STUDIES IN BINARY SYSTEMS.

PART II. HEATS OF ADSORPTION FROM BINARY MIXTURES OF TOLUENE AND ACETIC ACID BY CHARCOAL AND SILICA GEL.

By J. G. Kane and S. K. K. Jatkar.

INTRODUCTION.

Numerous attempts have been made to determine the heats of wetting of solid powders of various liquids. As early as 1822, Pouillet (*Ann. Chim. et Phys.*, 1822, **20**, 141) observed this phenomenon and attributed it to capillary forces. Afterwards, many papers followed, important amongst them being those of Tate [*Phil. Mag.*, 1860, **20** (4), 508], Rose (*Ann. d. Phys.*, **73**, 1), Jungk (*Ann. Phys. u. Chim.*, 1865, **125**, 292), Linebarger (*Phys. Rev.*, 1901, **13**, 48) and Parks [*Phil. Mag.*, 1902, **4** (6), 240]; Gaudechon (*Compt. rend.*, 1913, **157**, 209); Gurwitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 805); Patrick and Grimm (*J. Amer. Chem. Soc.*, 1921, **43**, 2144); Harkins and Ewing (*Ibid.*, 1921, **43**, 1795) and Berl and Andress (*Z. Phys. Chem.*, 1926, **122**, 81). Most of the work deals with heats of wetting of a solid by different liquids and of various solids by one liquid. Various theories such as the theory of solid solution, of chemical action, friction, compression, association of molecules, surface energy-changes, etc., were put forward to explain the liberation of heat. Out of these the theory of surface energy-changes has been successfully applied by Patrick and Grimm (*loc. cit.*) and Harkins and Ewing (*loc. cit.*) for obtaining a quantitative expression of the heat effects.

All the above-mentioned papers relate only to the measurement of heat effects when a solid is wetted by pure liquids. Comparatively less work has been done in the direction of measuring the heats of wetting or the heats of adsorption from various solutions. Gore (*Phil. Mag.*, 1894, **37**, 306) observed that when silica was wetted by various aqueous salt solutions, the rise in temperature was greater in some cases, and smaller in others than that with water alone. He also found that the heat evolved does not usually vary with the amount of dissolved substance abstracted by the powder. Kruyt and van der Spek (*Kolloid Z.*, 1919, **24**, 145) measured the heats as well as the amounts of adsorption with aqueous solutions of crystal violet on moist charcoal, and found that the amount of heat evolved depended on the strength of the wetting solution. Lachs and Lachman

(*Z. Phys. Chem.*, 1926, **123**, 303) determined the heats of wetting of animal blood charcoal by aqueous solutions of the nitrates of Ni, Na, Cs, in connection with precipitation experiments. Very little work has been done regarding the heats of adsorption from binary aqueous or non-aqueous solutions in low or high concentrations.

Bartell and Ying Fu (*J. Phys. Chem.*, 1929, **33**, 1758) have measured the heats of adsorption from binary non-aqueous solutions, on sugar charcoal.

The present work was started with the main idea of finding whether the amounts of the two components of a solution, adsorbed by a solid powder, bear any relation to the heats liberated in such processes.

EXPERIMENTAL.

The Calorimetric Arrangement.—The twin calorimeter used for the heat measurements is shown in Fig. 1. The temperature was measured by copper-constantan thermo-couples, one junction of which dipped into the cold calorimeter and the other into the reaction-calorimeter. The junctions of the thermo-couples were protected by thin glass capillaries sealed at one end and bent at the other. The bent portions were joined by a piece of narrow rubber tubing. Thin oil was put in the capillary for rapid conduction of heat to the junctions. Two silvered cylindrical brass vessels (C, C) each of about 30 c.c. capacity served as the calorimeters. Known quantities of the adsorbent were sealed into thin glass bulbs. The glass stirrer in the

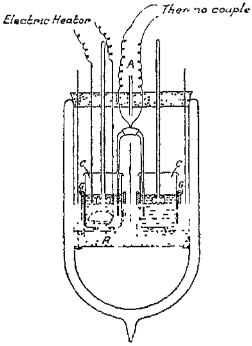

Fig. I.
Calorimetric Arrangement.

reaction-calorimeter had a pointed end for breaking the bulb. A th insulated manganin wire served as the electric heater. Its ends we brazed on to copper wires and the joints were protected by capilla glass sleeves. A protective coating of Bakelite solution was appli to the heater, which after being heated at 100° in an oven, w not affected by either toluene or acetic acid. The whole arrangeme was placed on a cork carrier (R) fitted with long glass rods, so th it could be very easily lowered into or taken out of the Dewar fla which served as the calorimetric jacket. In order to minimise t evaporation of the liquid inside, air saturated with the vapour of th liquid, was passed into the Dewar flask through (A), for a fe minutes, before beginning each experiment.

A mirror galvanometer of the suspended coil type having resistance (10 ohms), was used in conjunction with a lamp a a scale. The leads from the galvanometer to the thermo-couple we well paraffined so as to protect them from other electrical leaks. temperature difference of one degree between the cold and hot calo meters corresponded to a deflection of 25 cm. on the scale, when o thermo-couple was used. The heater could be connected to a batte supplying a steady current, which was adjusted by a variable resistanc The drop of potential across the heater was measured by means a voltmeter reading to 0.002 of a volt, the value of the resistan being found on a Post Office Box. The resistance of the heater und working conditions was further checked by passing the same heati current through a standard one ohm resistance and comparing t fall of potential across the heater, with the fall of potential across t standard resistance. The resistance of the leads of the heater, *i.* the portion not dipping into the liquid of the calorimeter was dete mined separately before they were brazed on to the heater. A co rection was applied for the lead resistance while calculating t subsequent results.

Equal volumes of the liquid or the solution were poured into t two calorimeters, the ratio between the weight of the adsorbent a the volume of the solution being the same as used in the adsorpti experiments (*cf.* Part I of this series, *This Journal,* **21A**, 331–44).

When steady conditions were attained, the bulb containing t adsorbent was broken by pressing the stirrer. The maximum deflecti as well as the time required to attain the same, was noted. Usual the total heat liberation was complete within two minutes. The coo ing correction was applied in the usual way.

The whole system was brought back nearly to its original conditi by passing cold air through the inlet tube. When steady conditio were attained, heating was started by passing a steady current throu the heater for a definite time. The value of the current and the peri of heating were so adjusted as to get nearly the same maximum deflection in the same period as obtained in the actual reaction.

The concentration changes due to adsorption in the calorimeter were found to agree with the values obtained in the regular adsorption experiments described in Part I.

(*a*) *Silica Gel.*—Heats of adsorption were measured with toluene-acetic acid mixtures. Simultaneously, the adsorption was also measured by determining the concentration of the solution in the calorimeter after the reaction was over. The results are given in Table I.

TABLE I.

1 gm. of silica: 10 c.c. solution.

ADSORPTION			HEATS OF ADSORPTION
% acid			cal./gm.
C_0	C	(C – C)	
0			17·9
2·57	1·65	1·92	21·1
12·65	10·25	2·40	23·5
39·54	37·59	1·95	26·1
57·68	56·20	1·48	26·5
100·0			30·3

The results are plotted in Fig 2. The maxima in the two curves occur at the same concentration. As acetic acid has a higher heat

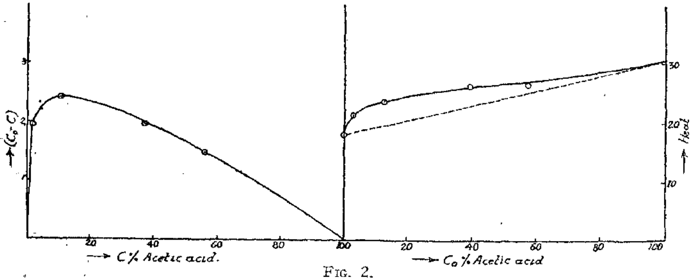

FIG. 2.

Toluene-Acetic acid-Silica.

of wetting than toluene, there is a proportionately greater heat liberation at the maximum adsorption of acetic acid.

(*b*) *Animal Charcoal.*—The heats of adsorption for animal charcoal are given in the following table (II).

TABLE II.

1 gm. of animal charcoal : 10 c.c. of solution.

Heats of Adsorption		Adsorption		
Liquid	Heats cal./gm.	C_0	C	$(C_0 - C)$
Toluene	22·1			
7·7% acetic acid ..	28·8	7·7	7·34	0·36
30·0 ,, ..	27·0	30·0	29·90	0·10
50·4 ,, ..	24·6	50·4	50·60	− 0·20
69·3 ,, ..	24·8	69·3	69·62	− 0·32
85·5 ,, ..	22·7	85·5	85·82	− 0·32
Acetic acid ..	24·8			

The curve for the above table is shown in Fig 3. It is interesting to see that the curve showing the relation of heats of adsorption to concentration is of the S type just as in the case of the adsorption isotherm. Acetic acid has a higher heat of wetting than toluene, though the difference is not so great as was in the case of silica (17.9 cal. for toluene and 30.3 cal. for acetic acid). At the point where toluene is selectively adsorbed, the heat liberation is proportionately less, because toluene has got a lower heat of wetting. Thus in

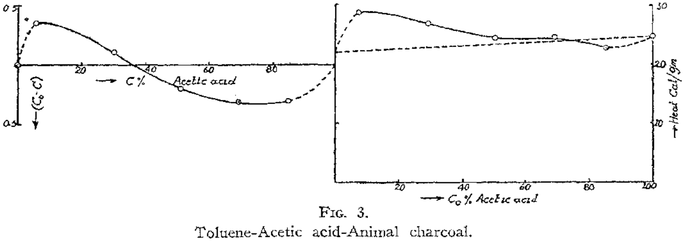

FIG. 3.
Toluene-Acetic acid-Animal charcoal.

very dilute concentrations of toluene, the main adsorbed component is toluene and probably very little acetic acid is adsorbed, while the reverse is the case in low concentrations of acetic acid.

(*c*) *Sugar Charcoal.*—Heat measurements with sugar charcoal are given in the following table (III).

TABLE III.

1 gm. of sugar charcoal : 10 c.c. of solution.

Adsorption			Heats of Adsorption	
C_0	C	$(C_0 - C$	Liquid	Heat cal./gm.
			Toluene	38·1
17·06	17·25	− 0·19	17·06% acetic acid ..	37·6
49·77	50·67	− 0·90	49·77 ,, ..	36·5
69·40	70·60	− 1·20	69·40 ,, ..	39·3
94·90	95·44	− 0·54	94·90 ,, ..	33·2
			Acetic acid	28·4

The curves for the heats and for the simultaneous adsorption are plotted in Fig. 4. The adsorption isotherm compares well with those obtained in the regular adsorption experiments (*cf.* Part I). As contrasted with silica, sugar charcoal has got a higher heat of wetting with toluene than with acetic acid. The maximum adsorption of toluene is between 70 and 80% of acetic acid (represented by the minimum point on the adsorption isotherm); similarly, the heat liberation also is maximum in this region.

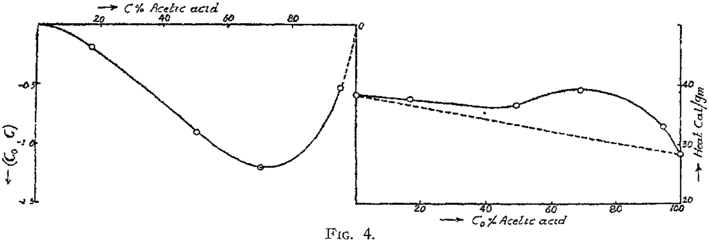

FIG. 4.
Toluene-Acetic acid-Sugar charcoal.

ADSORPTION ISOTHERMS AND THE HEATS OF ADSORPTION.

In the adsorption from binary mixtures, each component may be exclusively adsorbed or both may be simultaneously adsorbed. Even though the concentration of one of the components be decreased, the heat of adsorption may be the same as the heat of wetting of that component. When the quantity of the first component is insufficient to wet the whole of the surface of the adsorbent, the heat of adsorption decreases with change in composition, till it attains the value of the heat of wetting of the other component. The reverse is the case when the second component is preferentially adsorbed. If there is no preferential adsorption, the heats of adsorption will change linearly with the concentration. If there is preferential adsorption, the heat curve will be concave or convex to the concentration axis.

The results obtained in the present work show that both the components of the solution are adsorbed, one being adsorbed preferentially. The deviations of the observed values from linear relationship will be the greatest at the point where the preferential adsorption is also maximum. Such deviations have been plotted against concentrations (Fig. 5) and compared with their respective adsorption

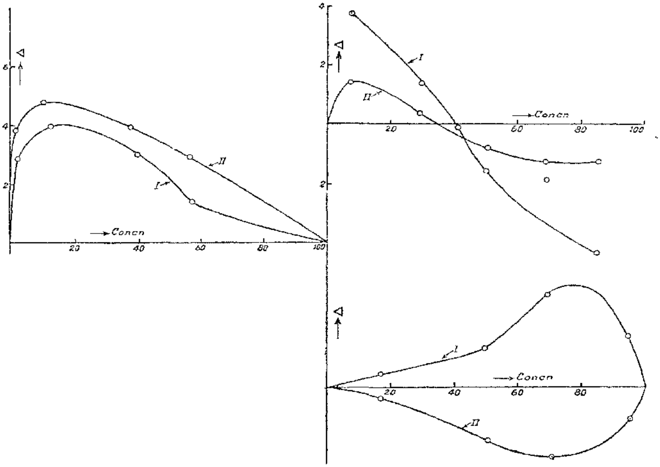

FIG. 5.
I. Deviation Curve
II. Adsorption Isotherm.

isotherms. In the case of sugar charcoal, the deviation curve does not follow the adsorption isotherm, because toluene has a higher heat of wetting than acetic acid, and since it is preferentially adsorbed, the heat of adsorption will be greater than what would be given by a linear variation. The following table (IV) gives the values of the deviations for the three systems. Column I gives the strength of acetic acid in the wetting solution (C_0) ; column II, the experimental heat of adsorption (H) ; column III, the heat as obtained from the dotted line in each case (H′) and column IV gives the deviations (△). (H′ is obtained on the assumption that the heat of adsorption varies linearly with composition).

TABLE IV.

SYSTEM (1)				SYSTEM (2)				SYSTEM (3)			
Toluene	Acetic acid		Silica	Toluene	Acetic acid		Animal charcoal	Toluene	Acetic acid		Sugar charcoal
C_0 I	H II	H′ III	△ IV	C_0 I	H II	H′ III	△ IV	C_0 I	H II	H′ III	△ IV
2·57	21·1	18·2	2·9	7·70	28·8	25·0	3·8	17·06	37·6	36·4	1·2
12·65	23·5	19·5	4·0	30·00	27·0	25·6	1·4	49·77	36·5	33·3	3·2
39·54	26·1	22·8	3·0	50·37	24·6	26·2	− 1·6	69·40	39·3	31·4	7·9
57·68	26·5	25·1	1·4	69·30	24·8	26·7	− 1·9	94·90	33·2	28·9	4·3
				85·5	22·7	27·1	− 4·4				

The resemblance between the deviation curves and the adsorption isotherms is quite marked. It is also evident that the heat of wetting is proportional to the activity of the adsorbent as shown by Herbst (*Kolloid Z.*, 1926, **38**, 314), and this holds good even in the case of the heats of adsorption from solutions.

INFLUENCE OF THE ADSORBENT.

The system toluene-acetic acid on silica, animal charcoal and sugar charcoal, affords a striking example of the influence exerted by the adsorbent on the adsorption isotherm. There is no doubt that all of them adsorb toluene as well as acetic acid, as is shown by the heats of adsorption, but the peculiarity enters only in the relative amount of each of them adsorbed. Silica is a polar compound while carbon is non-polar; toluene is non-polar while acetic acid is polar. Thus from a solution of one polar and one non-polar compound, silica prefers a polar compound while carbon prefers the non-polar one, and hence it is evident that the adsorption is more a function of the specific attractions operative between the solid and the liquid, than merely of the surface properties. The results for heat of wetting are given below:

Heats of Wetting cal./gm.

Liquid	Silica	Animal charcoal	Sugar charcoal
Acetic acid ..	30·3	24·8	28·4
Toluene	17·9	22·1	38·1

Thus, the heat of wetting of silica by a polar liquid as acetic acid is greater than by a non-polar liquid as toluene, while this is exactly the reverse in the case of sugar charcoal (*cf.* P. Rehbinder and Fr. L. Krajuschkina, *Z. Phys. Chem.*, 1929, **142A**, 282).

It was shown in Part I that the particles of the ash are more on the surface than inside. This conclusion is also supported by a consideration of the heats of wetting of toluene and acetic acid on silica, animal charcoal and sugar charcoal. Ordinarily, the heat of wetting of animal charcoal with toluene (non-polar) ought to be greater than with acetic acid (polar), if it contained pure carbon. The ash-content (15%) may lower the difference between the two heats, but not change the order of their magnitude. Actually, the heat of wetting of animal charcoal with toluene is slightly less than that with acetic acid. This can be explained on the assumption that the ash particles are more on the surface than in the interior, in agreement with conclusions given in Part I.

It was shown previously that the concentrations at which very flat maxima, minima and zero selectivity is shown by the adsorption isotherm of sugar charcoal and animal charcoal, occur at compositions corresponding to the formation of complexes of toluene with 1, 2, 3 and 4 double molecules of acetic acid. Referring to Fig. 3, the curve showing the heats of adsorption cuts the axis at about 73% of the acid, and the adsorption isotherm itself in the same figure cuts the axis at about 39%, and is flat between 70 and 84%, a characteristic which is also shared by the heat curve. Referring to Fig. 4 both the adsorption and the heats of adsorption curves show a maxima at 72% of the acid. Referring to Fig. 5 showing the deviation of the heats of adsorption from additive law, the system toluene-acetic acid-animal charcoal shows a zero deviation from the additive law at about 40% and the system toluene-acetic acid-sugar charcoal shows maximum deviation at about 70% of the acid, These results lend support to the theory put forward in Part I regarding the effect of formation of complexes on the adsorption isotherm: that the complexes that are preferentially adsorbed have a composition of the liquid mixtures giving zero selectivity or a maximum selectivity corresponding to the formation of $C_6H_5CH_3$ $(CH_3COOH)_2$, $C_6H_5CH_3$ $2(CH_3COOH)_2$, $C_6H_5CH_3$ $3(CH_3COOH)_2$, and $C_6H_5CH_3$ $4(CH_3COOH)_2$.

Thanks of the authors are due to Dr. H. E. Watson for his keen interest and helpful guidance during this investigation.

SUMMARY.

The heats of adsorption of mixtures of toluene-acetic acid by activated silica, animal charcoal and sugar charcoal have been determined using the method of twin calorimeters. The relation between the excess of heat observed over that calculated from the heat of wetting the compounds, and the composition of the binary mixture, is of the same nature as the adsorption isotherm.

The deviations of the heats of adsorption of the mixtures of toluene-acetic acid by activated charcoal and sugar charcoal from the additive law, occur at compositions corresponding to the formation of complexes of toluene with 1 to 4 double molecules of acetic acid.

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[Received, 13–10–1938.]

1709-38 Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent.