

Fig. 2.—Plot of  $\log K_p$  vs.  $1/T$  for the reaction:  $\text{FeCl}_2(\text{s}) + 1.14\text{H}_2\text{S}(\text{g}) \rightarrow \text{FeS}_{1.14}(\text{s}) + 2\text{HCl}(\text{g}) + 0.14\text{H}_2\text{S}(\text{g})$ .

shown in Fig. 2. This line may be represented by the equation

$$\log_{10} K_p = -(4,320/T) + 6.71$$

From this we find that the heat of reaction (5),  $\Delta H$ , assumed to be constant with temperature, is 19,800 calories.

It is not certain whether the composition  $\text{FeS}_{1.20}$

calculated at  $456^\circ$  is in error or whether the solubility of sulfur at this temperature is sufficiently large to account for this composition.  $\log_{10} K_p$  calculated from this run is not plotted in Fig. 2.

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#### Summary

An experimental study has been made of the equilibrium relationships existing between solid ferrous chloride and gaseous hydrogen sulfide at intermediate temperatures. For the temperature interval of  $620$ – $706^\circ\text{K}$ ., pyrrhotite (a solid solution of sulfur in  $\text{FeS}$ ) is formed rather than ferrous sulfide. Equilibrium constants were determined for the reaction:  $\text{FeCl}_2(\text{s}) + 1.14\text{H}_2\text{S}(\text{g}) = \text{FeS}_{1.14}(\text{s}) + 2\text{HCl}(\text{g}) + 0.14\text{H}_2(\text{g})$ . In the temperature interval the relation  $\log_{10} K_p = (-4,320/T) + 6.71$  was found between  $K_p$  and  $T$ .

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## Equilibrium Relationships between Fluid Interfaces: the System Methylene Iodide-Water-Air<sup>1</sup>

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Material relating to the equilibrium relationships between interfaces at their mutual edge has been included in most discussions of capillary phenomena since the earliest considerations of the subject.

For the condition where three phases meet at a common edge and one of the phases is a solid it has long been stated<sup>2</sup> that

$$T_{31} \cos \theta + T_{12} = T_{23} \quad (1)$$

where  $T$  is defined as the superficial tension of the interface acting on the mutual edge in a direction parallel to the respective interface (2 refers to the solid phase). Equation 1 is generally recognized as a fundamental equation of capillarity, but its use has never been experimentally justified.

For the condition where all three phases are fluids, it has been believed by many<sup>3</sup> that "If

(1) Dissertation submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. This material was included in paper number 16, delivered before the Division of Physical and Inorganic Chemistry at the 108th meeting of the American Chemical Society, New York, N. Y., September 12, 1944.

(2) Thomas Young, "Works," by Peacock, Vol. I, p. 464 (1855). Terminology is that used by Lord Rayleigh.<sup>4</sup>

(3) (a) Article on Capillary Action, 11th edition of Encyclopedia Britannica. Article by J. C. Maxwell, revised by Lord Rayleigh. The quotation included here is Lord Rayleigh's. (b) See also Franz Neumann, Vorlesungen über die Theorie der Capillarität, pp. 161–163, B. G. Teubner, Leipzig, 1894.

the three fluids can remain in contact with one another, the sum of any two of the quantities (referring to the tensions of the interfaces) must exceed the third, and by Neumann's rule the directions of the interfaces at the common edge must be parallel to the sides of a triangle, taken proportional to  $T_{12}$ ,  $T_{23}$ ,  $T_{31}$ . If the above-mentioned condition be not satisfied, the triangle is imaginary, and the three fluids cannot rest in contact, the two weaker tensions, even if acting in full concert, being incapable of balancing the strongest."

Where "pure" fluid phases were concerned, Rayleigh<sup>4</sup> has argued that from the hypothesis of Thomas Young "We are thus led to the important conclusion, so far as I am aware hitherto unnoticed, that according to this hypothesis Neumann's triangle is necessarily imaginary, that one of the three fluids will always spread upon the interface of the other two."

From Laplace, Rayleigh concludes that "According to Laplace's hypothesis, then, three fluids cannot rest in contact, but the case is altered if one of the bodies be a solid."

Those who attempted to investigate experimentally the utility of the relationships that might exist between three fluid interfaces at an edge of contact, were faced with difficulties in-

(4) Lord Rayleigh, "Scientific Papers," Vol. III, pp. 414, 416.

herent in their experiments which made their results difficult to interpret.<sup>5-12</sup>

For mutually saturated three phase fluid systems meeting at a common edge it has recently been demonstrated<sup>13</sup> how the equilibrium angle through the fluid phase of intermediate density can be determined. It also has been established that equilibrium with regard to the three fluid interfaces at their common edge is possible even when the angles through the phases are, respectively, 0, 180, 180°.

The experimental method already described, however,<sup>13</sup> does not permit self-dependent determination of the relative values of the tensions of the interfaces.

The general validity of the relationships<sup>14</sup> (see Fig. 1)

$$0 = \sigma_{1,2} + \sigma_{1,3} \cos \theta_e + \sigma_{2,3} \cos \phi_e \quad (2)$$

$$0 = \sigma_{1,3} \sin \theta_e - \sigma_{2,3} \sin \phi_e = \sigma_{1,3} \sin \beta_e - \sigma_{1,2} \sin \phi_e = \sigma_{2,3} \sin \beta_e - \sigma_{1,2} \sin \theta_e \quad (3)$$

in their application to such systems has not been established previously.

Furthermore, the measurement of the equilibrium angle through only one phase requires the knowledge of the relative value of the tensions of two interfaces in order to utilize these relationships to calculate the relative value of the tension at the edge of the third interface, and the angles through each of the other two phases.

The purposes of this investigation can therefore be resolved as follows: (a) to investigate the validity of equations 2 and 3 in their application to such systems; and (b) for a mutually saturated three phase fluid system meeting at a common edge, to present methods for the determination of the equilibrium angles through the phases of lowest and greatest density.

The system methylene iodide-water-air was selected for this investigation for the reason that comparative data on the relative values of the tensions of the interfaces of this system were available from a number of sources.<sup>10,12,15,16</sup>

(5) G. Quincke, *Phil. Mag.*, **41**, 454 (1871).

(6) W. B. Hardy, *Proc. Roy. Soc. (London)*, **A86**, 610 (1912).

(7) W. H. Coghill and C. O. Anderson, U. S. Bureau of Mines, Tech. Paper 262 (1923).

(8) N. Fuchs, *Kolloid Z.*, **52**, 262 (1930).

(9) C. G. Lyons, *J. Chem. Soc.*, 623 (1930).

(10) Joseph J. Jaspér, A Study of Liquid Lenses: A part of a dissertation submitted to the graduate faculty in candidacy for the degree of Doctor of Philosophy, Department of Chemistry of the University of Chicago, 1931. Reference made to the private edition printed 1933, distributed by the University of Chicago Libraries, Chicago, Illinois.

(11) N. F. Miller, *J. Phys. Chem.*, **45**, 1025 (1941); and others.

(12) In this regard, it may be noted that Harkins in presenting the theory of "spreading coefficients" stated (in referring to the concept of the "Neumann triangle") that "Some investigators appeared to doubt the general applicability of such a relation," 6th Colloid Symposium Monograph, p. 20, 1928.

(13) W. Fox, *J. Chem. Phys.*, **10**, 623 (1942).

(14)  $\sigma$  refers to the tension that manifests itself at the edge of each interface.

(15) E. G. Carter and D. C. Jones, *Trans. Faraday Soc.*, **30**, 1025 (1934).

(16) W. D. Harkins and A. Feldman, *THIS JOURNAL*, **44**, 2665 (1922).

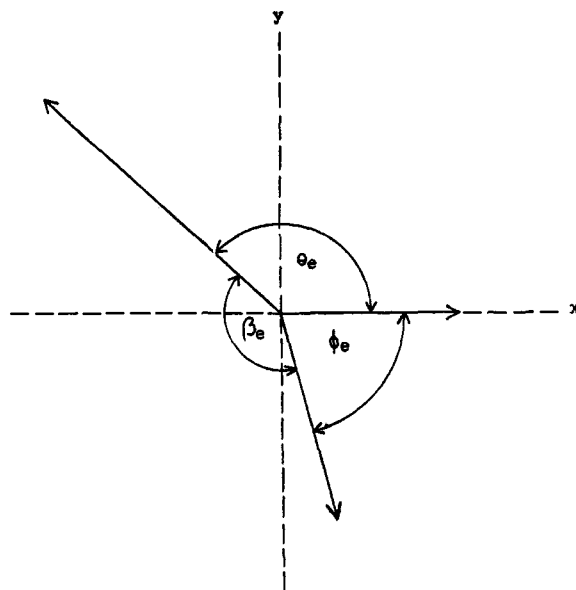


Fig. 1.—The vectors indicate the relative directions at which the tensions<sup>14</sup> of the interfaces act on the mutual edge:  $\theta_e$  = the equilibrium angle through the fluid phase of intermediate density (phase 1);  $\phi_e$  = the equilibrium angle through the fluid phase of greatest density (phase 2);  $\beta_e$  = the equilibrium angle through the fluid phase of lowest density (phase 3).

Investigations were conducted at  $25 \pm 1$ ,  $28 \pm 1$  and  $20 \pm 1^\circ$ , to approximate (respectively) the conditions of Carter and Jones,<sup>15</sup> Jasper,<sup>10</sup> and Harkins and co-workers.<sup>12,16</sup>

#### Materials

**Methylene Iodide.**—Samples of four different histories were used: (1) Eastman Kodak Co. 162, sample light brown in color, was distilled under reduced pressure. No appreciable decrease in color was effected by distillation. (2) A portion of the above noted distillate was further purified by repeated crystallizations at about  $6.1^\circ$ . That portion of the material which solidified last and melted first was rejected each time. In this manner a white crystalline solid was obtained which melted to a faintly yellow liquid. (3) This was another sample of Eastman Kodak Co. 162, which was light yellow in color. (4) Sample 3 was purified directly by crystallization at about  $6.1^\circ$  as described under (2).

**Water.**—Distilled water, available directly from a block tin system, was used throughout this investigation.

#### Apparatus

For the low-power photomicrographic work required, the following apparatus was used. (a) The camera was an  $8 \times 10$ " View Camera; by the use of reducing kits the plateholder was adapted to hold smaller size photographic plates.

(b) A Zeiss Tessar lens, focal length 7.5 cm.,  $f/4.5$ , mounted on Compur shutter was used. A lens shade prevented an excessive amount of extraneous light from reaching the lens.

(c) Incandescent tungsten filament lamps were used as the light source. A ground glass diffusing screen was placed between the glass cell and the light source, and a plano-convex condensing lens between the light source and the diffusing screen. The image of a rectangular glass slide, suspended in the cells used to hold the systems under investigation, showed no distortion on the ground glass focusing screen.

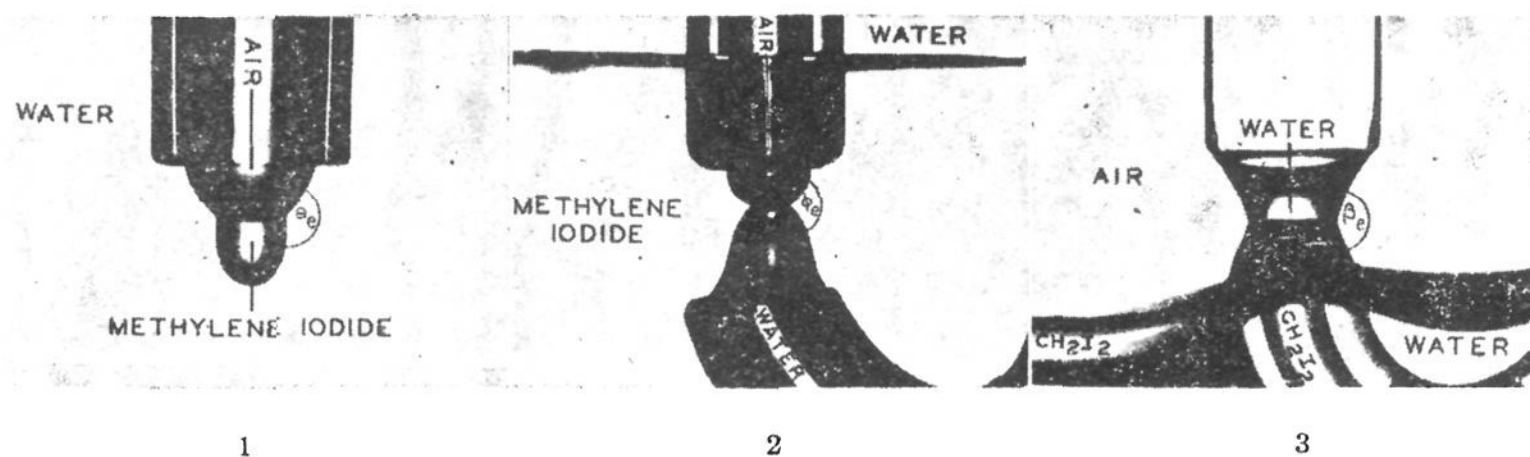


Fig. 2.

Glass apparatus coming into contact with the systems studied was washed in hot cleaning solution, tap water, and then distilled water.

Profiles outlining the equilibrium angles through each of the mutually saturated fluid phases can be secured by the methods indicated in Plates 1, 2, and 3 of Fig. 2.

The profile outlining  $\theta_e$ , the equilibrium angle through the fluid phase of intermediate density, was obtained by bringing a drop of the saturated organic liquid into contact with the gas bubble which was held suspended in the saturated aqueous phase (Plate 1). Care was taken to keep all three phases mutually saturated and to secure the profile cutting off the actual equilibrium angle. Plate 1 is a photograph of sample 2 at 20°.

The profile outlining  $\phi_e$ , the equilibrium angle through the fluid phase of greatest density, was secured in the manner indicated in Plate 2. Methylene iodide (saturated with water) was covered with the saturated aqueous phase in the observation cell. A curved glass tube containing the saturated aqueous phase was placed in the cell and enough of the saturated methylene iodide added so that it reached its limit in the cell, well above the opening of the curved glass tube. Pressure was increased on the end of the curved glass tube which extended from the observation cell. This caused the aqueous phase contained in the curved glass tube to project into the methylene iodide. The gas bubble on the end of the hollow glass tube could then be brought into contact with the saturated aqueous phase in the saturated methylene iodide. Since two approximately spherical masses were brought into contact in a third phase through which the angle is acute, considerable care had to be exercised to secure a profile which outlined the actual equilibrium angle. To be sure that the profiles of the gas and the aqueous phases were in the same vertical plane, a low power microscope was used for observation of the system, while the gas bubble and the aqueous phase were brought into contact. Plate 2 is a photograph of sample 4 at 25°.

The profile outlining  $\beta_e$ , the equilibrium angle through the gas phase, can be secured as indicated in Plate 3. A curved glass tube containing the

saturated methylene iodide was placed in the cell. Enough of the aqueous phase and of the saturated organic liquid were added to the cell so as to permit the mutual existence of an appreciable area of water-air and methylene iodide-air interfaces right up to the opening of the curved glass tube containing the saturated methylene iodide. A hollow glass tube sealed to a glass rod was filled with the saturated aqueous phase and lowered into the observation cell. Enough of the saturated aqueous phase was added with a curved pipet to the bottom of the hollow glass tube to form a hanging drop. Pressure was increased on the end of the curved glass tube which extended from the cell. This caused the saturated methylene iodide contained in the curved glass tube to project into the gas phase. Keeping the system under observation through a low power microscope, to ensure that the profiles of the aqueous phase and the organic liquid were in the same vertical plane at contact, the two liquid phases were brought together in the gas phase. The glass cell was then covered, the systems under investigation left in the dark, and photographed about twenty hours later. In this manner errors due to profile position and to unsaturation were minimized. Plate 3 is a photograph of sample 3 at 28°.

The image of the interfaces outlining the angles were brought to focus at lines marking the center of the ground glass focusing screen, after which the systems under investigation were photographed.

At each of the three temperatures noted,  $\theta_e$ ,  $\phi_e$  and  $\beta_e$  were determined on samples 1, 3 and 4. On sample 2 only the angles through the aqueous phase and the gas phase were studied.

The equilibrium angles through each of the phases, determined from the photographed images by lines parallel to the interfaces at their mutual edge, were measured directly with a protractor. Within the experimental precision of the measurement of the angles, or as determined by superimposing the photographed images, the respective angles were the same, reproducible when measured at different times, and independent of the temperature over the range studied.

The values of the angles, determined by direct measurement, were  $\theta_e = 137.6 \pm 0.9^\circ$ ,  $\phi_e = 75.9 \pm 1.2^\circ$ , and  $\beta_e = 146.2 \pm 1.7^\circ$ .<sup>17</sup> The sum of the mean values,  $359.7^\circ$ , indicates close agreement of the mean to the actual values of the angles.

From equation 3 and the measured values of the angles,  $\theta_e$ ,  $\phi_e$ , and  $\beta_e$ , it was found that<sup>18</sup>

$$\begin{aligned} (a) \quad \sigma_{2,3}/\sigma_{1,3} &= 0.695 \\ (b) \quad \sigma_{1,2}/\sigma_{1,3} &= 0.573 \\ (c) \quad \sigma_{1,2}/\sigma_{2,3} &= 0.825 \end{aligned}$$

In Table I these relative values are compared with those of previous workers. In the paper by Harkins and Feldman<sup>16</sup> data are not given for the tensions of the saturated water-air and saturated methylene iodide-air interfaces. The tension of the methylene iodide-water interface, of the mutually saturated system, reported in the paper by Harkins and Feldman is, therefore, compared with the tensions of the saturated liquid-air interfaces as reported in the paper by Harkins.<sup>12</sup>

TABLE I

	$\frac{\sigma_{2,3}}{\sigma_{1,3}}$	$\frac{\sigma_{1,2}}{\sigma_{1,3}}$	$\frac{\sigma_{1,2}}{\sigma_{2,3}}$	Temp., °C.
This investigation	0.695	0.573	0.825	20 25 28
Carter and Jones <sup>15</sup>	.728	.565	.775	25
Harkins <sup>12</sup>	.697	.635	.908	20
Harkins and Feldman <sup>16</sup>	...	.672	.960	20
Jasper <sup>10</sup>	.692	.628	.909	28.3

A conservative estimate of the precision of the method, determined by assuming an error of  $\pm 2^\circ$  in the measurement of each of the angles, and by adding the percentage errors of the numerator and denominator calculated from this deviation, would place the relative values  $\sigma_{2,3}/\sigma_{1,3}$ ,  $\sigma_{1,2}/\sigma_{1,3}$  and  $\sigma_{1,2}/\sigma_{2,3}$  in doubt by about 4.7, 6.1 and 9.1%, respectively.

For the relative value  $\sigma_{2,3}/\sigma_{1,3}$ , Harkins<sup>12</sup> and Jasper<sup>10</sup> agree with each other. Their values differ from that of Carter and Jones<sup>15</sup> by from about 4.2 to 5.0%.

For the relative value  $\sigma_{1,2}/\sigma_{1,3}$ , Harkins and Jasper also agree fairly well with each other. Their values differ from that of Carter and Jones by from about 12.4 to 11.1%.

For the relative value  $\sigma_{1,2}/\sigma_{2,3}$ , Harkins and Jasper are in agreement with each other. Their values differ from that of Carter and Jones by about 17.2%.

The tension of the methylene iodide-water interface, of the mutually saturated system, re-

(17) The value given for each angle represents the mean and a. d. of twenty measurements, five from each of four different plates.

(18) 1 = the saturated aqueous phase; 2 = the saturated methylene iodide; 3 = the saturated gas phase.

ported in the paper by Harkins and Feldman<sup>16</sup> is about 5.7% higher than the value reported in the paper by Harkins.<sup>12</sup>

The relative value  $\sigma_{2,3}/\sigma_{1,3}$ , reported by other workers is in good agreement with that determined in this investigation by the measurement of the angles. The relative value  $\sigma_{1,2}/\sigma_{1,3}$ , of Carter and Jones is also in good agreement with that determined in this investigation. A decrease of about 2.5 dynes/cm. in the reported value of Carter and Jones for the tension of the methylene iodide-air interface, of the mutually saturated system, would bring their other relative values into good agreement with the results of this investigation. In view of the high density of the methylene iodide, a deviation of that magnitude in the determination of these relative values by capillary measurements is not excessive.

A decrease of about 4.5 dynes/cm. in Harkins'<sup>12</sup> reported value for the tension of the methylene iodide-water interface, of the mutually saturated system, would bring his relative values into agreement with the results of this investigation.

**Acknowledgments.**—It is a pleasure to thank Professor Arthur W. Thomas, who encouraged, stimulated and sponsored this investigation; also the Administration of the City of New York, Police Commissioner Lewis J. Valentine, First Deputy Commissioner Louis F. Costuma and Chief Inspector John J. O'Connell, of the New York City Police Department, for permitting the working arrangements which made the conduct of this research possible.

### Summary

1. For a mutually saturated three phase fluid system meeting at a common edge, methods are presented for the direct determination of the equilibrium angles through each of the three fluid phases.

2. The validity of the fundamental relationships

$$\begin{aligned} 0 &= \sigma_{1,2} + \sigma_{1,3} \cos \theta_e + \sigma_{2,3} \cos \phi_e \\ 0 &= \sigma_{1,3} \sin \theta_e - \sigma_{2,3} \sin \phi_e = \sigma_{1,2} \sin \beta_e - \\ &\quad \sigma_{1,2} \sin \phi_e = \sigma_{2,3} \sin \beta_e - \sigma_{1,2} \sin \end{aligned}$$

in their application to the mutually saturated methylene iodide-water-air system is demonstrated.<sup>19</sup>

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(19) In this connection it should be noted that notwithstanding the fact that the vector sum of the tensions of the interfaces is zero at equilibrium, it is also apparent from these experiments (see Plate 1), that there exists a force after equilibrium with regard to the surfaces of discontinuity has been established, which prevents the methylene iodide from sliding off the gas phase. This will be discussed in another article.