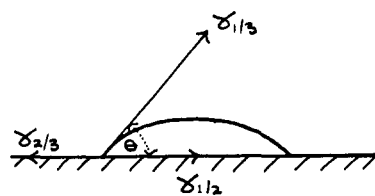
(a) Liquid Drop on a Solid Substrate
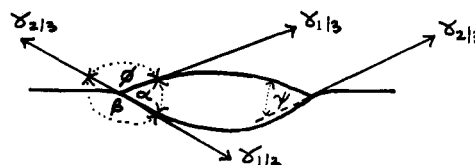
(b) Liquid Lens on a Liquid Substrate

(c) Contact Angle Hysteresis

Figure 26. Balance of forces acting at three-phase intersections.

sider the changes in free energy occurring on spreading in terms of Harkin's spreading coefficient,[163] S, where

$$S = \gamma_{2/3} - \gamma_{1/3} - \gamma_{1/2} \qquad (40)$$

From eq 37, 39, and 40

$$S = W_A - W_C \qquad (41)$$

For contact angles between 1 and 179, S is negative. When $\theta = 0$, $S = 0$, and when $W_A > W_C$, S is positive.

For liquid–liquid–liquid or liquid–liquid–gas systems, only one angle, θ, is measured.[440] The contact angle of a liquid on a solid substrate, however, usually varies, depending on whether the liquid is advancing or receding (Figure 26c). The difference between the advancing angle, θ_A, and the receding angle, θ_R, is called the hysteresis of the contact angle[442] and

$$\theta_A \geq \theta_{eq} \geq \theta_R$$

The magnitude of the contact angle hysteresis varies considerably with the nature of the solid surface, varying from 0 to greater than 100°. A detailed analysis of contact angle hysteresis has been given by Johnson and Dettre.[443]

A. EQUILIBRIUM WETTING

1. Mercury–Solid–Gas Systems

Many measurements have been made of the contact angle of mercury on different solid surfaces in air (ref 15, 57, 75, 147,

(438) T. Young, *Phil. Trans. Roy. Soc. London*, **95**, 65, 82 (1805).
(439) F. Neumann, "Vorlesungen uber die Theorie der Capillaritat," B. G. Teuber, Leipzig, 1894.
(440) W. Fox, *J. Chem. Phys.*, **10**, 623 (1942); *J. Amer. Chem. Soc.*, **67**, 700 (1945).
(441) W. D. Harkins and A. Feldman, *ibid.*, **44**, 2665 (1922).

(442) H. L. Sulman, *Trans. Inst. Mining Met.*, **29**, 44 (1920).
(443) R. E. Johnson and R. H. Dettre, "Surface and Colloid Science," E. Matijevic, Ed., Wiley-Interscience, New York, N. Y., 2, 1969, p 85.

155, 202, 438, 444–455) (Table XVII). There are several interesting observations. All the contact angles lie between about 130 and 150°, irrespective of the nature of the solid surface (except for Ag, Pt, and Cu). This is surprising since the surfaces range from very low energy ones, such as polytetrafluoroethylene, to high energy ones, such as metals and metal oxides. Further, there is little contact angle hysteresis on any of the surfaces.

The work of cohesion of mercury for itself is of the order 950 ergs/cm², a value less than the surface tension of most metal or metal oxide surfaces.[169] It would therefore be expected that mercury would exhibit low contact angles on these surfaces. However, it is known that it is exceedingly difficult to prepare "clean" metal and metal oxide surfaces, since, due to their high surface free energies, they readily adsorb impurities such as water vapor, grease, etc., from the external phase.

The contact angles that drops exhibit on surfaces are dependent on the nature of the substrate surface layers, and not on the bulk properties of the substrate. Thus, Bartell and Ruch[456] found that the contact angles that water, hexadecane, and several other liquids exhibited on chrome-plated steel with various fractions of monolayer coverage of n-octadecylamine on the surface depended strongly on the degree of coverage. For example, the advancing and receding contact angles of tetradecane and hexadecane changed only slightly as depletion of the monolayer increased from 0 to 50–60%. Above this level the angles dropped sharply to zero. Aldrich and Keller[457] found that the presence of 1 mm pressure of hydrogen or nitrogen, introduced into an apparatus containing an atomically clean surface of aluminum, drastically reduced the bond strength between a drop of indium and the aluminum at 160°. Introduction of the gas after the indium drop had been placed did not affect the bond strength. Further, the contact angle (118 ± 10°) and surface tension (of indium, 658 ± 60 dyn/cm) did not alter in either experiment. Presumably the surface coverage of aluminum by gas molecules (chemisorbed?) was sufficient to affect the mutual diffusion of indium and aluminum atoms across the interface, reducing the bond strength, but not sufficient to alter the wettability.[456] Thus, the contact angle is a sensitive measure of the presence of adsorbed impurity in amounts less than monolayer coverage. In fact it is often used as a criterion of surface purity.

Barlow and Planting[455] have shown that, for atomically clean metal surfaces, mercury exhibits a zero contact angle. In their experiments the metal surfaces were polished with 3-μ diamond, degreased with trichloroethylene, and then bombarded with argon ions for 5–10 min. Contact angles

recorded on placing a small mercury drop on these surfaces are given in Table XVII. Except for the case of the more soluble metals (Ag, Cu, Pt) the contact angles were only slightly smaller than those recorded by other workers who had not attempted to prepare atomically clean surfaces. However, Barlow and Planting found that if argon ion bombardment was reinitiated after drop placement, high speed spreading of the mercury occurred within several seconds (contact angles in parentheses). It can be concluded that only during the second bombardment was the surface completely free of contaminants; i.e., surface recontamination occurred rapidly.

Evidence that nonspreading of mercury was due to surface contamination was obtained by placing mercury drops on a nickel surface at different times after the cessation of ion bombardment. Contact angles after 1 min were about 25°, but at 20 min the angle was 100°. It is likely that an initially physically adsorbed layer of argon was replaced by residual traces of reactive gases (O_2, H_2O, CO, etc.) which were chemisorbed.

Since mercury spread completely (zero contact angle) on atomically clean metal surfaces, it is pertinent to consider whether the surfaces became covered with a monolayer of mercury atoms, or whether multilayers were formed. Since the metal surfaces were "imperfect," exposing different crystal faces, the considerations become more complicated; some crystal faces may be covered with a monolayer, while others may be covered with multilayers. In this respect Swanson, Strayer, and Davies[458] have found evidence for monolayer coverage of mercury atoms on tungsten and molybdenum surfaces at 300°K, and a relative coverage of about two monomolecular layers at 77°K.

The practical difficulties in creating and maintaining an atomically clean high-energy surface are very large, and only in the recent 2 decades have adequate techniques been devised. Thus, many of the contact angles for mercury on high energy surfaces given in Table XVII are probably not the true ones for clean surfaces. This particular aspect is demonstrated by the fact that when a metal bar is broken under mercury the fresh surfaces created are found to be coated with mercury, and in many cases an amalgam formed.[459]

Glass surfaces consist of tightly held layers of water and hydroxyl groups.[460] Over a century ago it was known[438] that the typical convex meniscus of mercury in a glass tube could be made concave by careful baking out procedures.[461] Temperatures as high as 300 to 500° are necessary to completely remove the last traces of water.[460,462] Water is one of the most common "contaminants," and it is known to adsorb very strongly on high-energy surfaces. The presence of adsorbed water on the surfaces of the high-energy solids listed in Table XVII could account for the high contact angles and similarity of contact angles. If the interaction between water and mercury is only via disperson forces,[154] then the "real" surface being exposed to the mercury has a surface free energy of about 22 ergs/cm². Thus, if the surface forces acting are considered as 22 dyn/cm for the substrate–air interface and 426 dyn/cm for the mercury–substrate interface (see sec-

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(445) H. K. Livingston, *J. Phys. Chem.,* **48**, 120 (1944).
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Table XVII

Contact Angles of Mercury on Various Substrates

Substrate	Author (ref)	θ_A, deg	θ_R, deg	θ, deg	Temp, °C
Glass	Bashforth and Adams (15)			139.4	9
Glass	Anderson and Bowen			>139	16
Glass	Furth (444)			128	18
Glass	Ellison, Klemm, Schwartz, Grubb, and Petrash (202)	133	134		25
Quartz	Ellison, Klemm, Schwartz, Grubb, and Petrash (202)	132	134		25
Quartz	Loman and Zwikker (75)			139.0	
Plate glass	Loman and Zwikker (75)			137.0	
Glass	Young (438)			140	
Glass	Livingston (445)			128–140	
Glass	Talmud and Lubman (446)			139	
Glass	Lomas (447)			138.4	
Glass	Ehrlich (448)			129.5–132.6	
Glass	Parvatikar (155)			136.9	
Glass	Staicopolus (147)			138.6	
Paraffin wax	Gray (449)	141.1	140.9		
Paraffin wax	Fowkes (450)			154	
Polytetrafluoroethylene	Gray (449)	151.7	150.2		
Polytetrafluoroethylene	Fox and Zisman (451)			152	
Polytetrafluoroethylene	Ellison, Klemm, Schwartz, Grubb, and Petrash (202)	134	132		25
Octadecylamine Monolayer on platinum	Shafrin and Zisman (452)			146	
Perfluorodecanoic acid Monolayer on platinum	Schulman and Zisman (453)			152	
Polyethylene	Gray (449)	148.0	140.9		
Tungsten	Ellison, Klemm, Schwartz, Grubb and Petrash (202)	130	132		
Stainless steel	Ellison, Klemm, Schwartz, Grubb, and Petrash (202)	133	132		
Nickel	Ellison, Klemm, Schwartz, Grubb, and Petrash (202)	133	132		
Nickel	Ellison, Klemm, Schwartz, Grubb, and Petrash (202)	139	138		
Steel	Owen and Dufton (57)			154	
Amalgamated copper	Owen and Dufton (57)			0	
Gold	Tamman and Arntz (454)			0	
Silver	Tamman and Arntz (454)			0	
Tin	Tamman and Arntz (454)			0	
Lead	Tamman and Arntz (454)			0	
Iron	Barlow and Planting (455)			130–145 (0–2)	
Nickel	Barlow and Planting (455)			110–145 (0–2)	
Molybdenum	Barlow and Planting (455)			140 (0–2)	
Tungsten	Barlow and Planting (455)			130 (0–2)	
Titanium	Barlow and Planting (455)			142 (90)	
Platinum	Barlow and Planting (455)			38 (0)	
Silver	Barlow and Planting (455)			0 (0)	
Copper	Barlow and Planting (455)			31–35 (0)	
Black marble	Loman and Zwikker (75)			151.7	
Limestone	Loman and Zwikker (75)			138.2	
Steatite	Loman and Zwikker (75)			144.5	
Calcite (polished)	Loman and Zwikker (75)			141.7	
Galenite (polished)	Loman and Zwikker (75)			145.5	
Sphalerite (polished)	Loman and Zwikker (75)			145.7	
Pyrite (cryst. 100)	Loman and Zwikker (75)			142.0	

tion V), then Young's equation would give the contact angle as 141°. This is in reasonable agreement with many of the values given in Table XVII.

Many solids such as organic crystals spread over the surface of mercury by surface diffusion processes. Bikerman[134,135]

has measured the decrease in surface tension of mercury due to the surface diffusion of molecules from a variety of solid organic crystals placed on the mercury surface. The final surface pressures, π_e, corresponding to complete monomolecular coverage, are given in Table XVIII.
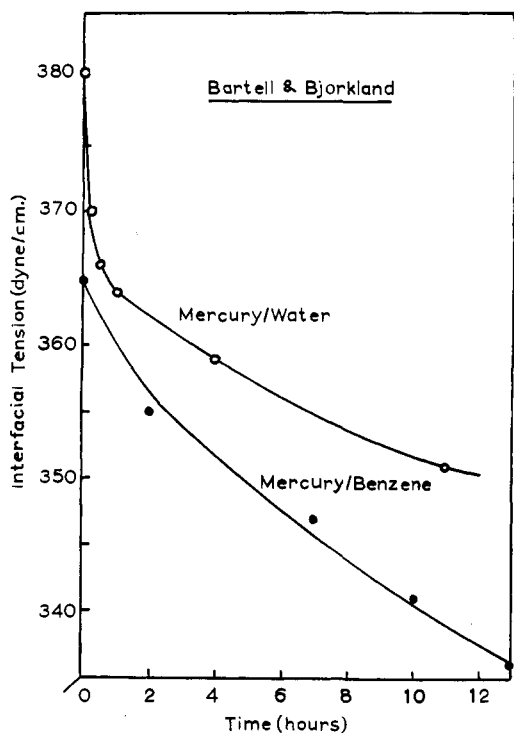
Figure 27. Influence of trace water and trace benzene on the mercury–benzene and mercury–water interfacial tension, respectively.

Table XVIII

Equilibrium Spreading Pressures on Mercury

Organic compd	π_e, dyn/cm	Organic compd	π_e, dyn/cm
Octacosane	50	Azoxybenzene	85
1-Hexadecanol	50	Ethyl palmitate	55
1-Octadecanol	40	2,4-Dibromophenol	140
Benzophenone	60		

2. Mercury–Solid–Liquid Systems

Few studies of these systems have been made, although they are of importance in manometers and other measuring devices.

Good, Givens, and Tucek[463] found that the contact angle of mercury in the mercury–gallium–glass system, at 25° and *in vacuo*, was zero. If the apparatus was exposed to air the contact angle increased rapidly during the first day (to 60°) and then more slowly. The equilibrium contact angle formed after about 10 days was 100°. Presumably the increase in contact angle in air was due to chemical interactions, probably oxide formation.

3. Mercury–Liquid–Liquid Systems

Bartell and Bjorkland[418] and Gaudin and Witt[464] have studied contact angles in the mercury–water–benzene system. The agreement between these workers was extremely good; for mercury in contact with degassed benzene and water the advancing and receding angles (measured through the water

(463) R. J. Good, W. G. Givens, and C. S. Tucek, *Advan. Chem. Ser.*, No. 43, 211 (1964).
(464) A. M. Gaudin and A. F. Witt, ref 463, p 202.

phase) were the same, namely 118 ± 2°. The contact angle calculated[418] by use of Young's equation, taking values for γ_{Hg/C_6H_6}, γ_{Hg/H_2O}, and $\gamma_{C_6H_6/H_2O}$ as 364.5, 379.5, and 34.0 dyn/cm, respectively, was 116°. The benzene and water phases were mutually saturated with each other.

Air, or specifically oxygen, had a radical affect on the magnitude of the contact angle. With time of exposure the advancing angle increased and the receding angle decreased. Bartell and Bjorkland were able to correlate these changes to variations in γ_{Hg/C_6H_6} and γ_{Hg/H_2O}; these both decreased with time (Figure 27). A comparison between the measured contact angle and the calculated contact angle is given in Table XIX, where the interfacial tensions have been taken from Figure 27.

Table XIX

Effect of Time of Exposure of Mercury to Benzene on Initial Advancing Contact Angles

Time of exposure, min	Exptl angle, deg	Calcd angle, deg	Time of exposure, min	Exptl angle, deg	Calcd angle, deg
6	118	119	300	144	145
25	119	126	1140	159	
60	122	129	1260	164	
150	138	138	1380	No attachment	

Butler[421] found no change in the mercury–water (saturated with benzene) and mercury–benzene (saturated with water) interfacial tensions over a 72-hr period. However, he found that the contact angle in the mercury–water–benzene system increased from 60 to 110° over about 60 hr. In one case he found that the contact angle was "very high" (probably greater than 110°) and only changed slowly with time. This latter result is in accord with the results of Bartell and Bjorkland, and Gaudin and Witt.

Gaudin and Witt studied the influence of pH on the contact angle in the mercury–benzene–water system. The contact angle hysteresis varied from zero to 141°; the results obtained are given in Table XX. Gaudin and Witt did not give values

Table XX

Effect of pH on Contact Angle (after 6 min) in Mercury–Benzene–Water System

pH	θ_A, deg	θ_R, deg	θ, deg	pH	θ_A, deg	θ_R, deg	θ, deg
1	111	111	0	9	126	83	43
2	116	116	0	10	129	30	49
3	118	118	0	11	130	52	78
4	119	111	8	12	132	38	94
6	119	104	15	13	134	0	134
7	119	98	21	14	141	0	141

of interfacial tensions, but it is probably that the mercury–water interfacial tension was varying with pH. Hysteresis in this case was due to a change in the properties of the mercury–water interface.

4. Mercury–Liquid–Gas Systems

Smolders and Duyvis[146] have studied the mercury–water–hydrogen system and found that measured contact angles agreed well with calculated ones. They found that the contact angle as measured through the water phase increased as the concentration of sodium decane sulfonate was increased; contact angles increased from about 23° in pure water to 83° at about 0.02 mol/l. They also showed that the mercury–solution–gas system exhibited the typical parabolic character of contact angle vs. applied potential curves, the maximum angle occurring at the point of zero charge. Thus, contact angle vs. potential curves are very similar to interfacial tension vs. potential curves.[409]

The results of Smolders and Duyvis may not be too reliable since they recorded a mercury–water interfacial tension of about 362 dyn/cm (although they took precautions to remove dissolved oxygen) and a surface tension for mercury in hydrogen of 434.6 dyn/cm. These values are consistent with their measured contact angle of 23°.

B. DYNAMIC WETTING

The spreading of a liquid over a substrate can occur by means of two different processes: (i) bulk wetting and the flow of a continuous viscous phase, and (ii) surface diffusion, the migration of molecules along the substrate surface. Both processes are known to exist, and in some cases they are both operative. The process of bulk wetting, which is common is most liquid–liquid–gas and liquid–liquid–liquid systems, can be followed by means of cine photography. Surface diffusion is more difficult to follow but is possible by the use of radioisotopes and autoradiographic techniques.[465]

The mechanism of spreading of one liquid over the surface of another has been discussed by Langmuir[391] and Adam.[168] When the molecules of the spreading substance have a definite affinity for the lower liquid (substrate), the mechanism is as follows. Molecules of the spreading liquid become attached to molecules of the substrate. The molecular agitation in the substrate allows more and more molecules of the spreading phase to reach the substrate surface, and a layer of the spreading phase diffuses over the substrate. Cohesion and viscosity in the spreading phase cause these adhering molecules to drag a layer of the bulk with them, thus spreading the drop as a whole. In many cases only the single adhering layer of molecules is stable and the excess liquid collects again into one or more drops (or lenses).

Rideal and Davies[466] have shown that, for many liquid–liquid–gas and liquid–liquid–liquid systems, the rate of spreading is given by

$$\text{rate of spreading} = \text{constant } x\frac{S}{\Sigma\eta} \qquad (42)$$

where S is the spreading coefficient and $\Sigma\eta$ is the sum of the viscosities of the phases.

Although the energy requirements for spreading on solids are the same as those for liquids, many other factors have to be taken into consideration. The microprofile of the surface and its state (presence of adsorbed impurities, oxide films, etc.), surface heterogeneity, structure of the subsurface regions, and the possibility of volume diffusion of the spreading liquid into the solid surface all have to be considered. In some cases modification of the solid surface may occur such as in the development and propagation of cracks and faults, the formation of liquid–solid complexes, and embrittlement.

Many different mechanisms have been proposed to describe the spreading of liquids over solid substrates. However, no generalized theory applicable to many different systems has been developed. This is almost certainly due to the complexity involved in describing the forces acting at solid interfaces.

1. Mercury–Solid–Liquid Systems

Goryunov and coworkers[467–471] have extensively studied the kinetics of spreading of mercury on metal surfaces, in particular nickel and zinc. Two different types of spreading occurred, wetting and surface diffusion, depending on the microprofile of the solid surface.

Deryaguin[472] found that a liquid can wet a rough surface along microdepressions and grooves if $K \cos \theta \geq 1$, where K (the roughness coefficient) is the ratio of the true to the apparent surface area, and θ is the contact angle on the ideally smooth surface. Since this is the case it should always be possible, in principle, for cases where $\theta < 90°$, to produce a degree of roughness sufficient to allow the liquid to wet the surface. This conclusion was confirmed by Goryunov, Pertsov, Summ, and Shchukin[468] in an investigation of the spreading of mercury on oxide-free zinc surface. They found that, on a highly smooth surface, mercury formed a contact angle of 7°. Surface diffusion from the drop occurred at a rate which followed the time law characteristic of Fickian[473] diffusion; i.e., $r \propto T^{0.5}$, where r is the radius of the diffused boundary and T is the time. On a roughened surface bulk wetting occurred where $r \propto T^{0.27}$.

The wetting of nickel and zinc surfaces free of oxide was carried out by allowing drops of mercury to spread at the metal–10% solution ammonia interface. (The ammonia dissolved the oxide film.) Three distinct stages were observed during the spreading process. The first, and shortest stage (a fraction of a second), consisted of rapid attachment and spreading under the influence of gravity and capillary forces. The second and main stage of spreading was described by the power law $r = A_1 T^{n_1}$, where the exponent n_1 was independent of the mass of the drop (m) and equal to 0.27. The coefficient A_1, however, increased as the mass of the drop increased. The third and final stage of spreading consisted of a continued, but very slow, drop growth, which ceased after several hours.

(465) S. Z. Bokshtein, "Diffusion, Structure, and Properties of Metals," translated from Russian by Consultants Bureau, New York, N. Y., 1965.

(466) J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York, N. Y., 1961.

(467) Yu. V. Goryunov, N. V. Pertsov, P. A. Rebinder, and E. D. Shchukin, "Surface Phenomena in Metals and Alloys and Their Role in Powder—Metallurgical Processes," in Russian, Izdatel'stvo Akademii Nauk Ukrainskoi SSR, Kiev, 1961, p 184.

(468) Yu. V. Goryunov, N. V. Pertsov, B. D. Summ, and E. D. Shchukin, Dokl. Akad. Nauk SSSR, 146, 638 (1962).

(469) Yu. V. Goryunov, G. I. Den'shchikova, N. V. Pertsov, B. D. Summ, and E. D. Shchukin (in Russian), Abstracts of Papers Presented to the Conference on Surface Phenomena in Melts and in Powder—Metallurgical Processes, Kiev, 1962, p 58.

(470) Yu. V. Goryunov, A. P. Dekartov, N. V. Pertsov, B. D. Summ, and E. D. Shchukin, All-Union Conference on Colloidal Chemistry, in Russian, Izdatel'stvo Akademii Nauk SSSR, Moscow, 76, 1962, p 76; Kolloid. Zh., 25, 253 (1963).

(471) Yu. V. Goryunov, Russ. Chem. Rev., 33 (9), 467 (1964).

(472) B. V. Deryaguin, Dokl. Akad. Nauk SSSR, 51, 357 (1946).

(473) S. D. Gertsriken and I. Ya. Dekhtar, "Diffusion in Metals and Alloys," in Russian, Fizmatgiz, Moscow, 1960.

The increased growth during this third stage was only a few per cent of the main stage.

By assuming that the mercury drop spread radially, and that at any stage the drop profile approximated to the cap of a sphere, Goryunov equated the viscous retarding force of the mercury layer to the driving force ($\Delta\gamma = \gamma_{\text{Zn/soln}} - \gamma_{\text{Hg/soln}} - \gamma_{\text{Hg/Zn}}$) and obtained the following relationship

$$r = \left(\frac{6}{\pi}m\frac{\Sigma}{K_1}\right)^{0.25} T^{0.25} \tag{43}$$

where m is the mass of the drop, Σ equals $\Delta\gamma/\eta\rho$ (η and ρ are the viscosity and density of mercury, respectively), and K_1 is the constant. The time exponential of 0.25 is in good agreement with the experimentally observed value of 0.27.

The spreading of a mercury drop along a 1-mm wide channel scribed on the surface of a zinc plate was found to obey the power law $r = A_2 T^{0.30}$. The coefficient A_2 increased with drop weight. Thus, spreading along a channel was appreciably faster than circular spreading. By similar analysis to that used for circular spreading Goryunov obtained the expression

$$r = \left(3m\frac{\Sigma}{K_2}\right)^{0.33} T^{0.33} \tag{44}$$

The time exponential of 0.33 is in good agreement with the experimentally observed value of 0.30.

The very slow third stage of spreading governs the final size of the spread mercury drop. For both the case of circular spreading, and spreading along a channel, the final distance from the center of the drop to the drop periphery, R, is given by

$$R = Bm^p \tag{45}$$

where m is the mass of the drop. The exponential p was found to be 0.40, and 0.59, for circular spreading and spreading along a channel, respectively.

Since the final coverages did not correspond to monolayer coverage, then volume diffusion or absorption into the zinc surface must have occurred. For example a 0.01-g drop of mercury spread radially to cover an area of 78.5 cm²; this corresponds to a film thickness of 9.4×10^{-6} cm. The importance of volume diffusion in spreading was confirmed by mechanical experiments. If the plate was bent immediately after the experiment (after stage II), the area the mercury covered developed a network of cracks; this is an example of embrittlement brought about by adsorption.[474] However, if the specimen was subjected to flexure after some time (after stage III), no surface cracking was observed. This suggests that practically all of the mercury originally present on the surface had diffused into the zinc. Further, since the diffusion coefficient is sensitive to temperature changes, it would be expected that the time for completion of spreading and the final radius would decrease with increase in temperature; this was borne out experimentally.

The surface diffusion of mercury along a very smooth zinc surface was followed by placing a drop of mercury at a zinc–10% ammonia interface. The mercury formed a contact angle of ~7°, but a matt, circular spot soon began to spread outwards from the drop. The radius of this spot was found to increase with time according to the equation $r = AT^{0.5}$. After

several hours the drop disappeared from the center of the spot and the growth of the spot departed from the law $r = AT^{0.5}$, and eventually growth stopped altogether. The final spot radius was related to the initial drop mass by

$$R = Cm^q \tag{46}$$

where q had the value 0.35 in every experiment.

For surface diffusion the proportionality coefficient A was found to be both independent of the mass of the drop, and to the angle of tilt of the plate to the horizontal (varied from 10° to 90°); the value was 0.2 mm sec$^{-1/2}$. Thus, the rate of diffusion is independent of gravity, as expected for surface diffusion. Similar experiments for wetting on roughened zinc plates, however, showed that A was strongly dependent on the angle of tilt of the plate to the horizontal.

The observed relationship between the radius of the dull spot and time agrees well with the expression derived for the two-dimensional diffusion in an infinite plane from a point source of mass m[473]

$$r = 2D_s^{1/2}[\ln(m/4\pi D_s C_0 t)]^{1/2} T^{1/2} \tag{47}$$

where D_S is the surface diffusion coefficient and C_0 the concentration of diffusion material at a point in the plane at distance r from the source. Since the logarithm term varies relatively slowly for a fairly long time, it can be ignored to a first approximation. Thus, eq 47 can be replaced by $r = $ constant $\times T^{1/2}$, which is in good agreement with the experimental results.

In order to determine whether the observed boundary for surface diffusion corresponded to the actual boundary Goryunov, Dekartov, Korobkov, and Summ[475] have carried out an autoradiographic study of the spreading of mercury on smooth zinc surfaces (immersed in 10% ammonia). ^{203}Hg was used. They found that the observed boundary coincided exactly with the boundary on the autoradiogram. If mercury was present beyond the boundary it was in quantities much less than monomolecular.

Tamman and Arntz[454] have studied the spreading of mercury on various surfaces immersed in different solutions (Table XXI). Contrary to the findings of Goryunov, et al., they found that in all cases the rate of spreading was linear. The rate of spreading does appear to be linear over limited sections of the distance spread vs. time plot, but a power law equation seems to best describe the entire process (refer to section VII.B.3).

2. Mercury–Liquid–Gas Systems

Quinke was probably the first to observe that pure water spreads on a fresh clean mercury surface. Spreading is not rapid and it usually takes several minutes for a drop of water to spread out to a thin film. Similar observations are recorded (ref 1, 62, 77, 125, 306, 310, 358, 369, 441, 476, 477) irrespective of whether the spreading occurs in vacuo[62, 477] in laboratory air, or in a pure nitrogen atomosphere.[310, 369] Further, the partial pressure of water vapor does not affect spreading until saturation is reached, at which stage spreading does not occur. These observations on spreading are so universal that Burdon

(474) V. I. Likhtman, E. D. Shchukin, and P. A. Rebinder, "Physicochemical Mechanics of Metals," in Russian, Izdatel'stvo Akademii Nauk SSSR, Moscow, 1962.

(475) Yu. V. Goryunov, A. P. Dekartov, V. I. Korobkov, and B. D. Summ, *Dokl. Akad. Nauk*, **191**, 331 (1970).

(476) R. G. Mitton, *Trans. Proc. Roy. Soc. S. Aust.*, **53**, 267 (1929).

(477) R. S. Burdon, G. R. Fuller, and E. S. H. Gibson, *Trans. Faraday Soc.*, **33**, 1528 (1937).

Table XXI

Rate of Spreading of Mercury in Various Solid–Solution Systems (mm/min)

| Substrate | Solution | | | |
	0.1 N H₂SO₄	0.1 N HCl	0.1 N HNO₃	0.5 N KCN
Gold	0.39 ± 0.03	0.36 ± 0.03	0.36 ± 0.03	0.35 ± 0.02
Silver	0.39 ± 0.04	0.35 ± 0.02	0.34 ± 0.04	0.30 ± 0.03
Copper	0.017 ± 0.003	0.007 ± 0.001	0.012 ± 0.003	0.45 ± 0.1
Tin	0.95 ± 0.10	0.90 ± 0.11	1.05 ± 0.10	0.28 ± 0.03
Lead	0.63 ± 0.05	0.69 ± 0.04	~ 2.5	0.70 ± 0.10
Cadmium			0.34 ± 0.03	0.42 ± 0.05
Zinc	0.41 ± 0.05	0.40 ± 0.04	0.42 ± 0.04	0.30 ± 0.04

has suggested that the spreading of pure water be used as a check of the surface cleanliness of mercury.

The slow spreading of water can be explained on the basis of the gradual decrease in the mercury–water interfacial tension with time. The initial magnitude of γ_{Hg/H_2O} on drop placement will probably be close to 426 dyn/cm (see section VI). With a surface tension for water of 72 dyn/cm, the maximum force acting against spreading will be 498 dyn/cm. If the three forces acting at the mercury–water–gas line of contact remained constant (γ_{Hg} at 475.5 dyn/cm), then the water drop would exhibit a finite contact angle of 51°. However, since the drop spreads it must be concluded that the mercury–water interfacial tension decreases with time (any effect of water vapor on γ_{Hg} would provide a surface pressure tending to reduce spreading).

Complete spreading ($\theta = 0°$) will be achieved when γ_{Hg/H_2O} falls to 403.5 dyn/cm. This, according to Bard,[430] will take up to 1 hr (see Figures 24 and 25) and depend on the nature and concentrations of dissolved gases present. For pure water containing dissolved oxygen and carbon dioxide at usual laboratory levels, a time of 1 to 2 min is to be expected. The initial gaseous concentrations obviously vary from system to system, and the range of spreading (30 sec to many minutes) can be adequately accounted for.

The problem of the effect of water vapor on the surface tension of mercury has not been resolved. Thus, results obtained for the spreading of aqueous solutions on a mercury surface may be questionable.

Burdon found that, whereas pure water spread on mercury at a rate of about 0.03 cm/sec, a 10^{-3} N solution of an inorganic acid spread at a rate of 5 cm/sec. Increasing the concentration of the acid did not increase the rate of spreading but did increase the final area covered. The area covered was directly proportional to the drop volume. Hydrochloric acid, nitric acid, and the straight-chain fatty acids from formic to valeric acid all behaved in the same manner. In all cases the area covered during spreading was close to 1 cm² for each 10^{14} molecules of monobasic acid. Dibasic acids, such as sulfuric acid, covered twice as great an area per molecule. Thus the area covered is apparently dependent on the number of H ions, each H ion causing water to cover about 10 atoms of mercury in the surface layer (1 cm² of surface of mercury contains about 10^{15} atoms). After the rapid stage of spreading the spreading rate dropped to that observed for pure water.

Solutions of inorganic bases such as the hydroxides of barium, calcium, sodium, potassium, and ammonium do not spread on mercury. The presence of OH groups actively prevents spreading, since a solution of sodium chloride is prevented from spreading by the addition of sodium hydroxide.

The effects described can be explained in terms of the elec-

trocapillary curve, the maximum of which occurs for the mercury–water interface at +0.51 V. Any variation in the double layer by incorporation of other ion species will lead to a different potential and lower interfacial tension. For example, Burdon found that he could increase the rate of spreading of a water drop by applying a charge across the mercury–water interface; the charge could be either positive or negative. However, if the drop had been forced to spread rapidly by application of say a positive charge, and then the charge was removed or reversed, the water drop would retract and then respread again in its normal manner. Similar observations were recorded for solutions of inorganic bases or acids; a drop could, by the application of charge be "forced" to spread to a larger area than normal, or be kept from spreading at all.

Spreading is controlled by the relative magnitudes of the "driving" (surface forces) and "retarding" forces (viscosity, friction, etc.). Whether the magnitudes of the surface forces are reached by adsorption of surface-active agents or accumulation of charge is unimportant with regard to the kinetics of the spreading process. Thus, Burdon found that the rate of spreading of drops of aqueous solutions on mercury were very nearly constant. This suggests that processes occurring at the drop periphery rather than over the interface is the deciding factor. The constant speed is typical of motions due to a steady force and opposed by a steady resistance.

Ellison, Lyerly, and Otto[369] have studied the effects of 2 ppm of gold, lead, and zinc on a mercury surface in a nitrogen atmosphere. They followed the change in the mercury surface by placing 5-μl drops on a mercury surface that had been aged for different periods of time. The mercury was contained in a Plexiglas trough and a fresh surface was produced by sweeping. Because the small drops evaporated quickly, measurements could be made as close as 15 sec apart.

Three stages of wetting were defined: (i) where the liquid spread to a thin film, contact angle 0°; (ii) the formation of a "low" contact angle (magnitude not specified); and (iii) formation of a "high" contact angle (magnitude not specified). The results obtained are presented in Table XXII.

There are several points of interest with regard to the results presented in Table XXII. The mercury surface becomes sufficiently contaminated within 2 min such that the spreading of water does not occur. Burdon's drops, which were much larger, spread completely in 3 to 4 min and evaporated without retraction. It is difficult to decide whether the influence of the metal additive is due to its interaction at the mercury surface, the mercury–liquid interface, or both of these. Semenchenko has deduced that gold and lead should affect the surface tension of mercury, but that zinc should be inactive. Thus, it is difficult to reconcile the results of Ellison, Lyerley,
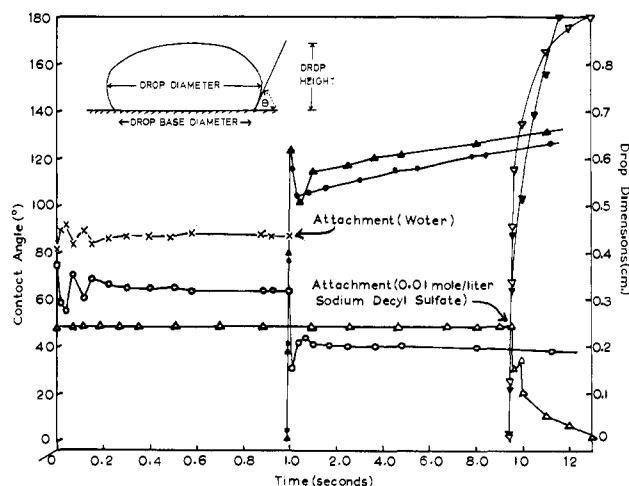
Figure 28. Variation in drop dimensions and contact angles with time for drops of carbon tetrachloride spreading at mercury–water and mercury–solution interfaces. Attachment marks the end of the induction period. Distilled water: $\theta_{eq} = 129°$; drop volume, 0.0343 ml; ●, contact angle; O, drop height; ▲, drop base diameter; ×, maximum drop diameter prior to attachment. Sodium decyl sulfate, 0.010 M: $\theta_{eq} = 180°$; drop volume, 0.0155 ml; ▼, contact angle; △, drop height; ▽, drop base diameter.

Table XXII

Effect of Metal Impurities on the Spreading of Water and Benzene on Mercury

Metal impurity (ppm)	Liquid	Initial effect	Time to "low" drop, min	Time to "high" drop, min
	Water	Complete spreading	2	2.5
	Benzene	Complete spreading	19	20
Gold (2)	Water	Complete spreading	2	2.5
Gold (2)	Benzene	Complete spreading	19	20
Lead (2)	Water	Complete spreading	0.5	6
Lead (2)	Benzene	Complete spreading	7	20
Zinc (2)	Water	"High" drop		
Zinc (2)	Benzene	"Low" drop		2

and Otto with simply effects at the mercury surface alone.

Sweeping of the mercury surfaces containing zinc and lead resulted in the collection of a "grayish, powery residue." This is indicative of oxide formation, although the experiments were apparently carried out in a dry nitrogen atmosphere. In fact, a residue was also observed for the system containing gold where oxide formation is not possible. Thus, the possibility of the "clean" mercury containing impurities is raised.

3. Mercury–Liquid–Liquid Systems

Wilkinson and Elliott[478] have studied, by means of high speed photography, the processes of attachment and subsequent spreading of carbon tetrachloride drops at mercury–solution interfaces. A typical set of measurements, where the drop dimensions and contact angle (measured through aqueous phase) are plotted against time, is given in Figure 28. The

(478) M. C. Wilkinson and T. A. Elliott, *J. Colloid Interface Sci.*, submitted for publication.
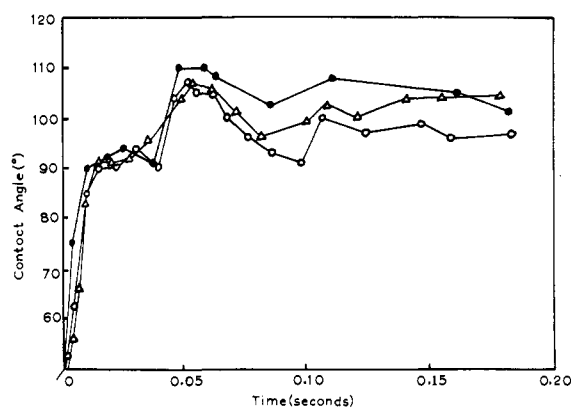
Figure 29. Induced drop oscillations due to attachment. Three repeat experiments are given for drops at the mercury–water interface. The degree of reproducibility was good.
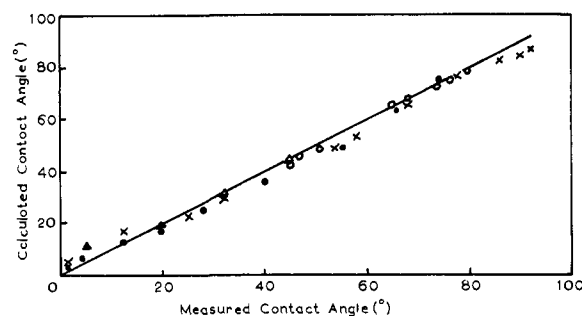
Figure 30. Comparison of measured contact angle (through oil phase) and value calculated from a cap of a sphere. The full line is drawn through equal values of measured and calculated contact angles. ●, 0.0100 M sodium decyl sulfate; ×, 0.0050 M sodium decyl sulfate; O, 0.0005 M sodium decyl sulfate; ▲, 0.0040 M sodium dodecyl sulfate; △, 0.00001 M sodium tetradecyl sulfate.

similarity of the contact angle vs. time and base diameter vs. time curves is readily apparent. For "self" spreading systems, the variation in contact angle with time can be considered as a measure of the rate of spreading of the drop.[479, 480]

Although the drops only fell 0.625 cm, they impinged on the mercury surface with sufficient kinetic energy to cause complete drop distortion, a "dish-like" structure being formed which reverted to a spherical shape in less than 0.01 sec. The drop usually rebounded once from the mercury surface before settling, the time taken from initial impact to consequent settling being less than 0.05 sec. Similar results were obtained in the presence of surface-active agents. The zero time on the plots in Figure 28 corresponds to the time at second impact and consequent settling. Oscillations, as depected by variations in the plots of drop height and diameter, died down very quickly. In all cases oscillations due to impact had ceased before attachment occurred.

The time taken for the trapped fluid (water) to drain from between the drop and the mercury surface is termed the induction period. Induction periods vary widely and depend on factors such as viscosity of the draining fluid, mass of the drop, concentration and nature of surface-active agents, and the

(479) T. A. Elliott and L. Leese, *J. Chem. Soc.*, 22 (1957); 1466 (1959).
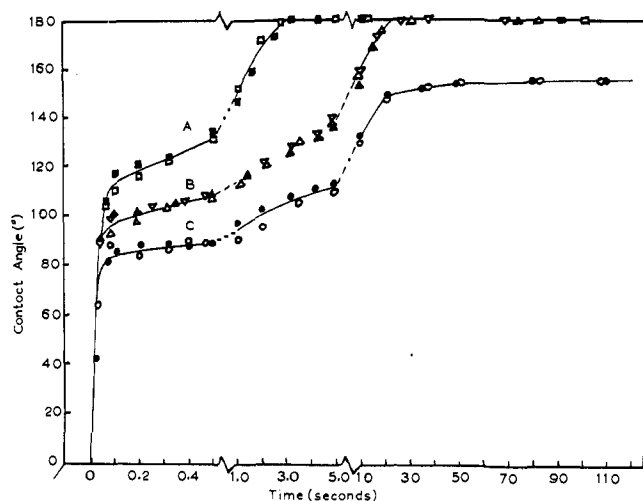(480) T. A. Elliott and M. Morgan, *ibid.*, 558, 563, 567, 570 (1966).

Figure 31. Reproducilibility obtained with drops in different solutions of surface-active agent (number of experiments, molarity of sodium decyl sulfate): (A) 2, 0.0100; (B) 3, 0.0075; (C) 2, 0.0025.
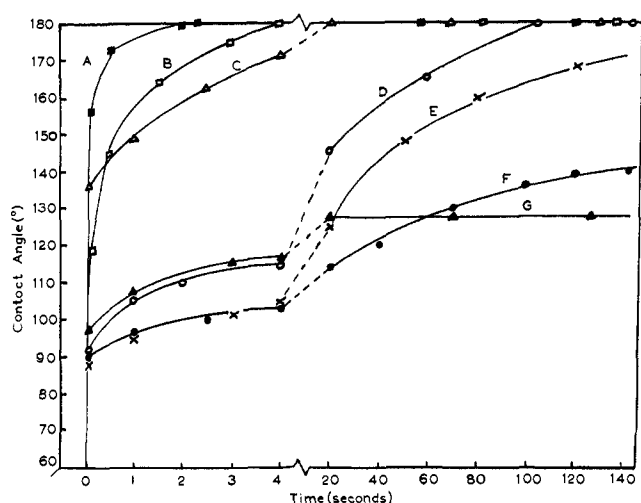

Figure 32. Dynamic contact angles in solutions of sodium dodecyl sulfate. Concentration (M), carbon tetrachloride–solution interfacial tension (dyn/cm), mercury–solution interfacial tension (dyn/cm), θ_{eq} (deg), respectively: (A) 0.0040, 10.3, 365.8, 180; (B) 0.0030, 14.4, 366.4, 180; (C) 0.0020, 18.5, 366.4, 180; (D) 0.0010, 25.3, 372.1, 180; (E) 0.0005, 29.9, 378.3, 180; (F) 0.0001, 38.8, 383.6, 145; (G) ..., 44.3, 395.0, 129.
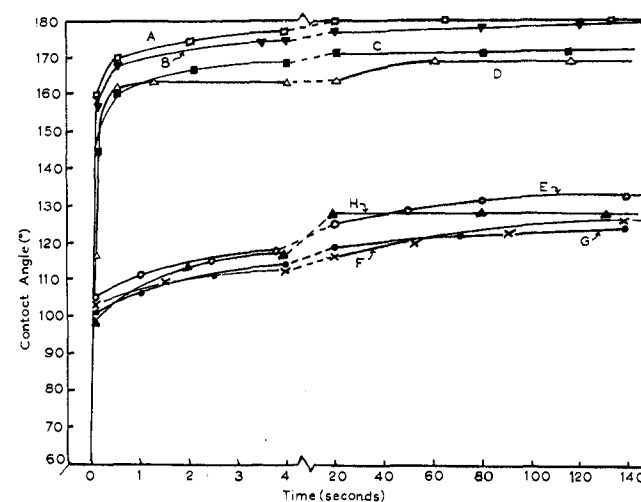
magnitude of any electrical forces.[481–483] For the present system water usually drained away in 0–2 sec, but with surface-active agents in solution induction periods were as large as 1–2 min.

Attachment of the drop at the mercury–water interface occurred in less than 0.0005 sec and over a relatively large basal area—not at a point contact. The contact angle on attachment was very close to 90° and remained at this value as the mercury–carbon tetrachloride interfacial area increased. The drop shape was retained during this period. Complete drop distortion occurred, however, as the mercury–carbon tetrachloride interfacial area exceeded the maximum cross-sectional area of the drop (at 0.005 sec); the contact angle then increased beyond 90°. The sides of the drop were initially pulled down as the advancing front moved across the mercury surface, and finally the apex of the drop collapsed. The oscillations set-up in the drop during this process are reflected in the contact angle $vs.$ time plot of Figure 29. Induced oscillations set up on attachment were rapidly damped, and the drop regained a shape of minimum surface area; this corresponded to the cap of a sphere (Figure 30).

The initial rate of spreading at the mercury–water interface was greater than 14000 mm/min, but this dropped rapidly, such that after 0.20 sec the rate was less than 100 mm/min. The final equilibrium contact angle was formed in a matter of seconds. The reproducibility between repeat runs was excellent (Figure 31); contact angles and interfacial areas on repeat experiments agreed to within 5%. Similar, excellent reproducibility was achieved in the presence of surface-active agents. These results demonstrate that, for well-defined liquid–liquid–liquid systems, not only can equilibrium wetting (such as contact angle) be reproduced, but also dynamic wetting (the dynamic contact angle).

The influence of sodium dodecyl sulfate and n-dodecylamine hydrochloride on the rate of spreading of carbon tetrachloride drops at the mercury–water interface was studied.

Figure 33. Dynamic contact angles in solutions of n-dodecylamine hydrochloride. Concentration (M), carbon tetrachloride–solution interfacial tension (dyn/cm), mercury–solution interfacial tension (dyn/cm), θ_{eq} (deg), respectively: (A) 0.0040, 19.5, 380.2, 180; (B) 0.0030, 23.7, 380.2, 178; (C) 0.0020, 29.3, 379.8, 171; (D) 0.0010, 36.0, 379.8, 132; (E) 0.0005, 40.0, 380.2, 126; (F) ..., 44.3, 395.0, 129.

The changes in contact angle with time are given in Figures 32 and 33. In both cases an increase in the concentration of the surface-active agent resulted in an increase in the rate of spreading, $i.e.$, increase in the rate of contact angle change. The equilibrium contact angles were all higher than the values recorded in the absence of surface-active agent. Further, the time taken for an equilibrium contact angle to be formed decreased with increase in concentration of the surface-active agent.

At particular, "critical" concentrations sudden large increases in the rate of spreading occurred. This phenomenon was observed for a number of surface-active agents and found

(481) M. H. Baird, *Trans. Faraday Soc.*, **56**, 213 (1960).

(482) B. Biswas and D. A. Haydon, *Third Congr. Surface Activity*, *Cologne*, **2**, 580 (1960).

(483) G. A. H. Elton and R. G. Picknett, *Second Congr. Surface Activity*, *London*, **1**, 288 (1957).
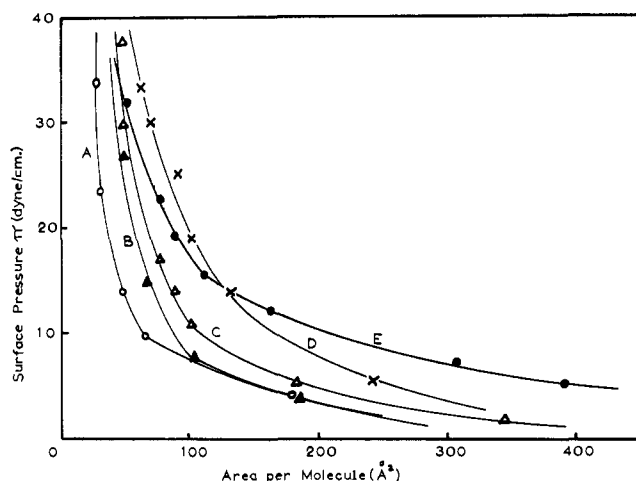
Figure 34. Variation in surface pressure with area per molecule for different surface-active agents adsorbed at the mercury-water interface: (A) sodium tetradecyl sulfate, (B) n-dodecylamine hydrochloride, (C) n-decylamine hydrochloride, (D) sodium dodecyl sulfate, (E) sodium decyl sulfate.

Table XXIII

Critical Concentration Regions for Various Surface-Active Agents in the Mercury–Carbon Tetrachloride–Water System

Surface-active agent	Critical concn, M
Sodium decyl sulfate	0.0075–0.0100
Sodium dodecyl sulfate	0.0020
Sodium tetradecyl sulfate	0.0002
n-Decylamine hydrochloride	0.0030
n-Dodecylamine hydrochloride	0.0010–0.0015

to be very reproducible. Values of these "critical" concentrations are given in Table XXIII. They were different for different surface-active agents and decreased with increase in chain length. For a given carbon chain length the "critical" concentration of the cationic surface-active agent was about one-half that of the anionic surface-active agent.

The surface-active agents used (Table XXIII) are known to be chemisorbed at the mercury-water interface.[484,485] However, since the surface atoms of mercury are quite mobile, the film is compressible to a certain extent. At low surface coverages the approach of the carbon tetrachloride drop to the mercury surface (during the induction period) acts to "squeeze" out the trapped layer of water and also the adsorbed surfactant species. Attachment thus occurs at the mercury surface, creating a mercury-carbon tetrachloride interface. In this instance spreading is governed by the magnitudes of the mercury-solution, mercury-carbon tetrachloride, and carbon tetrachloride-solution interfacial tensions.

As the concentration of adsorbed surface-active agent at the mercury/water interface increases, the area per molecule decreases, and more force is required to compress the film (Figure 34). Eventually a surface concentration is reached where further compression is not possible. The carbon tetrachloride drop then spreads over the adsorbed layer of surface-

(484) K. Eda, *Nippon Kagaku Zasshi*, **80**, 343, 461 (1959); **81**, 879 (1960).
(485) K. Eda and K. Takahashi, *ibid.*, **85**, 828 (1965); *Third Congr. Surface Activity*, Cologne, **2**, 291 (1960).
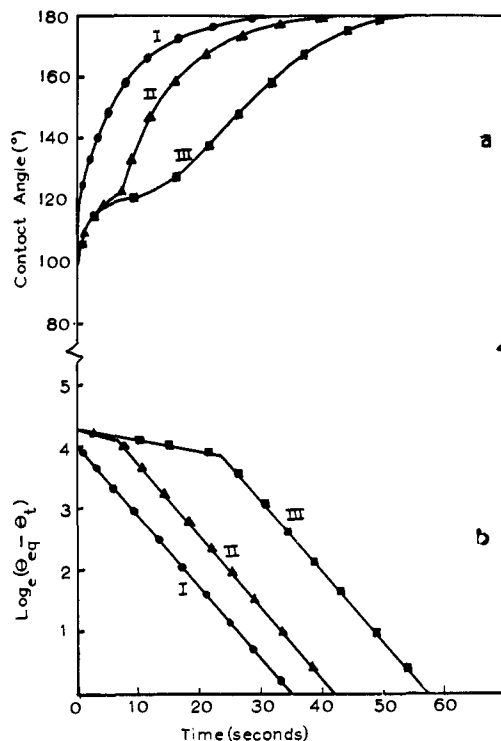

Figure 35. Different experiments carried out at the critical concentration of sodium dodecyl sulfate.

active agent. Since the interfacial tension mercury/adsorbed layer surface-active agent/carbon tetrachloride is much lower than the mercury/carbon tetrachloride interfacial tension the rate of spreading increases.[153] This particular surface concentration of adsorbed surface-active species has a corresponding unique value of bulk concentration in the water phase—referred to as the "critical" concentration.

Occasionally repeat experiments carried out at the "critical" concentration of a surface-active agent were very different (Figure 35a). In experiments II and III initial spreading is typical of that observed for drops spreading below the "critical" concentration region. However, after an unpredictable time period, spreading suddenly increased, and the equilibrium contact angle formed was the same as that in I. In experiments II and III the drop initially makes contact forming a mercury-carbon tetrachloride interface. After a certain amount of spreading a "metastable" state is reached; at this stage the area per adsorbed dodecyl sulfate ion at the mercury-water interface has reached a limiting stage (Figure 34), and the surface pressure increases rapidly. Any slight thermal or mechanical variations are sufficient to upset this "metastable" condition and surface-active agent infiltrates into the mercury-carbon tetrachloride interface, reducing the value of the interfacial tension. A further rapid increase in spreading then occurs.

The "metastable" states of Figure 35 should correspond to unstable equilibrium states where no surface-active agent molecules had penetrated the mercury-carbon tetrachloride interface. As such Young's equation (eq 34) should apply. Taking a value for the contact angle of 60° and substituting the experimentally determined values for the interfacial tensions

$$369.0 = 361.0 + 18.5 \cos 60 = 370.2 \text{ dyn/cm}$$

Good agreement was also obtained at the "critical" concentrations of the other surface-active agents.

It is of note that, when the spreading mechanism changed, the order of the process (first order, see eq 48) during the second rapid stage was the same (Figure 35b), irrespective of the time spent in the "metastable" state. In Figure 35a, experiments were found to follow first-order kinetics of the form

$$\frac{d\theta}{dT} = K'(\theta_{eq} - \theta_t) \qquad (48)$$

where θ_{eq} is the contact angle at t_∞, θ_t is the value at time t, and K' is a constant only for a particular type and concentration of surface-active agent. K' is proportional to the rate of the spreading process. This general relationship was found to apply for drops spreading in solutions of anionic, cationic, and nonionic surface-active agents. Wolstenholme and Schulman[486] found that the same law was obeyed for the spreading of oxygen bubbles at copper–solution interfaces. Since the processes obey a pseudo-unimolecular law the surface excess of surface-active agent at only one of the three interfaces must be varying. This must be at the carbon tetrachloride–solution interface, since the surface-active agent at the other interfaces is chemisorbed and the surface excesses are constant.

VIII. Summary

Mercury can routinely be prepared in purities far higher than almost all other elements, and it therefore might be expected that its surface properties would be known with some exactitude. Unfortunately, this is not the case; the literature concerned with the surface properties of mercury shows a very wide discordance. The purpose of this review has therefore been to critically and comprehensively examine all pertinent literature dealing with the surface properties of mercury. The reasons for the discrepancies are examined, and the factors affecting the determination of reliable values are discussed.

An analysis of almost 200 independent determinations of the surface tension of mercury (since 1773) shows that the values are normally distributed about an average of 466.3 dyn/cm with one standard deviation (σ) being 33.0 dyn/cm. The range has varied from 359 to 563 dyn/cm. The distribution has not narrowed over the last 30 years, the average being 469.7 ($\sigma = 34.2$) dyn/cm.

The normal methods of purification, e.g., distillation, are extremely efficient and even the cheaper commercial grades of mercury probably contain impurities at levels no higher than 1 ppm. Purer grades may contain impurities at levels from 1 in 10^6 down to 1 in 10^{10}. At these levels, however, the effects on the surface properties of mercury, if any, are time dependent. For the preparation of pure mercury of a reliable standard it is recommended that the Hulett-type air still be employed.

Various factors affecting the surface tension of mercury have been considered.

1. The surface tension does not vary with time; reported time variations are due to the accumulation of impurities at the surface.

2. The temperature coefficient of the surface tension, from 28 independent determinations, is -0.224 ($\sigma = 0.032$) dyn/

(cm °C). This is applicable between the freezing and boiling points.

3. Normal atmospheric gases, such as nitrogen, oxygen, carbon dioxide, carbon monoxide, hydrogen, and the rare gases do not affect the surface tension of mercury. The surface tension of mercury in vacuo and dry air is reliably 475.5 $\pm$ 10 dyn/cm at 25°.

4. Water vapor has spurious effects on the surface tension of mercury. In the absence of other gases it adsorbs on mercury reversibly and by physical (van der Waals) forces alone. Adsorption obeys the Gibbs–Volmer relationship up to relative vapor pressures of about 0.9. In the presence of air, or specifically oxygen and/or carbon dioxide, complex and time-dependent surface chemical reactions occur. This results in an apparent lack of effect on the surface tension until the saturation vapor pressure is approached.

5. Many organic vapors adsorb physically and reversibly on mercury, although some are chemisorbed. Adsorption obeys the Gibbs–Volmer relationship up to relative vapor pressures approaching unity. In some cases phase changes can be identified as the reorientation of molecules at certain surface packing densities occurs.

6. Dissolved metals produce complex variations in the surface properties of mercury. Intermetallic compound formation and polynary alloys occur, and the effect of these on the surface tension of mercury is at present unknown. The greatest complicating factor in these measurements is the fact that dissolved metal impurities are very reactive toward trace gases when they come into the mercury surface layers. This can result in chemical reactions and compound formation. A great deal more work in this important area is required before any definitive statements can be made.

7. Mercury has an interfacial tension against degassed water of 426 $\pm$ 2 dyn/cm at 25°. Both oxygen and carbon dioxide lower this value, in the extreme to 390 and 320 dyn/cm, respectively. Also the effects vary with time. Normally, interfacial tensions of between 370 and 390 dyn/cm will be recorded for pure water containing dissolved laboratory air.

The wide discordance in surface tensions reported for mercury can be explained mainly on the basis of the interaction of external contaminants, e.g., water vapor and organic materials, at the high-energy surface. Poor experimental technique accounts for a smaller percentage and the effect of internal impurities, e.g., base metals, is probably only of importance in a few cases.

Various equilibrium, and dynamic, spreading and wetting phenomena of mercury in different systems have been discussed. Mercury is found to be an "ideal" atomically smooth surface, and, since it can be well characterized, should prove to be an almost perfect "high-energy" surface for general studies in the field of surface chemistry.

(486) G. A. Wolstenholme and J. H. Schulman, *Trans. Faraday Soc.,* 46, 488 (1950).