

**ADSORPTION IV.—ADSORPTION BY COCONUT CHARCOAL FROM BINARY MIXTURES OF SATURATED VAPOURS. THE SYSTEMS METHYL ALCOHOL-BENZENE, ETHYL ALCOHOL-BENZENE, *N*-PROPYL ALCOHOL-BENZENE, AND *N*-BUTYL ALCOHOL-BENZENE.**

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It has been shown in previous communications<sup>1</sup> that the adsorption of a binary saturated vapour mixture by charcoal occurs in three well-defined stages. The first is the adsorption of the two components in a constant ratio which is close to that existing in the saturated vapour phase. This process is complete in a few hours and, in the systems previously examined, terminates quite sharply. Reasons have been advanced for regarding the end of this stage as coincident with the condensation of the adsorbed vapour to the liquid phase. In the second stage a somewhat slow change occurs in the composition of the adsorbed phase. This change may occur without much alteration in the total number of adsorbed molecules, and entails the partial replacement of one component by the other. At the end of this stage the composition of the adsorbed phase approaches, although it is

<sup>1</sup>Tryhorn and Wyatt, *Trans. Far. Soc.*, 1926, **22**, 139.

never coincident with, that of the bulk liquid in contact with the saturated vapour mixture. It has been suggested that the selective adsorption powers of the charcoal manifest themselves during this stage, and that the extent of this selective adsorption is measured by the difference between the composition of the adsorbed phase at the end of this stage and that of the bulk liquid remaining in contact with the vapour mixture.

The third stage of adsorption is indefinitely prolonged and consists in an isothermal distillation of the bulk liquid into the interstitial spaces of the charcoal. Theoretically this will continue until the radius of curvature of the liquid surfaces in these spaces becomes infinite.

To confirm the existence of these three stages of adsorption and to investigate further the nature of the second stage, an examination has been made of the adsorption by coconut charcoal from mixtures of benzene with the first four members of the normal aliphatic alcohol series. The results for the system ethyl alcohol-benzene have already been communicated.

### Experimental.

The alcohols were purified and carefully dried by standard methods. The benzene was distilled over potassium permanganate and subsequently frozen out thrice. The charcoal used in the series methyl alcohol-benzene and propyl alcohol-benzene was the remainder of the batch prepared for the earlier work. It was necessary to prepare a fresh batch of charcoal for the system butyl alcohol-benzene. The charcoal previously prepared was a portion of a large batch of coconut shells which had been charred under sand in a gas-fired annealing furnace, and was activated before use by heating to  $600^{\circ}\text{C}$ . for two hours. The new sample of charcoal was a further portion of the large batch of charred shell, but was separately activated under conditions as close as possible to those maintained during the activation of the first batch.

In the determination of the adsorption curves for the system butyl alcohol-benzene, these two charcoal preparations were used alternately in order to test the reproducibility of the adsorbent. That the reproducibility was satisfactory was shown by the fact that the points obtained lay on smooth curves irrespective of the sample of charcoal used.

The experimental methods of measuring the adsorption curves and the compositions of the vapours in equilibrium with the binary liquid mixtures were those previously described. The liquid mixture placed in the adsorption tubes at the beginning of an experiment is referred to as the bulk liquid mixture, and the liquid and vapour present in the tube at the end of any experiment are described as the bulk equilibrium liquid and the equilibrium vapour respectively.

### Results and Discussion.

The essential results for the four systems are shown in Fig. 1. In these diagrams, which are selected to show principally the second stage of the adsorption process, the composition of the adsorbate is represented as a function of the total amount of the adsorbed phase, expressed in moles per gram of adsorbent. In every case the first and third stages of adsorption were found to be represented by straight lines, and the individuality of the adsorption process for a given mixture may therefore be illustrated by reference to the second stage alone.

*The First Stage.*—It has been mentioned above that the first stage is considered to consist in the packing of molecules, still in the vapour state,

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into the pores of the charcoal. The proportions in which the components of a binary vapour mixture will be adsorbed in this stage will depend primarily on the composition of the vapour, and on the partial pressures

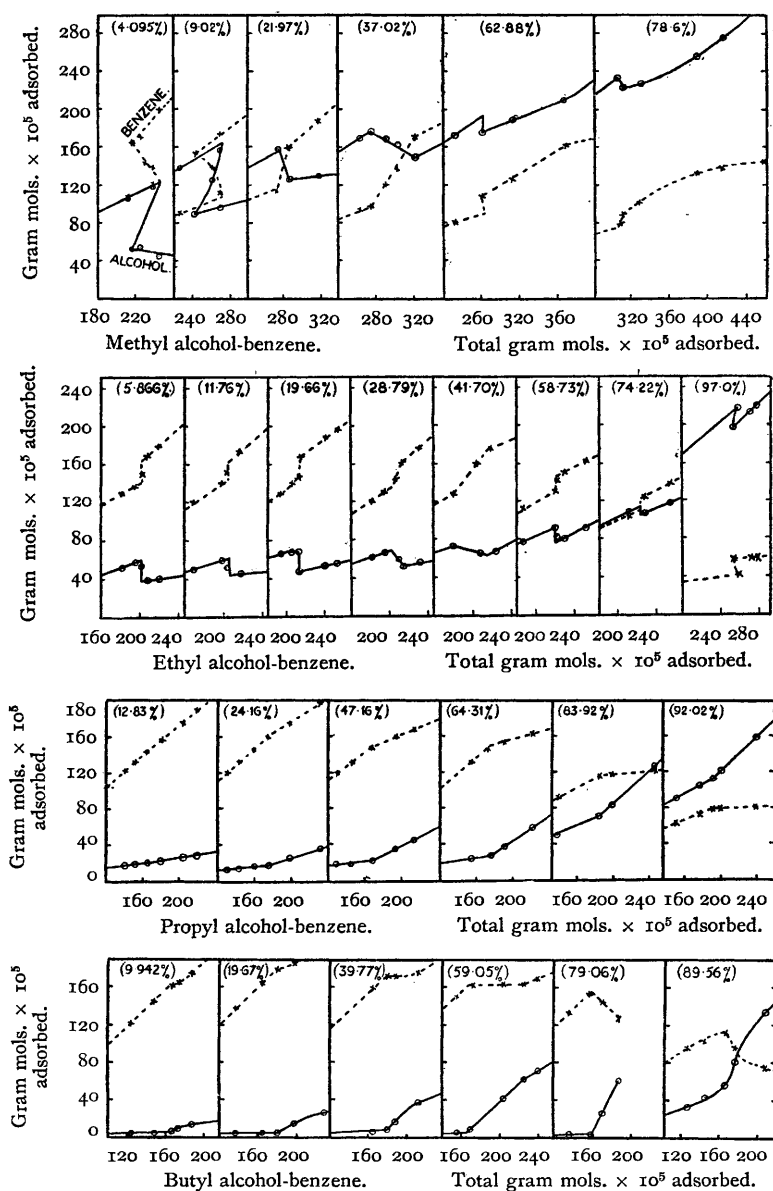


FIG. 1.

and the diffusion coefficients of the components. It has been pointed out by Mack<sup>2</sup> that if a porous substance adsorbs vapour molecules as quickly

<sup>2</sup> Mack, *J. Amer. Chem. Soc.*, 1925, **47**, 2468.

as they are presented to its surface, the weight of vapour  $g$  taken up in the time  $t$  is given by the expression  $g = DAdt/l$ , where  $A$  is the cross-section of the diffusion area,  $D$  the diffusion coefficient, and  $d$  the density of the vapour in gms. per c.c. at the surface of the evaporating liquid. For a binary mixture the ratio of the weights of the two components adsorbed at the time  $t$  becomes  $g_1/g_2 = D_1d_1/D_2d_2$ , where  $D_1$ ,  $D_2$  are the diffusion coefficients, and  $d_1$ ,  $d_2$  the densities of the two components in the vapour phase. This ratio should thus be independent of time, and indeed is found experimentally to be so. This is shown by the straight lines forming the first stage of the adsorption process in Fig. 1. For, although the abscissæ in these figures represent the total number of moles of the adsorbate, they may be regarded as representing implicitly a function of time. At the same time, it must be remembered that adsorption is becoming slower the further it proceeds, and the first stage of the process is therefore not necessarily represented by straight lines when the amounts of the two components adsorbed are plotted against time, as has been done by other observers.<sup>3</sup> Nevertheless, even when results are so plotted the constancy of the above ratio may be seen to persist up to the point at which the curvature changes abruptly at the end of the first stage.

It is not possible to apply Mack's equation quantitatively to the present results owing to lack of knowledge of the true densities and diffusion coefficients of the components of a binary mixture. A rough calculation of the composition of the adsorbed phase may, on the other hand, be made by the use of Langmuir's equation<sup>4</sup>  $\mu = p\sqrt{2\pi MRT}$ , for the number of gram moles  $\mu$  of a gas, of molecular weight  $M$ , which strike each square cm. of a surface per second, at the absolute temperature  $T$ . For a binary mixture the ratio of the numbers of moles of the two components adsorbed becomes  $\mu_1/\mu_2 = p_1\sqrt{M_2}/p_2\sqrt{M_1}$ , provided that the molecules can be adsorbed as rapidly as they reach the adsorbing surface. In the early stages of adsorption we may assume this to be the case. If now  $X_1$  and  $100 - X_1$  are the molecular percentages of the two components in a binary vapour mixture over a liquid mixture of which the total vapour pressure is  $P$ , then, regarding as an approximation the partial pressures of the two components as proportional to their mole fractions in the vapour phase, we may write for these partial pressures  $p_1 = (X_1/100)P$ , and  $p_2 = [(100 - X_1)/100]P$ . The molar ratio in which the two components will be adsorbed then becomes  $\mu_1/\mu_2 = X_1\sqrt{M_2}/(100 - X_1)\sqrt{M_1}$ . Thus  $\mu_1/\mu_2$  may be calculated if the composition of the vapour in contact with the bulk liquid mixture is known. The table shows the calculated and observed values of the adsorbed phases during the first stage for the four series studied.

In the methyl alcohol-benzene, and ethyl alcohol-benzene series the discrepancies between the observed and calculated compositions of the adsorbed phase are not great, when the approximate nature of the calculation is taken into account. In making these calculations it has been assumed that the partial pressure of each component in a binary mixture is proportional to its mole fraction. This is inaccurate, especially in dealing with saturated vapours at temperatures considerably removed from the natural boiling-points of the liquid components. It is noteworthy that in the two latter series, in which the mixed liquids possess considerably higher boiling-points than in the former, the numerical values of the discrepancies

<sup>3</sup> Williams, *J. Soc. Chem. Indus.*, 1924, 43, 97T.

<sup>4</sup> Langmuir, *Trans. Far. Soc.*, 1922, 17, 625.

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System.	Composition of Bulk Equilibrium Mixture. (Molar Per Cent. Alcohol.)		Composition of Adsorbed Phase. (Molar Per Cent. Alcohol.)		Difference Between Observed and Calculated Values.
	Liquid.	Vapour.	Observed.	Calculated.	
Methyl alcohol-benzene	4.7	36.0	50.0	46.7	+ 3.3
	14.7	46.8	60.7	57.9	+ 2.8
	39.0	48.5	57.0	59.5	- 2.5
	53.4	51.7	64.6	64.0	+ 0.6
	81.75	63.75	68.1	73.2	- 5.1
	91.0	73.7	76.1	81.5	- 5.4
Ethyl alcohol-benzene	7.9	19.9	29.1	24.45	+ 4.65
	17.5	26.8	30.2	32.2	- 2.0
	29.0	29.9	33.0	35.7	- 2.7
	41.1	31.3	33.65	37.2	- 3.55
	56.2	34.5	36.3	40.6	- 4.3
	72.6	42.0	41.3	48.6	- 7.3
	85.2	53.2	50.9	59.7	- 8.8
	97.9	87.0	83.9	89.4	- 5.5
n-Propyl alcohol-benzene	16.4	10.6	12.1	11.9	+ 0.2
	30.8	14.4	9.1	16.0	- 6.9
	56.5	18.5	13.0	20.46	- 7.46
	74.4	20.4	14.75	22.5	- 7.75
	90.9	46.2	37.3	49.3	- 12.0
	96.5	70.0	59.25	72.5	- 13.25
n-Butyl alcohol-benzene	11.1	3.25	3.13	2.85	+ 0.28
	22.3	4.0	3.0	4.1	- 1.1
	44.0	4.5	2.9	4.61	- 1.7
	64.3	5.2	2.41	5.34	- 2.93
	84.8	13.0	1.91	13.3	- 11.39
	94.8	36.0	25.35	36.6	- 11.25
	95.3	39.5	32.9	40.2	- 7.3

are greater. Further, in any one series a change of sign in the divergence occurs and if these divergences are plotted against the molar percentage of the alcohol in the vapour phase from which adsorption has occurred, an S-shaped curve is obtained, indicating zero divergence at some particular point. These zero values occur, for the methyl alcohol series at 51 per cent., for the ethyl alcohol series at 28 per cent., for the propyl alcohol series at 10 per cent., and for the butyl alcohol series in the neighbourhood of 3 per cent. These values agree closely with the compositions of the minimum boiling-point mixtures of these alcohols with benzene, which from the measurements of the composition of the vapours in equilibrium with the liquids have been found to be, at 20° C., 51.5 per cent., 30 per cent., 9.5 per cent., and 2.5 per cent. respectively. This suggests that the above discrepancies may be due to the error introduced in treating the partial vapour pressures of the vapour components as proportional to their mole fractions.

Inasmuch as for a minimum boiling-point mixture the composition of the liquid phase is the same as the composition of the vapour phase, the divergences of the true vapour pressure of each component from the value calculated from the molar percentage composition of the liquid phase may be regarded as equal for these mixtures. Thus, if  $p_1$  and  $p_2$  are the true

partial pressures of the two components, and  $p_1'$ ,  $p_2'$  those calculated from the composition of the vapour, then  $p_1 = k_1 p_1'$ ,  $p_2 = k_2 p_2'$ . For the minimum boiling-point mixture  $k_1 = k_2$ , and thus  $p_1/p_2 = p_1'/p_2'$ . In these circumstances it is obvious that zero discrepancy should be found between the calculated and the observed compositions of the adsorbed phase, if the bulk equilibrium liquid has the composition of the minimum boiling-point mixture. Approximately these conditions have been encountered in the case of the 53.4 per cent. mixture of methyl alcohol and benzene.

Further proof of the close relation between the composition of the adsorbed phase during the first stage, and the form of the vapour pressure curve of the binary system is afforded by a study of the results previously communicated for the system acetone-benzene. If a comparison is made for this series between the experimental values of the composition of the adsorbate and those calculated from Langmuir's equation the change of sign in the discrepancies is absent, and in all cases the calculated values are less (by 0.5 to 4.7 per cent.) than the experimental ones. This is to be anticipated since acetone and benzene do not form a minimum boiling-point mixture.

It may be mentioned here that the present method of studying adsorption appears to offer, by the application of Langmuir's equation, a method of determining indirectly the true, or effective, partial pressures of the components of a binary vapour mixture by a reversal of the above calculation, for systems in which molecular association of the components may be presumed to be negligible or absent.

Additional evidence that this first stage is a purely diffusional process is afforded by a comparison of the times necessary for its completion in the different series. In the methyl alcohol-benzene series the first stage is complete in from 3 to 4 hours; in the ethyl alcohol-benzene series, from 4 to 9.5 hours are necessary, the time increasing with the percentage of alcohol in the mixture; in the propyl alcohol series, the time required is from 18 to 48 hours, while for the butyl alcohol series, from 6 to 24 hours are necessary. The propyl alcohol series is anomalous inasmuch as the second stage is absent, or rather, overlaps the first and third stages. Consequently the above times for this series include part of the second stage, and are greater than the true values. Since, as will be shown later, the numbers of molecules adsorbed at the completion of the first stage do not vary greatly, the time required for the process, if purely diffusional, will vary inversely with the mean value of  $p/\sqrt{M}$  for the system in question. The values of  $p/\sqrt{M}$  for methyl alcohol, benzene, ethyl alcohol, propyl alcohol, and butyl alcohol decrease in that order from 14.4 to 0.59 at 20° C. The increase in the time required for the first stage from system to system is thus parallel with the decrease in the value of the average  $p/\sqrt{M}$  for the mixtures, except in the case of propyl alcohol, to which reference has been made above.

*The Volume of the Adsorbate at the First Break Point.*—Assuming that liquefaction of the adsorbate occurs at the first break point, we can calculate the volume occupied by that adsorbate by dividing the weight of each component at the break point by its density in the liquid state. When this is done the total volume of adsorbate is found to be approximately constant at 0.16 c.c. per gram of charcoal. The mean values for the four systems, methyl alcohol-benzene to butyl alcohol-benzene, are 0.1618, 0.1622, 0.156, and 0.150 c.c. respectively, per gram. of charcoal. The average variation for the various series in a system was about 3 per cent. The mean value

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for the free spaces in a gram of the charcoal, calculated from the four systems, is 0.1575 c.c. This confirms the value of 0.16 c.c. previously obtained by a more direct method. Since the volume of adsorbate is constant at the first break point, the number of molecules actually present will vary inversely with the molecular volume of the components, and we thus find that in each series, as well as in different systems, slight but regular variations in the number of molecules present at the first break point. The molecular volumes at 20° C. of the substances methyl alcohol, ethyl alcohol, propyl alcohol, benzene, butyl alcohol, are respectively 40.6, 58.3, 74.6, 88.7, and 91.4 c.c.s. Accordingly, we find that the greatest number of molecules is adsorbed at the first break point in the methyl alcohol series, and that within this system, the total number of molecules adsorbed increases as the individual mixtures become richer in methyl alcohol. Numerically the increase is from  $1.50 \times 10^{21}$  to  $1.86 \times 10^{21}$  molecules per gram. of charcoal. In the ethyl alcohol series the corre-

sponding figures are  $1.2 \times 10^{21}$  and  $1.55 \times 10^{21}$ , whilst for the butyl alcohol series the average value falls to  $1.0 \times 10^{21}$  molecules.

In Fig. 2 the numbers of gram mols. of the four alcohols adsorbed at the first break point are plotted against the molar percentages of alcohol in the vapour phase. An interesting point arises from these curves inasmuch as the points at the extremities of the full lines represent the maximum amount of

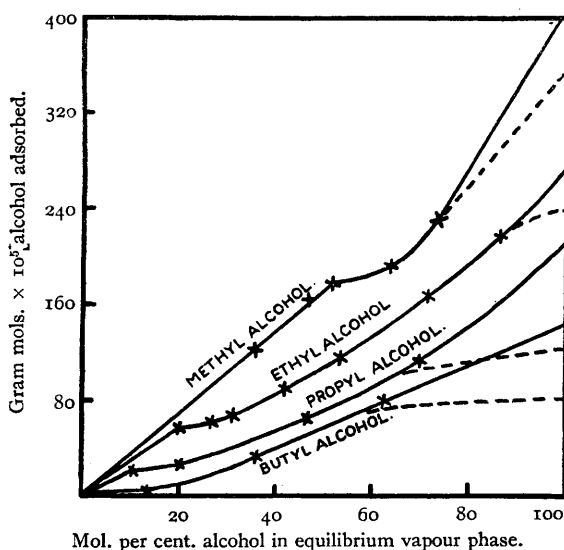


FIG. 2.

the alcohol adsorbable by a gram of charcoal, as determined by the continuous adsorption method for pure vapours described in a previous paper. The points at the 100 per cent. alcohol ends of the dotted curves refer to the break points on the adsorption curves for the pure liquids, and indicate the points at which condensation occurs in the pores of the charcoal when one substance only is present. The maximum values on the same curves represent a complete filling of the charcoal pores, the volumes lying close to the value 0.16 c.c. It is evident, therefore, that the appearance of a liquid phase occurs more readily when one substance only is in the pores than when a binary mixture is present. The same rule holds for the benzene, the break point in the adsorption curve for pure benzene occurring at  $120 \times 10^{-5}$  gram mols. per gram of charcoal. When curves for benzene adsorption in the binary mixtures are plotted in a manner similar to that of Fig. 2, it is found that above 55 per cent. the adsorption of the benzene is almost proportional to the molar percentage of benzene in the vapour, the straight line representing such adsorption



terminating at the maximum value for the adsorption of pure benzene. Below about 55 per cent., the adsorption of the benzene is considerably more than proportional to the percentage of benzene in the vapour. It thus appears that in adsorption from a polycomponent system, the tendency to condensation of each component is decreased by the presence of the others. Reference will be made to this point after dealing with the second stage of adsorption.

*The Second Stage.*—It is obvious from Fig. 1 that the sharpness and extent of the second stage in the adsorption process varies greatly from system to system. In the methyl alcohol-benzene and ethyl alcohol-benzene systems this stage is extremely sharp and well-defined. In the propyl alcohol-benzene series it is indistinguishable, while in the butyl alcohol-benzene series it becomes more prominent and extensive as the amount of butyl alcohol in the bulk liquid is increased. During this stage in the methyl and ethyl alcohol systems, a change of composition occurs in the adsorbed phase, without much change in either volume or total number of molecules adsorbed, by a process of replacement of alcohol molecules by benzene molecules. In the lower series of the methyl alcohol-benzene system this change is accompanied by a slight decrease in the total number of molecules in the adsorbed phase, owing to the fact that the benzene molecule is considerably larger than the methyl alcohol molecule, and therefore to fill a given pore volume the number of methyl alcohol molecules ejected must be greater than the number of benzene molecules taking their places. In the ethyl alcohol series, where the difference in molecular volume of the components is less marked, replacement occurs practically without change in the total number of adsorbed molecules, except from the mixture containing 95.04 weight per cent. of alcohol, in which case there is a slight decrease in the total number of molecules in the adsorbate during the replacement process. Irregularities were found when the initial liquid mixtures were close to the minimum boiling-point mixtures. In these cases, presumably owing to the high vapour pressure exhibited by such mixtures, and the consequent acceleration of adsorption, the replacement process was synchronous with a steady increase in the number of molecules adsorbed, and there appeared a tendency for this second stage of adsorption to coalesce with the third. This is shown in the curves for mixtures containing 37.02 wt. per cent. of methyl alcohol, and 28.79 and 41.7 wt. per cent. of ethyl alcohol.

In the propyl alcohol-benzene series the above tendency towards coalescence appears to have become complete, for it was not possible to detect any definite second stage. The only evidence of a second stage in this system is in the bunching of points which occurred after the first break point. In the butyl alcohol series the emergence of a definite second stage is clearly shown by reference to the curves for this system in Fig. 1. In no mixture of this series was the second stage as completely masked as in the propyl alcohol series, but as the amount of butyl alcohol in the original liquid increased, the second stage became more marked, involving at first an increase in the number of alcohol molecules while the number of benzene molecules remained practically constant, and then later, as in the curves for mixtures containing 79.06 and 89.56 wt. per cent. of alcohol, a replacement of benzene by alcohol molecules. The replacement in this series is opposite in direction to that in the methyl alcohol and ethyl alcohol series.

The cause of this replacement process is to be found in the effort of the liquid adsorbate, newly formed at the first break point, to come into



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equilibrium with the remaining bulk liquid mixture. By reference to Table I. it is possible to see in which direction replacement should occur during the second stage to set up this equilibrium. In the methyl alcohol series, with bulk liquid mixtures containing up to 53.4 molar per cent. of methyl alcohol, the adsorbed phase at the first break point contains more alcohol than the bulk liquid, and therefore to reach the second equilibrium methyl alcohol should be displaced by benzene. This is found experimentally to be the case. But by the same argument, mixtures containing more than 81.75 molar per cent. of methyl alcohol should show the reverse displacement, although experimentally the alcohol is replaced by benzene throughout the series.

In the ethyl alcohol-benzene series an inversion of the direction of replacement should occur between mixtures containing 29.0 and 41.1 molar per cent. of alcohol. Here again no inversion is found, but throughout the series benzene replaces alcohol. In the propyl alcohol-benzene series, no inversion of replacement in the mixtures studied should occur, but propyl alcohol should always replace benzene. In the butyl alcohol-benzene system, in each series butyl alcohol should replace benzene, and this is found to be the case wherever any replacement occurs. In consequence of these discrepancies, a comparison of the compositions of the adsorbate at

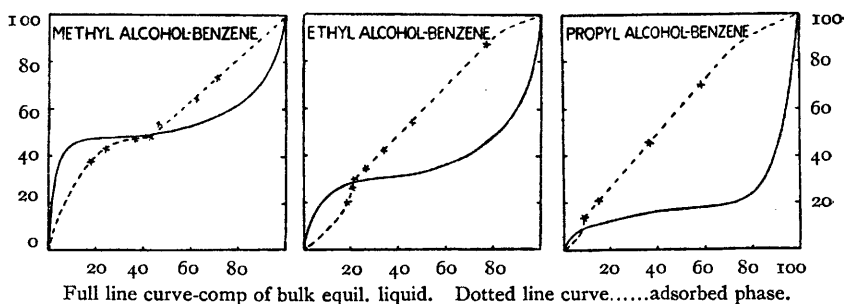


FIG. 3.

the second break points with those of the equilibrium bulk liquids shows that equality of composition is never attained. Now this equality of composition should be reached if the total and partial vapour pressures of a liquid mixture in a pore are the same as those of a bulk liquid mixture, and we are therefore forced to infer that the effect of the so-called selective properties of a charcoal must act in such a direction as to modify the total and partial vapour pressures of adsorbed substances. It must be pointed out here that such action cannot be assigned to the effect of a radius of curvature on the vapour pressures of the components of the adsorbate, for as has been mentioned above, at this stage of adsorption, the pores of the charcoal are full, and the radius of curvature is infinite. The differences in composition between the adsorbate and the bulk liquids at the second break points are shown in Fig. 3. In this diagram the broken lines represent the compositions of the adsorbed phase at the second break points and the full lines those of the bulk equilibrium liquids, plotted in each case against the compositions of the equilibrium vapours. For the propyl alcohol-benzene system the values of the first break points have been used, since these are coincident with the second break points. The curve for the butyl alcohol system is not shown, owing to the difficulty of determining exactly the end of the second stage as a result of the overlap-

ping of the second and third stages. An attempt was made to calculate the compositions of the adsorbates in this system at the second break points by a method referred to later. The curve so obtained was of a form similar to the experimental ones for the other two series.

The selective action of the charcoal is shown by the areas between the full and broken curves. The decrease in selective adsorption as the minimum boiling-point mixtures are approached is clearly shown, since the full and broken curves cross in each system close to those mixtures. The chief point of interest in this diagram lies in the fact that with bulk mixtures containing more alcohol than the minimum boiling-point mixture, the composition of the adsorbed phase is almost a linear function of the composition of the equilibrium vapour. In each case, however, this linear curve is displaced approximately parallel with the diagonal of the diagram, indicating that the adsorbed phase contains less alcohol than the vapour, but that the deficiency is a constant quantity. The physical significance of this appears to be that the partial vapour pressure of the alcohol in the adsorbate is enhanced in comparison with that of the benzene. This is in agreement with the recent work of Baker, who finds that certain adsorbent substances<sup>5</sup> possess the property of altering the vapour pressures of pure liquids into which they are placed. Charcoal, for example, was found to cause an increase of 12 mms. in the vapour pressure of methyl alcohol at 35° C., and of 2 mms. in that of benzene. It is therefore suggested that the mechanism of selective adsorption in this second stage may be found in the relative changes effected by the charcoal in the partial pressures of the components. Further than this it is not possible to go at present, but whereas Baker suggests that these changes are to be attributed to alterations in the degree of association of the molecules, it is also possible that we are dealing with molecular phase changes of the type suggested by Baly.<sup>6</sup>

These phase changes may conceivably be occasioned by the effect of the force fields which must exist in the charcoal pores on those existing among the molecules of the adsorbed phase. The source of the energy changes between different molecular phases of the adsorbate might then be found in the transfer of quanta of energy between the charcoal surfaces and the adsorbate molecules, the direction of the transference depending on whether the charcoal increases or decreases the vapour pressure of the adsorbent.

It may further be suggested that these energy transfers occur in the infra-red region in the neighbourhood of the carbon band at  $3.5\mu$ . An observation pointing to this possibility was made when investigating the effect of the air contained in the charcoal pores on the accuracy of the present adsorption measurements. This air is displaced during the experiment, and thus while the initial weight of charcoal is that of the charcoal plus the air in the pores, after the experiment the charcoal is weighed plus the adsorbate, but minus the expelled air. To determine the error thus introduced, charcoal was sealed up in glass bulbs which could be broken by a brass screw working through an air-tight sleeve in a brass cylinder which was connected to a water-jacketed gas burette. By these means, the bulb containing the charcoal could be broken in the cylinder under an excess of any given liquid, and the air expelled could be measured. Of sixteen liquids so examined fourteen displaced between 6.5 and 6.8 c.c.s of air (*N.T.P.*) per gram of charcoal in periods varying from 5 minutes to 20

<sup>5</sup> Baker, *J. Chem. Soc.*, 1927, **130**, 949.

<sup>6</sup> Baly, *Rice Inst. Pamphlet*, 1925, **12**, 1.

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hours. The error introduced into the adsorption measurements by this loss is slight and is balanced by the small loss of vapour which occurs after opening the tube at the end of the experiment. Carbon tetrachloride and tetrachlorethylene, however, after 20 hours had expelled less than 1.0 c.c. of air per gram of charcoal. The abnormal behaviour of these two substances cannot be explained by their rather large molecules blocking the pores of the charcoal, since ethylene dibromide, with a still larger molecular volume, displaced the maximum amount of air in a few minutes. Nor is any explanation possible in terms of the varying solubility of air in the liquids examined, for *n*-pentane, with an extremely low solubility for air, displaced the full quantity of air from the charcoal in a short time. Further, since this same reluctance to enter the charcoal is found for carbon tetrachloride in the vapour phase, the anomaly cannot be due to a low penetration coefficient for the liquid. It is, however, striking that of the numerous organic substances examined by Coblenz<sup>7</sup> in the infra-red region these two alone failed to show the characteristic carbon band at  $3.5\mu$ . If the above tentative suggestion of the importance of the infra-red band of carbon in connection with the adsorptive power is considered, it is evident that carbon should have a negligible adsorptive power for carbon tetrachloride and tetrachlorethylene, since these substances could not take part in energy transfers occurring in the region of  $3.5\mu$ .

*The Third Stage.*—In the majority of adsorption curves shown in Fig. 1, it will be seen that the third stage of adsorption is represented by straight lines, which are not parallel to those found for the first stage. If, however, lines are drawn representing the composition of the bulk equilibrium liquids in the various series, it will be found that they are, within extremely small limits parallel with those representing the third stage of adsorption. Thus the third stage consists in the isothermal distillation of the bulk liquid over to the charcoal. In one or two series in which this process was carefully followed for more than three weeks, it was found that the lines representing the third stage did not become strictly parallel to those representing the composition of the bulk liquid until 14 to 20 days had elapsed. These lines are therefore to be regarded as approaching asymptotically to lines parallel to those of the bulk liquid composition. For this reason, the third stage is considered to consist in the gradual filling up of the intergranular spaces of the charcoal, after the internal pores of the charcoal have been filled with adsorbate which has come into equilibrium with the vapour phase. This intergranular condensation will begin at the points of contact of the charcoal particles, and in its initial stages will give rise to surfaces having a marked concave curvature, and therefore vapour pressures somewhat different from that of the bulk liquid. As the spaces are gradually filled, the liquid condensing will gradually approach in composition that of the bulk liquid giving rise to adsorption curves of the type observed. The nature of the third stage renders possible the calculation of the composition of the adsorbate at the second break point in those cases in which coalescence of the second and third stages has occurred. In those series in which all three stages were sharply defined, it was shown that the replacement in the second stage occurred practically without change in the volume of the adsorbate, and that the mean value of this volume, for a gram of the charcoal used was 0.1575 c.c. Thus if we produce the lines representing the third stage backwards towards the origin, and calculate at what number of total mols. adsorbed, the sum of the volumes of the two components

<sup>7</sup> Coblenz, *Carnegie Inst. Pubs.*, 35 (1905).

adsorbed, as represented by points on the above lines, is 0.1575 c.c., we shall have determined, *ipso facto*, the composition of the adsorbate at the second break point. This was done, as mentioned above, for the butyl alcohol-benzene series.

### Summary.

The adsorption by a coconut charcoal has been measured for the binary vapour systems methyl alcohol-benzene, ethyl alcohol-benzene, *n*-propyl alcohol-benzene, and *n*-butyl alcohol-benzene at 20°.

Adsorption occurs in three stages which represent respectively (*a*) the adsorption of a vapour phase, (*b*) the condensation of the vapour phase followed by a change in composition of the liquid so formed in an effort to reach equilibrium with the bulk equilibrium liquid, and (*c*) capillary condensation in the inter granular spaces of the charcoal.

The first stage is mainly diffusional in character, and selective adsorption is either absent or slight.

The selective action of the charcoal is exhibited chiefly in the second stage.

It is suggested that the selective adsorption is the result of the adsorbent altering the vapour pressures of the components of the adsorbate in different degrees, with the result that a liquid adsorbate may have the same vapour pressure as a bulk liquid of different composition.

A possible quantum mechanism involving energy transfers in the infra-red region is suggested for the above effect.

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