

# INTERFACIAL TENSION STUDIES ON MERCURY IN REACTING SYSTEMS\*

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## *Introduction*

DURING the course of an investigation in this Laboratory on the reaction between hydrogen sulphide and sulphur dioxide in non-aqueous solutions, B. S. Rao and M. R. A. Rao<sup>1</sup> noticed that the gases did not interact in the presence of mercury or of carbon tetrachloride. When mercury, however, was brought in contact with a carbon tetrachloride solution of the two gases, reaction took place. The authors suggested that the primary product of the reaction between hydrogen sulphide and sulphur dioxide was thio-sulphonic acid (thiosulphurous acid) and that its decomposition at the interface between mercury and carbon tetrachloride caused greater union between the two gases.

A systematic study of the interfacial tension of the system :

Solution of hydrogen sulphide and sulphur dioxide in carbon tetrachloride		Mercury
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and of the allied system :

Solution of sulphur in carbon tetrachloride		Mercury
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has now been carried out and the results are presented in this paper.

## *Experimental*

### *Purification of Materials*

*Mercury.*—Commercial mercury was passed several times in the form of fine spray through a column of dilute nitric acid containing 1% mercurous nitrate. The metal was then washed with water, dried at 200° C. and filtered through a pin-hole in filter-paper. The mercury was distilled in air under reduced pressure (25 mm.) and was again passed through a pin-hole in filter-paper to remove the oxide impurities. Finally, the air-distilled mercury was distilled twice in vacuum to free it from the last traces

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of oxide; and the purified product was stored in a phosphorus pentoxide desiccator.

*Water.*—Ordinary distilled water, after freeing it from carbon dioxide and ammonia was redistilled in an all-glass apparatus. The double-distilled water was suitably protected from contamination during storage.

*Carbon tetrachloride.*—Carbon tetrachloride of c.p. quality was kept over phosphorus pentoxide and mercury for some weeks with frequent shaking. The clear liquid was then decanted into a round-bottomed flask and distilled in an all-glass apparatus. Moisture was excluded by means of suitable guard tubes. The middle fraction boiling at  $72.6^{\circ}\text{C}$ . was collected and was preserved in glass-stoppered bottles. The liquid was freshly distilled before use.

*Sulphur.*—Merck's extra pure sulphur was used.

*Sulphur dioxide.*—Sulphur dioxide from a cylinder was dried over phosphorus pentoxide and was passed to saturation through pure dry carbon tetrachloride, atmospheric moisture being carefully excluded by means of suitable guard tubes.

*Hydrogen sulphide.*—Hydrogen sulphide was prepared by the action of water on aluminium sulphide. The sulphide had been prepared by the union between aluminium and sulphur on the lines of the thermite process. The gas, dried over phosphorus pentoxide, was passed through carbon tetrachloride to saturation. The resulting solution was carefully preserved.

#### *The Technique of the Drop Weight Method*

Harkins and co-workers<sup>3,4,5</sup> have standardized a method for the determination of surface tension of mercury by the drop-weight method. Their method consists in siphoning out mercury through a fine capillary tube bent twice at right angles, with one end of the tube dipping in a reservoir of mercury. The other end of the tube is well ground and serves as the dropping tip. Three to five drops are collected and weighed. The authors claim a high degree of accuracy.

In their apparatus for surface tension measurements, Bartell, Case and Brown<sup>6</sup> use a tip of razor edge sharpness obtained by cutting the capillary tube with a tungsten knife. They point out that drops formed at this tip are quite reproducible, being of uniform weight. They further state that drops formed at a tip obtained by grinding are bound to be non-uniform on account of the jaggedness of the tip. Our experiments confirm the above observations. A tip prepared by the method of Bartell and co-workers<sup>6</sup> has been employed in the present work. In order to get reproducible results it is necessary to regulate carefully the rate of formation of the drop.

For this purpose Harkins and co-workers employ a fine capillary. They observe that the capillary required is so fine that it often gets clogged. This difficulty has also been experienced by Gliddon<sup>7</sup> who has therefore devised a new arrangement for controlling the rate of formation of the drop. But his arrangement appears to be rather elaborate.

In the present work, the rate of formation of the drop is controlled by a simple device. The apparatus used (Fig. 1) consists of a flat-bottomed flask of about 125 c.c. capacity, a cooling column of fine capillary tube of U form to which the dropping tip is attached, through two ground glass joints  $G_1$  and  $G_2$  which move at right angles to one another, enabling one to secure the proper position of the tip. The edge of the tip is adjusted to be a level higher than any of the ground glass joints or stop-cocks so that no grease is needed for rendering the joints air-tight.

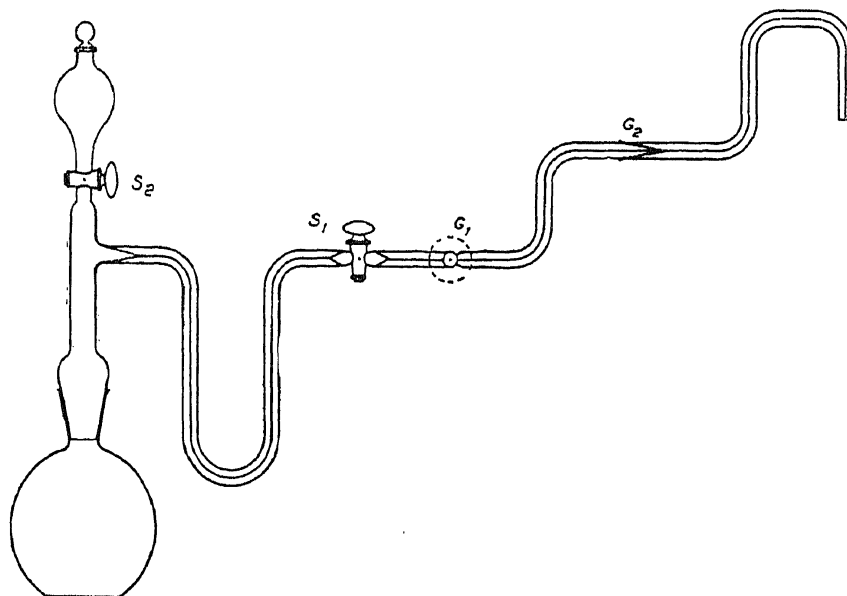


FIG. 1

The apparatus is set upon a reinforced concrete table, in order to avoid vibration. Air draughts are prevented by having proper screens. The apparatus is filled with purified mercury, all air bubbles being expelled. The capillary portion of the apparatus is filled by suitable manipulation of the stop-cocks and ground joints.

It is essential that the edge of the tip should be parallel to the surface. The drops obtained from a tube kept at an angle to the vertical do not form and tear off from a circular bore but from an elliptical one. Since the radius of the bore is involved in the calculations, it is obvious that an error will be introduced if the correct position for the tip is not secured. For this purpose a flat glass dish containing mercury is placed on an adjustable platform. The mercury surface is brought close to the tip. By observing

in between the edge and its reflection any tilt of the edge from the horizontal can be discovered and set right by operating the ground joints.

The drops are generated by gently warming the mercury reservoir by means of a carbon filament lamp. The rate of dropping can be controlled by adjusting the distance of the lamp from the reservoir. An asbestos sheet is used to screen the tip from the lamp.

The mercury drops are collected in clean weighing bottles (of known weight) kept ready in a desiccator. The first two drops are rejected in each case; the subsequent drops are collected and weighed in batches of three to five drops.

To find out whether the drops formed are uniform in size, the weights of successive drops of mercury have been determined. The results of a typical experiment are indicated below.

TABLE I

No. of the drop	Weight of the drop in air	No. of drop	Weight of the drop in air
	gm.		gm.
1st	0.1527	9th	0.1521
2nd	0.1523	10th	0.1522
3rd	0.1520	15th	0.1520
4th	0.1522	20th	0.1522
5th	0.1518	26th	0.1518
6th	0.1520	30th	0.1519
7th	0.1521	32nd	0.1516
8th	0.1524	Mean	0.1520

As can be gathered from the above values the drops are quite uniform. The diameter of the inner bore of the tip is accurately measured by means of a "Photo-measuring Micrometer" which can be read correct to 0.001 mm. Measurements are made along eight even diameters and the average values employed in the calculations. The following formulæ have been used in the calculations.

$$(1) \quad T = \frac{Mg}{2\pi r} \cdot \frac{1}{F(a)} \quad \dots \text{for surface tension of mercury ;}$$

$$(2) \quad T = \frac{Mg}{2\pi r} \left\{ \frac{\rho - \sigma}{\rho} \right\} \frac{1}{F(a)} \quad \dots \text{for interfacial tension measurements,}$$

where

$M$  = mass of falling drop ;

$r$  = radius of the bore ;

$g$  = acceleration due to gravity ;

$F(a)$  = correction factor whose values are given by Harkins and co-workers ;

$\rho$  = density of mercury at a known temperature ;

$\sigma$  = density of the liquid at the same temperature.

Interfacial tension measurements are carried out in an exactly similar manner. A stoppered weighing bottle containing the freshly distilled liquid is kept near the tip for acclimatization. Meanwhile the first two drops are collected in a separate portion of the same liquid and rejected. After some time the stopper of the bottle is removed and the platform holding the weighing bottle is slowly raised until the tip is below the surface of the liquid. After collecting three to four drops of mercury the liquid is carefully removed by suction. The metal is then washed and dried at as low a temperature as practicable. In the case of water the mercury is washed with absolute alcohol a number of times and dried at 40° C. In general, six determinations have been made for each liquid. The results obtained are indicated in Table II.

TABLE II. *Tension Values of Mercury at Air, Water and Carbon Tetrachloride Interfaces at 23.2° C.*  
(Diameter of the Inner Bore 0.1386 cm.)

Interface	Uncorrected drop weight	Correction factor (Harkins)	Tension dynes/cm.	Values obtained by	
				Harkins	Bartell
	gm.				
Air ..	0.1520	0.72024	473.9	464.4	..
Water ..	0.1272	0.71264	371.3	374.8	371.1
Carbon tetra-chloride ..	0.1384	0.71510	373.7	362.2	..

*Results*

Having standardized the method of determination of surface tension by the method of drops, the interfacial tension of mercury in the following reacting systems has been measured.

- (i) Mercury | Saturated solution of sulphur dioxide in carbon tetrachloride.
- (ii) Mercury | Saturated solution of hydrogen sulphide in carbon tetrachloride.
- (iii) Mercury | Carbon tetrachloride saturated with hydrogen sulphide and sulphur dioxide.
- (iv) Mercury | Different dilutions of hydrogen sulphide and sulphur dioxide in carbon tetrachloride.
- (v) Mercury | Sulphur in carbon tetrachloride at different concentrations.

The experimental error in these measurements is less than one dyne/cm.

It has to be noted that it is not practicable to carry out any interfacial tension measurements in system (v), when the sulphur concentration in carbon tetrachloride exceeds 0.05%, as the mercury drops get covered with sulphide rapidly and crumble to small droplets making the measurements impracticable. It may also be pointed out that the measurement of the interfacial tension of mercury cannot be made in carbon tetrachloride containing even minute quantities of dissolved iodine.

The results obtained are presented in Tables III and IV.

TABLE III. *Interfacial Tension between Mercury and Saturated Solutions of Hydrogen Sulphide and Sulphur Dioxide in Carbon Tetrachloride and their Mixtures at 23.2° C.*

Solution	Uncorrected drop weight	Correction factor (Harkins)	Interfacial tension dynes/cm.
	gm.		
Saturated solution of H <sub>2</sub> S ..	0.1345	0.7153	372.6
Saturated solution of SO <sub>2</sub> ..	0.1292	0.71321	364.4
Mixtures of H <sub>2</sub> S and SO <sub>2</sub> in CCl <sub>4</sub> —			
(i) Saturated solution ..	0.1372	0.71593	379.9
(ii) Ten times diluted ..	0.1334	0.71470	370.1
(iii) Twenty times diluted ..	0.1340	0.71490	371.6
Pure carbon tetrachloride ..	0.1348	0.71510	373.7

TABLE IV. *Interfacial Tension between Mercury and Sulphur Solutions in Carbon Tetrachloride at 23.2° C.*

Concentration of sulphur in CCl <sub>4</sub> mg./100 g. of CCl <sub>4</sub>			Uncorrected drop-weight gm.	Correction factor	Interfacial tension dynes/cm.
1.	Pure CCl <sub>4</sub>	.. ..	0.1348	0.71510	373.3
2.	2.21 mg.	.. ..	0.1470	0.71883	405.5
3.	6.66 mg.	.. ..	0.1525	0.72007	419.9
4.	29.19 mg.	.. ..	0.1555	0.72103	428.7
5.	32.12 mg.	.. ..	0.1529	0.72047	420.7
6.	47.45 mg.	.. ..	0.1500	0.72023	417.3

In an attempt to elucidate the nature of the changes in the interfacial tension in systems studied above, measurements have been made of the interfacial tension between mercury and aqueous solutions of complex salts of the metal.

The iodides and cyanides of mercury and potassium employed in the investigations are of A. R. quality.

*Complex Iodide Solution.*—Mercuric iodide prepared by interaction between aqueous solutions of mercuric chloride and potassium iodide is shaken up with molar potassium iodide to give a saturated solution. The complex iodide of mercury thus obtained is mixed with an equal volume of the stock potassium iodide and the resulting solution is used for the measurements, after suitable dilution.

The complex cyanide solution is prepared in the same manner as indicated above for the iodide. Densities of the solutions used have been measured at 23.5° C. using specific gravity bottles.

Interfacial tension between mercury and aqueous solutions at 23.5° C.

TABLE V. *Mercury and Aqueous Solutions of Potassium Iodide*

Concentration in moles of KI/litre				Uncorrected drop-weight gm.	Correction factor (Harkins)	Interfacial tension dynes/cm.
1.	Pure water	..	..	0.1272	0.71264	371.3
2.	0.1 mol.	..	..	0.1012	0.70214	299.2
3.	0.5 „	..	..	0.1220	0.70675	361.4
4.	0.75 „	..	..	0.1115	0.70645	332.8
5.	1.00 „	..	..	0.1114	0.70787	339.6

TABLE VI. *Mercury and Aqueous Solutions of Potassium Mercuric Iodide*

Concentration in moles of HgI <sub>2</sub> /litre				Uncorrected drop-weight gm.	Correction factor (Harkins)	Interfacial tension dynes/cm.
1.	Pure water	..	..	0.1272	0.71264	371.3
2.	0.10 mol.	..	..	0.1122	0.70694	336.5
3.	0.50 „	..	..	0.0938	0.70013	282.9
4.	0.75 „	..	..	0.1163	0.70890	344.4
5.	1.00 „	..	..	0.1293	0.72220	374.1

TABLE VII. *Mercury and Aqueous Solutions of Potassium Cyanide*

Concentration in moles of KCN/litre				Uncorrected drop-weight gm.	Correction factor (Harkins)	Interfacial tension dynes/cm.
1.	Pure water	..	..	0.1272	0.71264	371.3
2.	0.50 mol.	..	..	0.1100	0.70607	323.4
3.	1.00 „	..	..	0.1230	0.71710	361.6



TABLE VIII. *Mercury and Aqueous Solutions of Potassium Mercuric Cyanide*

Concentration in mols of HgCy <sub>2</sub> /litre			Uncorrected drop-weight gm.	Correction factor (Harkins)	Interfacial tension dynes/cm.
1.	Pure water	.. ..	0.1272	0.71264	371.3
2.	0.50 mol.	.. ..	0.1072	0.70501	315.2

*Discussion*

The results show that the lowering in interfacial tension of mercury in mixtures of carbon tetrachloride solutions of hydrogen sulphide and sulphur dioxide noticed by B. S. Rao and M. R. A. Rao<sup>1</sup> is confined to very dilute solutions and that with an increase in the concentration of the gases the interfacial tension actually rises. It is of interest to note that neither sulphur dioxide nor hydrogen sulphide can individually bring about any increase in the interfacial tension. With sulphur dioxide, in fact there is lowering in interfacial tension by several dynes.

With solutions of sulphur in carbon tetrachloride, the interfacial tension of mercury rises, reaches a maximum and then drops in value. There is in this case no initial fall in interfacial tension followed by a rise. Interfacial tension measurements in this system are practicable only when the solutions are so dilute that the rate of production of mercury sulphide is insignificant; with iodine, which seems to react with mercury more vigorously, measurements are not practicable even in dilute solutions. The interfacial tension-concentration curve with solutions of sulphur in carbon tetrachloride is strongly suggestive of the usual electro-capillary curves obtained with mercury when aqueous solutions are used. Very little, however, is known at present about electro-capillary effects at mercury surfaces in contact with non-aqueous solutions; for, the practical difficulties involved in studying such effects in non-conducting media seem to be very formidable.

We are of opinion that the initial decrease in interfacial tension noticed with mercury and aqueous solutions of complex salts, are due to adsorption phenomena while the subsequent increase in interfacial tension as the concentration of salt increases, is analogous to the effects noticed by Lenkewits<sup>8</sup> and Goebel<sup>9</sup> (*cf. International Critical Tables*, 1928, 4, 439).

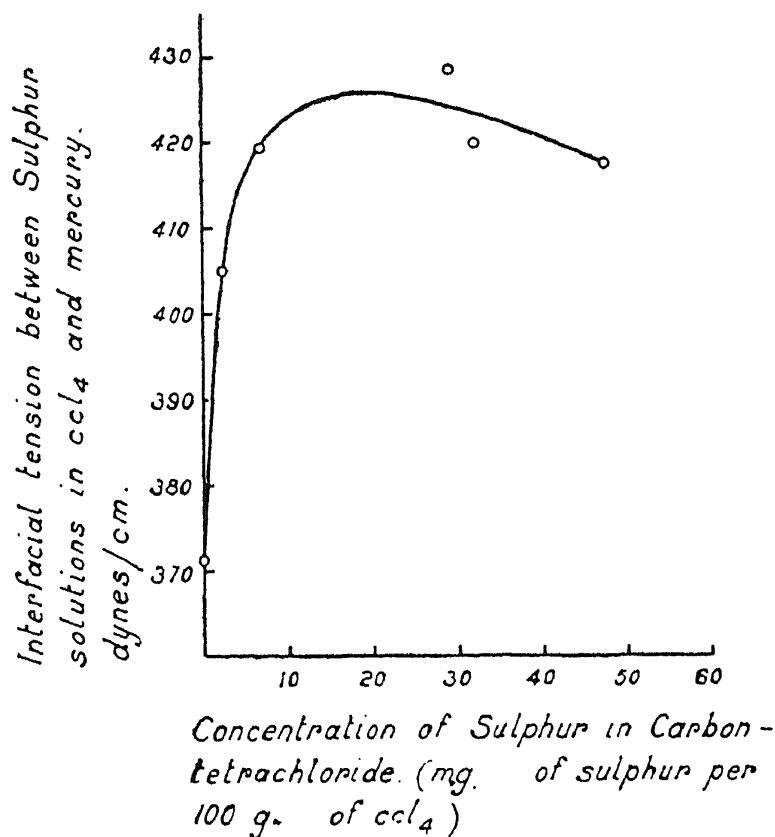


FIG. 2

The changes in interfacial tension with an increase in the concentration of the two gases (hydrogen sulphide and sulphur dioxide) cannot satisfactorily be explained on the basis of liberation of sulphur and the subsequent formation of the sulphide of mercury at the interface. The effect of concentration on the interfacial tension even in the simpler system (sulphur solution in carbon tetrachloride and mercury) does not at present admit of a satisfactory explanation and we are inclined to believe that interfacial tension changes of mercury in a chemically reactive system cannot profitably be studied by the technique adopted in this paper. We have tried using in the above systems the double capillary rise method described by Speakman<sup>10</sup> but the results are in no way encouraging.

### Summary

A new method has been described for controlling the rate of formation of drops in the drop-weight method for the determination of surface tension and interfacial tension with mercury as one of the phases.

Interfacial tension of mercury has been measured in systems containing (a) hydrogen sulphide and sulphur dioxide in carbon tetrachloride solution, (b) sulphur in carbon tetrachloride solution, (c) potassium mercuric iodide in aqueous solution, and (d) potassium mercuric cyanide in aqueous solution. Certain interesting features of the results obtained, are discussed.

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