the weight of the sample vaporized, will be the required molecular weight.

In carrying out molecular-weight determinations by this method, it is of course important that all connections be air-tight. Certain devices in use for dropping the sample make this difficult. The best method is to let the capsule containing the sample rest on an iron wire projecting from the delivery tube into the vertical stem of the vaporization tube. When all connections have been made tight and the pressure in the apparatus has been somewhat decreased by lowering *C*, the sample is dropped by moving the wire with a magnet.

Illustrative Results.

M. V. Del Rosario very kindly carried out a number of determinations with the instrument that has been described, and reports the following results:

Determination of Nitrogen in Potassium Nitrate:

Reaction carried out in tube *A*.

C. P. sample recrystallized and dried at 110°.

$T = 302.5°$; $P = 762.5$ mm.; $k = 2$; $W' = 226.7$.

Results: 13.82%, 13.96%, 13.81%, 13.72%, 13.78%, av. 13.81%.

Calc. 13.75%.

Determination of Hydrogen Peroxide:

Commercial sample.

$T = 302°$; $P = 764$ mm.; $m = 2$; $W' = 276.3$.

Results: 2.79%, 2.79%.

Duplicate determinations by titration with potassium permanganate solution, standardized with oxalic acid, gave 2.79%.

Determination of Carbon Dioxide in Calcium Carbonate:

C. P. reprecipitated sample, dried at 110°.

$T = 301°$; $P = 764.5$ mm.; $m = 2$; $W' = 358.8$.

Results: 44.11%, 44.16%, 43.76%, av. 44.01%.

Calc. 44.00%.

Summary.

This paper describes a gas-volumeter in which a tube graduated in terms of the weight of sample has been substituted for the correction tube of the Lunge gas-volumeter. This instrument reads directly in percentages of any desired constituent, for any weight of sample, no matter what the nature of the substance analyzed.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 303.]

THE SURFACE TENSIONS OF THE CO-EXISTING LAYERS OF SYSTEMS OF MUTUALLY SOLUBLE LIQUIDS.

BY J. LIVINGSTON R. MORGAN AND WARD V. EVANS.

Received July 24, 1917.

The object of this investigation was to secure accurate data in regard to the surface tensions of the separate layers of some of those non-homogeneous liquid systems in which the concentrations of the two co-existing layers automatically adjust themselves with temperature. The literature contains but few results of surface tension for such systems, the only workers of importance apparently being Antonow[1] and Whatmough,[2] whose results are decidedly discordant.

The tip used to determine the surface tension, using the drop-weight method,[3] was standardized by the use of specially purified benzene with the following result, each drop-weight value being the mean of at least three results agreeing to within a few hundredths of one per cent.:

TABLE I.—BENZENE.

t.	Wt. 1 drop. (Mg., w.)	Surface tension. (Dynes, γ.)	Constant ($= \gamma/w$).
25°	28.628	27.263	0.9523
30°	27.944	26.625	0.9528
35°	27.284	25.991	0.9526
			Av., 0.9526

The values of the surface tensions of benzene (γ) employed here were calculated to the temperature of the drop-weight determinations by the acid of the formula

$$\gamma_{C_6H_6,\, t} = 30.514 - 0.1321t + 0.000082t^2,$$

found by the method of least squares, and which represents the average of the results of the investigators who have studied this liquid by the capillary-rise method. To find the surface tension of any proper liquid in dynes per cm. from the drop weight in mg., at the same temperature, from this tip, then, we have:

$$\gamma_{l,t} = 0.9526\ w_{l,t}{}^{4}$$

The tip was found to give normal drop profiles with all the liquids employed, as it must if the above equation is to be used.

Experimental Results.

The sample of phenol was the same as that used by Morgan and Egloff. It was twice redistilled under reduced pressure and recrystallized, its melting point being 39.70°.

The surface-tension values for this liquid are given in Table II, together with the values found by Morgan and Egloff.[5]

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[1] *J. chim. phys.*, **5**, 371 (1907).

[2] *Z. physik. Chem.*, **39**, 129 (1901).

[3] Morgan, THIS JOURNAL, **37**, 1462 (1915).

[4] This constant led to a result at 25° for toluene of 26.97 dynes, as compared with the value 27.00 found by Morgan and Griggs with a different tip, which will show the consistency of the method. The mean diameter of the tip here is calculated, from the constant, to be approximately 5.33 mm. (see Morgan, *loc. cit.*).

[5] THIS JOURNAL, **38**, 844 (1916).

TABLE II.—PHENOL.

t.	γ obtained.	γ Morgan and Egloff.
35°	38.06[1]	38.02[2]
41°	37.42[1]	37.43[1]
45°	36.97[1]	36.96[2]

The values obtained by the use of this tip are shown thus to accord very well with those of previous workers by the capillary-rise method, for the results of Morgan and Egloff were in excellent agreement with those of Worley,[3] Hewitt and Winmill[4] and Ramsay and Aston.[5]

The sample of amyl alcohol was made to order[6] for a previous piece of work. It was not redistilled for this work, as it gave sensibly the same surface tension as that found earlier by Morgan and Neidle.[7] The surface tensions found for this liquid, together with a formula connecting surface tension and temperature obtained from them, are given in Table III.

TABLE III.—AMYL ALCOHOL.

t.	γ obs.	γ calc. (from formula below).
0°	24.47	24.45
30°	22.26	22.26
50°	20.78	20.79

$$\gamma_{\text{amyl alcohol}} = 24.450 - 0.07308t \quad (0° \text{ to } 50°).$$

The sample of triethylamine used in the work was an especially pure one and was twice redistilled, the second distillation not changing the surface tension. The values of the surface tension at various temperatures are given in Table IV.

TABLE IV.—TRIETHYLAMINE.

t.	γ obs.	γ calc. (from formula).
0°	22.00	21.99
10°	21.00	20.99
20°	19.96	19.99
30°	18.99	18.99
40°	18.02	18.00

$$\gamma_{(C_2H_5)_3N} = 21.987 - 0.09970t \quad (0° \text{ to } 40°).$$

The two-layer systems (phenol–water, amyl alcohol–water, and triethylamine–water) in each case were made up of the purified liquid with specially purified water, taking about equal parts of each, and making additions of one or both of the constituents from time to time during the work as was necessary in order to keep both layers present. The system composed of two layers was then placed in a bottle, suspended in a temperature bath held constant to 0.05°, a certified thermometer being used.

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[1] Direct observation.

[2] Calculated from the equation $\gamma_{C_6H_5OH,\, t} = 41.701 - 0.1053t$.

[3] *J. Chem. Soc.*, **105**, 267 (1914).

[4] *Ibid.*, **91**, 446 (1907).

[5] *Ibid.*, **65**, 168 (1894).

[6] By the Hoffman and Kropff Chemical Co.

[7] THIS JOURNAL, **35**, 1856 (1913).

The ordinary form of supply vessel was not used on the drop-weight apparatus in this work, as it was found necessary, with such systems, in order to be certain that they attain and retain equilibrium, to have both layers continuously present in the supply vessel, from which the one being studied can be drawn over with the least possibility of a change in temperature and consequently in concentration. This end was achieved by the use (in place of the supply vessel on the plug of the apparatus)[1] of a small cup of about 25 cc. capacity, placed on the bottom of the large outer vessel, which is used in general to prevent the water of the bath from coming in direct contact with the supply and weighing vessels fastened to their respective plugs. This cup was so fixed that it could be raised or lowered to such an extent that the supply end of the ∩-shaped dropping tube could be made to dip into either layer of the system desired. Further, the cup was provided with an L-shaped stirring rod (passing through the large tube entering the large outer air vessel and originally intended for a thermometer) by the revolving of which at intervals the attainment of final equilibrium could be hastened.

For the determination of the drop weight of either layer, then, of the two-layer system, this supply cup was filled with the gently shaken system from the bottle, always kept in the thermostat at the temperature to be studied, and the apparatus set up, the cup being elevated so that the supply end of the dropping tube entered the vessel to that point occupied by the layer to be studied. The mixed liquids were then allowed to segregate into two layers, being stirred at intervals, and the drop weights found by combinations of 30-drop determinations with 5-drop blanks. This gave the weight of 25 drops, free from all loss by evaporation.

In addition to the two-layer systems studied, it seemed of interest to extend somewhat the work of Morgan and Egloff on homogeneous solutions of phenol and water, of known and fixed content, in order to settle more certainly the effect of small amounts of water added to phenol at various temperatures, as that work left some slight uncertainty perhaps in that one region of the curve.

In Tables V, VII and VIII are given the results of surface tension, against air saturated with vapor, for the two layers which co-exist at various temperatures in the three systems studied, as well as the values for that pure component (toward which the γ values of the layers tend) at like temperatures. Each result here is the mean calculated from at least three drop-weight determinations, *i. e.*, at least three each of a 30-drop determination and a 5-drop blank, which agreed to within a few hundredths of one per cent. In Table VI are given the new results for the homogeneous phenol–water systems of known content, as well as those of Morgan and Egloff, for comparison.

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[1] See Morgan, THIS JOURNAL, 33, 352 (1911).

TABLE V.—SURFACE TENSIONS.[1]

		Co-existing layers.	
t.	Pure phenol.	Phenol layer.	Water layer.
15°	40.121*[2]	39.402	39.201
20°	39.595*	39.003	38.851
25°	39.068	38.580	38.485
30°	38.542	38.172	38.104
35°	38.015	37.761	37.711
40°	37.489	37.322	37.330
45°	36.962	36.945	36.949
50°	36.436	36.545	36.560
55°	35.909	36.107	36.187
60°	35.383	35.703	....

TABLE VI.—PHENOL-WATER SOLUTIONS OF KNOWN CONTENT.

% = g. of water per 100 g. of mixture.

t.	% = 0. γ.	% = 1.77. γ.	% = 4.68. γ.	% = 13.76. γ.
25°	39.07	...	39.16†[3]	...
30°	38.54	...	38.65†	...
35°	38.01	...	38.15†	...
40°	37.49	...	...	...
45°	36.96	37.03†	37.13†	37.16†

t.	% = 16.14. γ.	% = 23.40. γ.	% = 26.00. γ.	% = 29.6. γ.
25°	...	...	...	...
30°	38.51†	38.29	38.22	38.09
35°	...	37.89	37.83	37.72
40°	...	37.50	37.41	37.33
45°	37.14†	37.08	36.99	36.96

TABLE VII.—AMYL ALCOHOL.

		Co-existing layers.[4]	
t.	γ amyl alcohol.	γ alcohol layer.	γ water layer.
0°	24.45	24.25	26.40
15°	23.35	23.25	25.72
25°	22.62	22.57	25.22
25°	21.89	21.90	24.80
45°	21.16	21.24	24.36
55°	20.43	20.58	23.90

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[1] The total number of drop-weight determinations, 30's and 5's, made and used in the preparation of this table was two hundred and five, the system being brought to equilibrium before each determination.

[2] The starred values for phenol are extrapolated values, the others being interpolated from the Morgan and Egloff formula $\gamma_{C_6H_5OH} = 41.701 - 0.1053t$ (t equal to 23 to 60°), tested in Table II.

[3] The marked values are new experiments, the others are taken from Morgan and Egloff.

[4] One hundred and ten drop-weight determinations were necessary for the preparation of this table.

TABLE VIII.—TRIETHYLAMINE.

		Co-existing layers.[1]	
t.	γ triethylamine.	γ amine layer.	γ water layer.[2]
25°	19.49	20.38	22.37
30°	18.99	19.75	23.54
35°	18.50	19.11	24.15
40°	18.02	18.51	26.08
45°	17.50	17.93	27.52

The Establishment of Equilibrium in the Systems.

The three two-layer systems selected for study in this work were chosen because of their characteristic differences in behavior in regard to changes in temperature; differences which make them representative, practically, of all such systems possible.

Phenol-water systems,[3] for example, exist in two layers only *below* a certain definite critical solution temperature, above which the components are completely miscible in all proportions, to form homogeneous solutions. The co-existing layers of such non-homogeneous systems, in general, have concentrations of the two components which are fixed automatically by the temperature and are unlike, except in the immediate vicinity of the critical solution point. In the case of this particular system, the concentration of each component in the other's layer increases with increasing temperature, up to the critical solution point.

Triethylamine and *water*,[4] on the other hand, form two-layer systems only *above* a certain fixed critical solution temperature, 18.5°, below which the components are miscible in all proportions to form homogeneous solutions. In the case of the two-layer systems here, the water dissolves a *decreasing* amount of the triethylamine with increasing temperature above the critical point, while the concentration of water in the triethylamine layer remains practically constant at all temperatures above one about 5° beyond its critical solution point, having decreased very suddenly in that interval.

The *amyl alcohol–water* system, finally, is one which forms homogeneous solutions in all proportions at temperatures above a certain fixed point, similar to that of phenol and water, but the water layer in this case at temperatures below this point contains a decreasing amount of amyl

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[1] One hundred and twenty-five drop-weight determinations were necessary for the preparation of this table.

[2] These results are by no means of the same order of accuracy as the others presented, differences in successive results as high in some cases as 0.8 dyne being found, though they were generally smaller. At any rate, these results being an average, can be taken as giving a band of the width of less than 0.4 dyne in place of a sharp line, and will be sufficient to show the trend of the curve.

[3] See Rothmund, *Z. physik. Chem.*, **26**, 433 (1898).

[4] See Rothmund.

alcohol with increasing temperature,[1] the amyl alcohol layer showing an increasing amount of water with rising temperature, up to the critical point.

In general, the last two-layer system which can exist immediately before an infinitesimal change in temperature causes the system to be transformed into a homogeneous one, is characterized by the fact that the two layers become identical in composition. In consequence of this, the trend of the magnitude of the content of each component in the other's layer can usually be predicted from a state of known concentration and the direction of the temperature change necessary to attain the critical point.

The greatest difficulty encountered in work of this sort lies in obtaining at the desired temperature, a stable equilibrium of the two layers as they co-exist in the supply cup. The only criterion of equilibrium at any one temperature we have here is the constancy and reproducibility of the drop weights obtained, especially when new samples of the same mixed liquids are substituted for the old in the cup.

The non-aqueous layer, as a rule, gave little trouble, the drop weights being reproducible for any system at any one temperature with great exactness, even when the system was prepared in several different ways.

The aqueous layer, however, gave considerable trouble throughout, although a general procedure was found which led to results which, with one exception, are to be regarded as burdened with only the same very slight error as those of the non-aqueous layer.

The reason for this difference in the behavior of the two layers of such systems, in regard to the speed and ease with which they are obtained in stable equilibrium, judged by the surface-tension result, is not difficult to grasp. For as Morgan and Egloff have shown, the water layer is always on, or just off, the steepest part of the concentration—surface-tension curve, so that under- or supersaturation shows its effect in an exaggerated way on the surface tension. The non-aqueous layer, on the other hand, lies in that region where the slope of the concentration—surface-tension curve is almost imperceptible, so that under- or supersaturation would not be so sharply indicated by the surface tension. In addition to this, however, there is a reason for the difference in behavior of the layers which can be noticed visually, *viz.*, the water layer shows the existence of emulsions which are much more persistent than any appearing in the other layer, and which, also, are more difficult to avoid.

The existence of equilibrium, in certain cases, can be predicted, even as the first drop of the aqueous layer is run over, and is always confirmed

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[1] This is true for the region studied in this paper. At a higher temperature, however, after having passed through a minimum at 80°, the amyl alcohol content increases with increased temperature, as it must of course, if the two layers are later to be of identical composition.

by the obtaining of reproducible drop weights. This visual test of equilibrium is the gradual appearance of a cloudiness in the first clear drop when it is run over and allowed to hang to saturate with vapor the empty weighing vessel in which the fallen drops will ultimately be collected. The drop in this case is simply drawn back into the supply cup and brought over again, etc., the process being repeated until a clear drop as brought over remains clear. This cloudiness, naturally, is due to the change in the composition of the layer caused by the evaporation, and would only appear when the liquid previous to the drawing over had been really saturated. Later, when the drop is brought over again, the weighing vessel now being saturated with the vapor, no further evaporation takes place, and the composition of the liquid remains what it was in the equilibrium present in the supply cup. When this cloudiness fails to appear, in these cases, it is observed that the drop weights are not reproducible.

The production of a cloudy layer in preparing the system not only depends upon the amount and violence of the shaking to which the system is subjected, but also the direction of the temperature change of the system when it is removed from the main supply to the supply cup of the apparatus. No matter how this change is made, since the supply cup must be placed in the apparatus at room temperature, there must be a change in temperature which will change the equilibrium which has already been established in the supply bottle. Naturally, when working at or near the room temperature itself, this change is negligible, and the same equilibrium state existing in the bottle is carried over unchanged to the supply cup.

When the temperature of observation was higher than room temperature, with the phenol–water system, the temperature was momentarily lowered in transferring the liquid and setting up the apparatus, and consequently less of each component was present in the other's layer than would have been if the temperature had been unchanged. This, naturally, would cause the value of the surface tension of the water layer to be too high at first. Many hours (10) in such cases were necessary to complete the saturation and lead to reproducible drop-weight results.

At temperatures below room temperature with this system, the equilibrium was raised in temperature during the transfer, and consequently the first results, not reproducible, were too low for the water layer; but, again, continued standing produced constant, reproducible results. Persisting emulsions in the water layer were a source of great trouble at times. At the crossing point of the two layers, in fact, where the surface tensions, as well as the densities, were alike, they often persisted for 24 hours. This can be avoided partly by not shaking the equilibrium in the supply bottle (just before its transfer to the supply cup) vigorously enough to disperse the layers in too fine a state of subdivision, although mixing thoroughly.

The emulsions produced by the change in temperature, on the other hand, were found to clear by the gentle stirring of the system in the supply cup with its enclosed stirrer. Even after this, however, the system had to remain standing for some time before reproducible drop weights are obtainable. All the results for this system, given above, were obtained from equilibrium states which were reproducible from either side, as respects temperature, and consequently are to be taken as of permanently persisting states.

With the *amyl alcohol–water* system, again little trouble was experienced with the non-aqueous layer. The water layer, however, gave the same difficulties described above for phenol–water, except that here supersaturation phenomena, at the lower temperatures, were not common, and a result could be obtained rapidly by going from a low to a higher temperature. In the opposite direction, from a high to a lower temperature, as much as 12 hours were required to attain saturation. Again, here, the results are those reproducible ones obtained not only from different directions in the temperature change, but also with different samples from the supply bottle.

In the case of *triethylamine and water*, the aqueous layer only caused trouble, but that in such an exaggerated form that the results obtained can only be regarded as an average and to represent a band rather than a line on the plot.

When a drop of the water layer here is first carried over it seems to form two layers; at least globules of a second layer appear, in the drop, which falls before it assumes its true form, the later irregularity in size of drop being plainly apparent to the eye. This solution, in fact, is the most sensitive to temperature changes of any investigated, for a change of even 0.05° causes a cloudiness to appear. When the solutions were brought from a high to a lower temperature no reliable results could be obtained, as saturation could not readily be secured.

The concentration here changes very rapidly with the temperature, and the slope of the concentration-surface-tension curve at any one temperature is very steep. These two factors seem to be the cause of the difficulty. Thus the concentration of triethylamine in water changes from 7.3% to 15.5% between 20° and 25°, a change in concentration of 0.16% for a change of 0.1°, while Morgan and Egloff have shown that a 4.79% solution of triethylamine lowers the surface tension of water from 72.82 to 31.78 dynes per cm. at 19.20°, a lowering of 41.04 dynes per cm.

Granting these quantities to be proportional, it would mean that a change of 0.1° in temperature would effect the surface tension by 1.4 dynes per cm. At 25°, the lowest temperature at which it was found possible to get workable solutions, and where of course this depression would be less per 0.1°, the lowest value for the surface tension was 22.95, the highest being 23.78, a difference of 0.83 dyne per cm.

All the results given for this layer are the means of at least ten and in some cases of twenty-five determinations.

Antonow also found great trouble with one of the layers of the aniline-amylene system, and it was the layer containing the larger percentage of the component with the higher surface tension, just as in this work.

Discussion of the Results.

Treating the results in Tables V, VII and VIII by the method of least squares, we find the equations accurately representing the results to be:

$$\left\{\begin{array}{l}\text{Phenol } \gamma_t = 41.701 - 0.1053t \quad (23° \text{ to } 60°);\\ \text{Phenol layer } \gamma_t = 40.636 - 0.08218t \quad (15° \text{ to } 60°);\\ \text{Water layer } \gamma_t = 40.367 - 0.07595t \quad (15° \text{ to } 55°);\end{array}\right.$$

$$\left\{\begin{array}{l}\text{Amyl alcohol } \gamma_t = 24.450 - 0.07308t \quad (0° \text{ to } 50°);\\ \text{Amyl alcohol layer } \gamma_t = 24.248 - 0.06685t \quad (0° \text{ to } 55°);\\ \text{Water layer } \gamma_t = 26.391 - 0.04348t \quad (0° \text{ to } 55°);\end{array}\right.$$

$$\left\{\begin{array}{l}\text{Triethylamine } \gamma_t = 21.987 - 0.0997t \quad (0° \text{ to } 40°);\\ \text{Triethylamine layer } \gamma_t = 23.426 - 0.1226t \quad (25° \text{ to } 45°);\\ \text{Water layer } \gamma_t = 15.747 + 0.2568t \quad (25° \text{ to } 45°).\end{array}\right.$$

This last equation (the water layer of the triethylamine–water system), although representing results burdened with a greater error than the others, shows in itself, perhaps, the very cause of that error, *viz.*, its excessively high temperature coefficient. Further, the relationship is almost unique, for it shows that the surface tension *increases* with increased temperature. In other words, the loss in surface tension the layer might undergo by an increase in temperature is very much more than compensated by the loss of triethylamine (and the consequent approach to the higher value of water) in the same interval.

Before discussing the co-existing layers at equilibrium further, it will be well here to consider the effect of small additions of water to pure phenol at various temperatures (Table VI), since such data will be useful later. The results for the surface tension of homogeneous phenol–water systems, plotting them against the known concentration, are shown graphically in Fig. 1.

These isotherms would indicate that the addition of water to phenol always increases its surface tension slightly, the maximum points of the curves being sharper at the lower temperatures.

Antonow, in his work on aniline-amylene, noted the same phenomenon and states that the addition of small quantities of aniline to amylene invariably raised its surface tension, but that it soon fell again, and then remained sensibly the same. The results of Moles[1] on mixtures of iso-

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[1] *Anales de la Sociedad Espanola de Fisica y Quimica,* 9, 157 (1911).

butyric acid and water also indicate the same phenomenon when water is added to the acid, but he apparently does not observe it, or at least does not comment upon it.

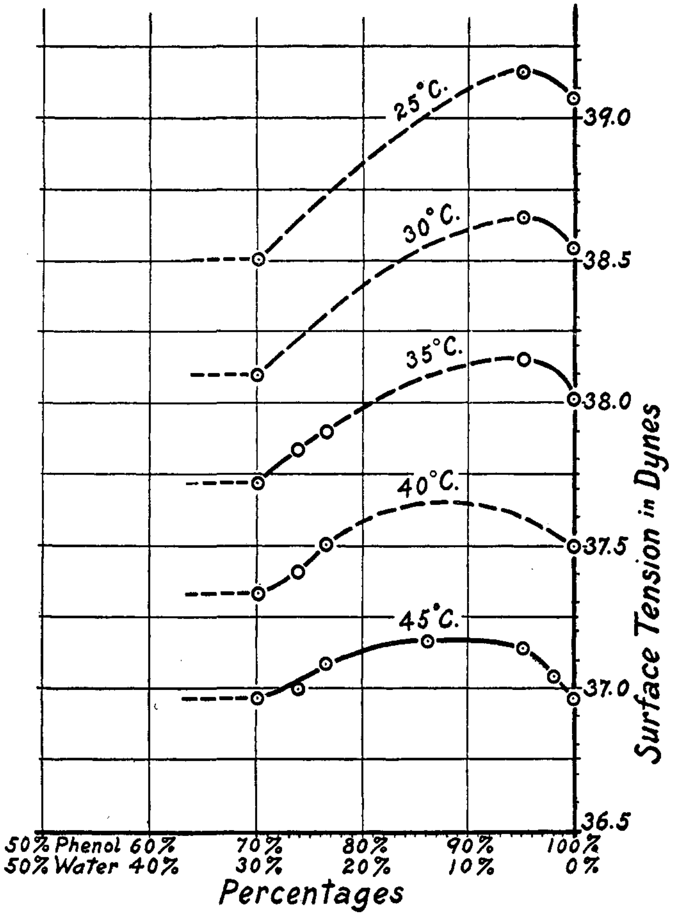

Fig. 1.

The plots representing the results for the co-existing layers (Tables V, VII and VIII) are given in Figs. 2, 3 and 4, so we are now prepared to consider the individual systems in detail.

Phenol-Water Systems.

In the case of this system, it will be noted that the crossing point of the curves representing the surface tensions of phenol, the phenol layer, and the water layer is at about 45°.[1] This is the only case in this work where the surface tensions of pure non-aqueous liquid and the two layers approach

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[1] This value naturally can be calculated from the three equations of the system

one another so closely. As will be observed, of the two layers of this system co-existing in equilibrium, the aqueous layer invariably exhibits the lower surface tension at all temperatures below 45°. Above this point, on the other hand, up to 55° at any rate, the aqueous layer exhibits the higher value of surface tension, the difference between the values increasing continuously with increasing temperature. It is well known, however, from the previous study of this system, that the content of phenol in the layers co-existing in equilibrium at any one temperature is a function of the temperature (*i. e.*, is changed automatically by the temperature), that in the aqueous layer increasing, that in the phenolic layer decreasing, until at 68.8°, the critical solution temperature of the system, the two layers become identical in composition and hence identical in all properties, the concentrations being 35.9% of phenol and 64.1% of water in each. At this point the layers, of course, become indistinguishable, and the system homogeneous.

It is evident from the above reasoning that the region studied experimentally above represents, on a surface-tension temperature plot, Fig. 2, the straighter portion of a curve for both layers, and that instead of diverging more and more, as would be indicated by an extrapolation from the linear equations, the values for the two layers, somewhere between 55° and 68.8°, where the change in concentration in each with the temperature has become excessive, begin to approach each other again, to meet and become identical at 68.8°.

In order to calculate the identical surface tensions of the two co-existing layers just before an infinitesimal increase in temperature causes them to merge into a homogeneous system; or, what is practically the same thing, the surface tension of that homogeneous system at a temperature, which if decreased by an infinitesimal amount would cause the appearance of two layers, *the law of rectilinear diameters*[1] (first used by Cailletet and Mathias for curves representing the densities of a liquid and its saturated vapor as found at co-existing temperatures, which must meet at the critical density) has been employed. This law may be stated as follows: The mean of the values of a common property, as found for two states at the various temperatures at which they co-exist, is a linear function of the temperature. Naturally, then, knowing the temperature at which the two states become indistinguishable, the mean value of the

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given above. The crossing point being the temperature of identical surface tension, it follows from the solution for t of the following equations:

$$41.701 - 0.1053t = 40.636 - 0.08218t = 40.367 - 0.07595t;$$

and is 45.6°. At this temperature the individual values of the surface tension are $\gamma_{\text{phenol}} = 36.899$; $\gamma_{\text{ph. layer}} = 36.900$ and $\gamma_{\text{water layer}} = 36.904$, all of which reduce practically to the identical value 36.90 dynes per cm.

[1] *J. physique*, [2] **5**, 549 (1886).

property of the two, which is also the value of each then, can be found by extrapolation.

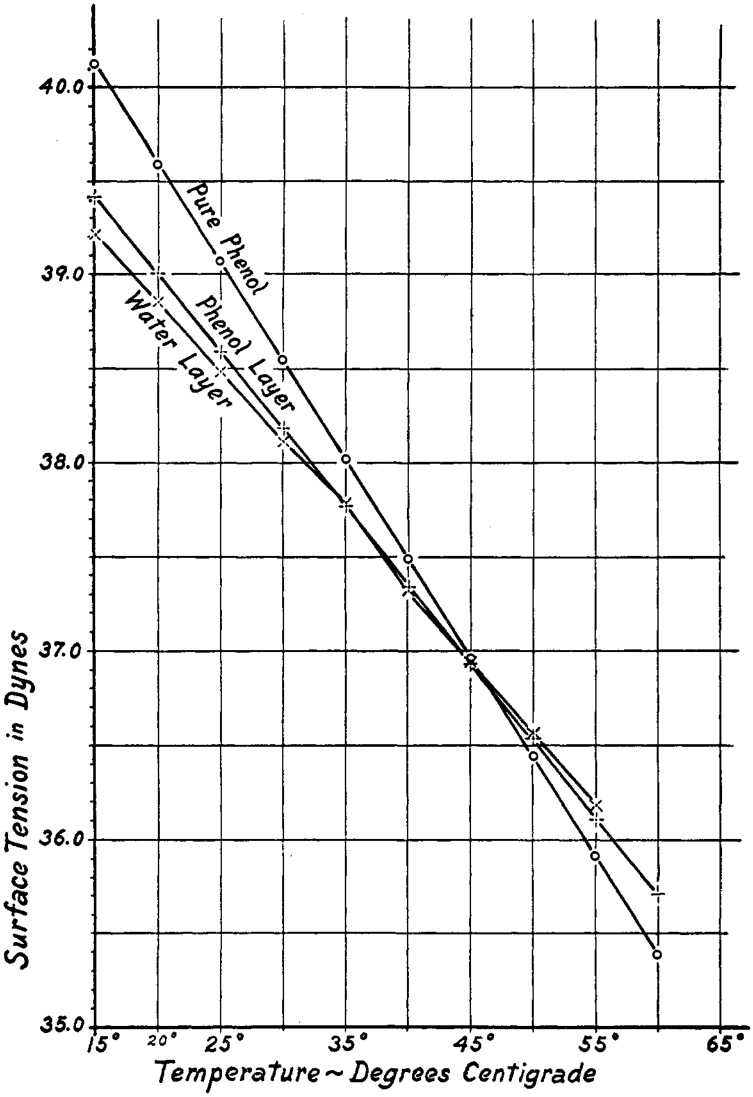

Fig. 2.

The values to be employed for the obtaining of such a linear equation for the means of the surface tensions of the co-existing layers of the water–phenol system, *i. e.*,

$$\frac{\gamma_1 + \gamma_2}{2} = A + a\,t,$$

taken from the above results are presented in the table below together with the least squares equation, and the values calculated from it:

TABLE IX.—PHENOL-WATER.

Mean surface tension of the layers co-existing at various temperatures.

t.	$\frac{\gamma_1 + \gamma_2}{2}$ obs.	$\frac{\gamma_1 + \gamma_2}{2}$ calc.	Δ.
15°	39.301	39.316	+0.015
20°	38.928	38.920	—0.008
25°	38.533	38.525	—0.008
30°	38.138	38.130	—0.008
35°	37.736	37.734	—0.002
40°	37.326	37.339	+0.013
45°	36.947	36.943	—0.004
50°	36.553	36.548	—0.005
55°	36.147	36.153	+0.006

$$\frac{\gamma_1 + \gamma_2}{2} = 40.502 - 0.07908t \quad (15^\circ \text{ to } 55^\circ)$$

The excellent holding of the equation here is indicated by the fourth column.

At 68.8°, the critical solution temperature of this system, the common value of the surface tension of the two co-existing layers is found by aid of this equation to be 35.061 dynes per cm. Although this is an extrapolation of 13.8°, it must be remembered that it is certainly as accurate as an interpolation from a equation referring simply to one layer, for this equation is obtained from two other equations and the quantity found indicates the common melting point of the lines representing the two.

It is now possible to consider the individual co-existing layers from the point of view of content of phenol and surface tension. Using the concentrations at various temperatures (as given by Landolt-Börnstein-Roth, "Tabellen," 1912, p. 592) and recalculated at every five degrees from the work of Rothmund) and the above experimental values of surface tension, we can arrange the following table:

TABLE X.—PHENOL-WATER.

	Phenolic layer.		Aqueous layer.			
t.	γ.	c_{ph}.	c_{ph}.	γ.	$\frac{c_1 + c_2}{2}$.	$\frac{\gamma_1 + \gamma_2}{2}$.
35°	37.76	68.28	9.34	37.71	38.810	37.735
40°	37.32	66.81	9.78	37.33	38.295	37.325
45°	36.95	65.02	10.62	36.95	37.820	36.950
50°	36.55	62.83	12.08	36.56	37.455	36.555
55°	36.11	60.18	13.88	36.19	37.030	36.150

Treating these results for concentration and surface tension by the law of rectilinear diameters, the following equation is obtained involving the variation in the *mean* of the concentrations of phenol in the two layers with a change in the *mean* of their surface tensions, as they co-exist at any one temperature. The surface tension here cannot be treated as the temperature was above, but only as a mean, as usually it is not the same for the two layers.

$$\frac{c_1 + c_2}{2} = -2.742 + 1.0997\left(\frac{\gamma_1 + \gamma_2}{2}\right).$$

When the value of surface tension 35.061, found above, is substituted for $(\gamma_1 + \gamma_2)/2$, in this equation it leads to a value of the concentration of

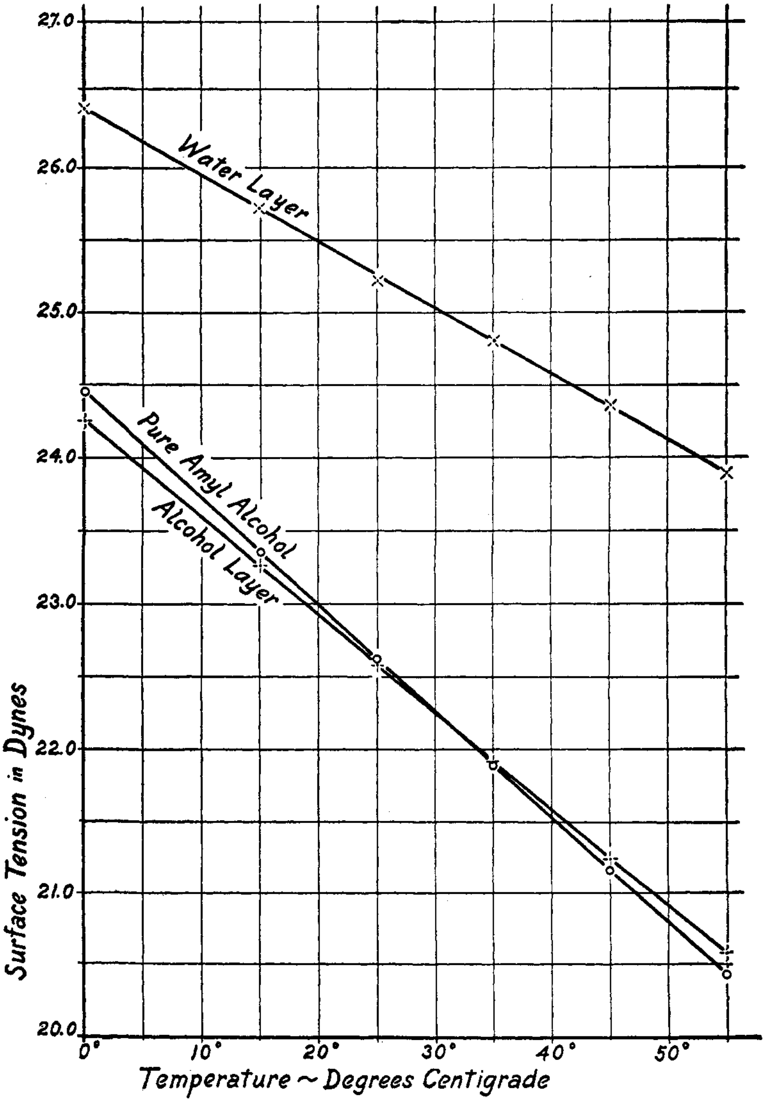

Fig. 3.

phenol (*i. e.*, $(c_1 + c_2)/2$) of 35.82%, as compared to the value 35.90%, usually accepted as the content of phenol in each layer just as the two layers become homogeneous at 68.8°.

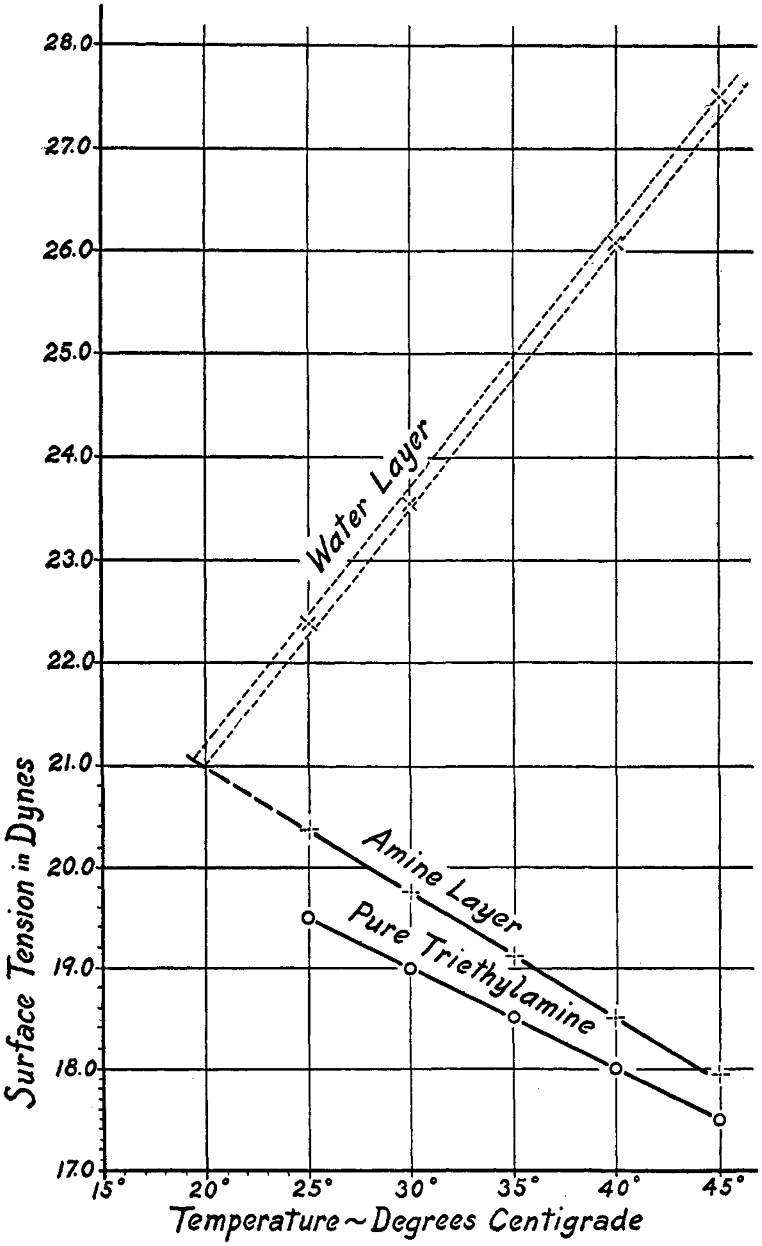

Fig. 4.

From what has been observed directly, together with the concentrations in the layers and the quantities calculated with very considerable accuracy, above, it is now possible for us to plot a *complete* diagram showing the relationships existing between concentration and surface tension in both co-existing layers of the water–phenol system. The data used in this curve are accumulated in the following table, where although the coördinates are concentration and surface tension, the temperatures to which they correspond are also given in the interest of complete information:

TABLE XI.—DATA FOR CURVES REPRESENTING $c_{ph.}$ AND γ.

	Phenolic layer.			Aqueous layer.	
t.	γ(dynes).	$c_{ph.}$%.		$c_{ph.}$%.	γ(dynes).
20°	39.00	72.24	...	8.40	38.85
25°	38.58	71.38	...	8.71	38.49
30°	38.17	69.95	...	8.92	38.10
35°	37.76	68.28	...	9.34	37.71
40°	37.32	66.81	...	9.78	37.33
45°	36.95	65.02	...	10.62	36.95
50°	36.55	62.83	...	12.08	36.56
55°	36.11	60.18	...	13.88	36.19
60°	35.70	56.10	...	...	...
68.8°	35.06	...	35.90	...	35.06

It has been possible to obtain equations for the curves of both layers in terms of surface tension and concentration of phenol, which hold very accurately for the points on the curved portions, although not so satisfactorily for those on the straighter portion. From these equations it has thus been possible to interpolate values lying upon the curves. Drawing lines through all these points then produces the curve shown in Fig. 5, the line of rectilinear diameters intersecting the curves at their meeting point, the critical solution temperature of the system, *i. e.*, the point of equal concentration and equal surface tension of the two layers. The equations mentioned above as found for the two branches of the curve are

$c_{ph.} = -19131.62 + 785.514\gamma + 0.6704\gamma^2 - 0.213400\gamma^3$ (phenolic layer)

and

$c_{ph.} = 216555.79 - 17704.8851\gamma + 482.61905\gamma^2 - 4.38612\gamma^3$ (aqueous layer)

when $c_{ph.}$ in both cases represents the number of g. of phenol in 100 g. of the layer.

The average content of phenol in the two co-existing layers, by the law of rectilinear diameters, being a linear function of the temperature, it is now possible from the Landolt-Börnstein-Roth figures above to derive a quantitative equation by aid of least squares. This relation is

$$\frac{c_1 + c_2}{2} = 42.185 - 0.0936t,$$

or, expressed for the summation of the concentration of phenol in the two co-existing layers,

$$c_1 + c_2 = 84.37 - 0.1872t.$$

If it is desired now to find the individual surface tensions of the two co-existing layers at any desired temperature between 55° and 68.8°, for example, we simply have to proceed as follows: (1) Find $c_1 + c_2$ for the desired temperature from the above equation. (2) Find $\gamma_1 + \gamma_2$ corresponding to this $c_1 + c_2$ by the equation $c_1 + c_2 = -5.484 + 1.0997 (\gamma_1 + \gamma_2)$. (3) Knowing $c_1 + c_2$ and $\gamma_1 + \gamma_2$ and the individual equations relating c_1 to γ_1 and c_2 to γ_2 find the individual values of c_1, c_2, γ_1 and γ_2.

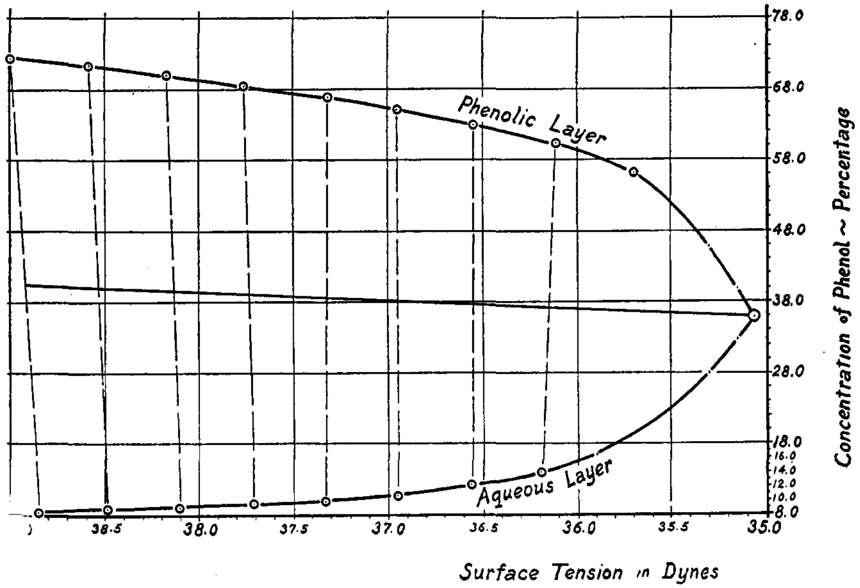

Fig. 5.

The simplest way of doing this is on a plot like Fig. 5 on a large scale. Since from $c_1 + c_2$ and $\gamma_1 + \gamma_2$ we can find $(c_1 + c_2)/2$ and $(\gamma_1 + \gamma_2)/2$, we have at once on the line of rectilinear diameters, the point through which a line must be drawn, and which by its intersection with the curves will give the individual values of c_1, c_2, γ_1 and γ_2 such as will produce the necessary values of the terms $c_1 + c_2$ and $\gamma_1 + \gamma_2$. Working in this way with the plot and checking up the values take from the c_1 and γ_1 and c_2 and γ_2 equations, values of γ_1 and γ_2 can be found at temperatures beyond the range of experimental work possible here and yet with great accuracy. In this way the following surface tensions have been calculated for the two layers:

Table XII.

Phenolic layer.			Aqueous layer.	
c_{ph}.	γ.	t.	γ.	c_{ph}.
56.1	(33.70)[1]	60°	35.84	17.1
47.2	35.35	65°	35.40	25.0
42.0	35.20	66°	35.26	30.0
39.8	35.14	67°	35.16	32.0
35.9	35.06	68.8°	35.06	35.9

This furnishes, then, a complete survey of the surface-tension-concentration-temperature relationship of the component and co-existing layers of the system phenol–water.

Amyl Alcohol–Water Systems.

With the amyl alcohol system little further can be brought out than that already shown by the experimental results themselves. As the concentration of amyl alcohol in the aqueous layer in the region studied is decreasing continuously with increased temperature (later to pass through a minimum and then to increase with temperature) and since the critical solution temperature 187.5° is so very far away from the experimental temperatures, there are not sufficient data available to apply the law of rectilinear diameters. In the region studied, although the surface-tension-temperature curves for pure amyl alcohol and the amyl alcohol layer (Fig. 3) lie near together, the curve for the water layer is very considerably removed. The two curves representing the layers diverge with increased temperature as would be expected, since the alcoholic content of the water layer is decreasing in the region studied. After passing through the *minimum* alcoholic content, however, they must again converge, becoming identical at 187.5°.

Triethylamine–Water Systems.

Even though great difficulty was experienced with the water layer of this system, and the surface-tension results do not even approach in accuracy those of the other layer or of the other systems, it is interesting to apply the laws of rectilinear diameters to the results. Here it is not possible to work below 25° satisfactorily. Although this is but 6.2° above the critical solution temperature, these 6.2° correspond to a change in concentration of triethylamine, of from 51.9% to 95.2% in the non-aqueous layer, and from 51.9% to 7.3% in the aqueous layer.

The application of the law to the relationship existing between the mean surface tension of the two co-existing layers and the temperatures at which they co-exist is based upon the experimental results given above. The mean values with their temperatures are presented in Table XIII.

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[1] Experimental.

TABLE XIII.—TRIETHYLAMINE–WATER.

Mean Surface Tension of Co-existing Layers at Various Temperatures.

t.	Mean γ $\left(i.\ e., \frac{\gamma_1 + \gamma_2}{2}\right)$.
25°	21.38
30°	21.65
35°	21.63
40°	22.30
45°	22.73

The equation obtained by least squares here is

$$\frac{\gamma_1 + \gamma_2}{2} = 19.589 + 0.067t,$$

holding with an accuracy less marked than that for phenol–water, the maximum difference between the observed and calculated values being 0.3 dyne at 35°, but less than 0.12 elsewhere. Applying t = 18.8° in this equation, which is the critical solution temperature of the system, we find the mean surface tension of the two co-existing layers, which at this point is also the common value for the layers, to be approximately **20.85** dynes per cm.

In view of the uncertainty in the values of the surface tension of the water layer here, no further attempt was made to complete the survey of the system, as was done in the case of phenol–water.

The most striking result in this system is the fact that the aqueous layer *increases* in surface tension with increased temperature (Fig. 4); a unique case, as far as is known.

Summary.

The results of this work may be summarized briefly as follows:

I. By the drop-weight method applied to three characteristic two-layer systems (phenol–water, amyl alcohol–water, and triethylamine–water), the surface tensions of the individual layers, co-existing at various temperatures, have been found. Further, the effect of small and known amounts of water upon the surface tension of phenol in homogeneous solution has been studied at several temperatures.

II. It is shown that at every temperature investigated the addition of water to phenol, in homogeneous solution, invariably raises its surface tension, and that there is a certain, small amount of water which will increase the surface tension of phenol to a maximum extent, a lesser or a greater addition having less influence. The lower the temperature, the smaller is the amount of water necessary to produce this maximum change, and the sharper is the maximum of the curve representing concentration and surface tension.

III. The surface-tension-temperature curves for pure phenol, the phenolic layer and the aqueous layer, of non-homogeneous systems, are found to cross and become identical at about 45°, a point 23.8° below

the critical solution temperature. Above 45° they diverge again, however, before becoming identical once more at the critical solution temperature, where the two layers become identical. In other words, the water layer has a lower surface tension than the phenol layer up to 45°, where they are identical, and then becomes the larger with an increase in temperature, before they converge again at 68.8°. This behavior is entirely unforeseen by any theory of such systems.

By the aid of the known concentrations and temperatures of this system, through the temperature relationship of the surface tension, a complete survey of this system has become possible, by the use of which one can find the concentrations of the two co-existing layers and their surface tensions at any desired temperature.

IV. Although with the amyl alcohol–water system the surface tensions were studied at a number of temperatures, its high critical solution temperature makes it impossible to prepare a complete survey of this system.

In accord with the results of the other systems, however, it is shown that the values of the surface tension of the two layers always approach very closely that of the non-aqueous component, and have no relations apparently to the value of the other component, water.

V. With the system triethylamine–water great difficulty was experienced in studying the water layer, owing to the fact that the change in concentration with the temperature is very large, and the true equilibrium under the conditions of the experiment very difficult to attain.

Here, again, a complete survey is possible, even though not as accurate as that of the phenol–water system. The most striking thing about the water layer of this system lies in the fact that its surface tension *increases* with increased temperature, due to the loss of triethylamine with the increased temperature.

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THE REDUCTION OF SELENIC ACID.[1]

BY E. B. BENGER.

Received August 18, 1917.

Ever since the time of Mitscherlich, who discovered selenic acid, his statement[2] that selenic acid is not decomposed by hydrogen sulfide has stood unquestioned in the literature. Some observations[3] made in this

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[1] Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] *Ann. Phys.*, [1] 9, 629 (1827).

[3] Victor Lenher, private communication, Lenher and Diemer, private communication, H. H. Morris, *Proc. Wis. Acad. Sci. Arts Letters*, 19 (1917).