with potassium soaps, but tended to break emulsions containing gelatin or free fatty acids as stabilizers. Homogenization with atmospheric pressure in the receiver caused a breaking of the emulsion in the cases investigated.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE UNIVERSITY OF BRISTOL]

THE SORPTION OF TOLUENE AND ACETIC ACID AND THEIR MIXTURES BY CARBON

BY A. M. BAKR[1] AND J. W. McBAIN

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In a previous paper[2] a general method was described for determining the true sorption of both solvent and solute in place of the merely relative values obtained in the usual way for solutions. This is done by reaching equilibrium through the vapor phase, the carbon being kept at a temperature higher than that of the liquid to prevent capillary condensation of liquid in the pores. From the increase in the weight of the carbon and analysis of the residual liquid, the absolute amount of each component sorbed is directly determined. The amount of solvent sorbed from a solution is much less than that which is sorbed when the pure solvent alone is taken.

In the present paper it will be seen that a maximum value for sorption is obtained with pure toluene and with pure acetic acid which is independent of the absolute temperature; that the ratio between the saturation values is that of the molecular weights (acetic acid being present as double molecules); and that when solutions are employed, the total amount sorbed still corresponds to a complete film in which a certain number of double molecules of acetic acid have replaced a corresponding number of molecules of toluene.

Experimental Method

The apparatus used is illustrated in the paper referred to, except that here two electrically heated thermostats were employed for the upper and lower bulbs, respectively, so that they could be kept at any pair of temperatures desired. The upper bulb was of 40 cc. and the lower bulb of 20 cc. capacity. The charcoal was weighed into the upper bulb and after the addition of the liquid, the whole was immersed in a mixture of liquid carbon dioxide and ether, evacuated and sealed. In a "direct" experiment, the liquid is placed initially in the lower bulb so that the carbon has

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[1] Experimental work by A. M. Bakr. Presented at the New York meeting of the American Chemical Society, Sept., 1921.

[2] *J. Chem. Soc.*, **119**, 454 (1921).

subsequently to adsorb the vapor; whereas in the "reverse" experiment the liquid is placed with the carbon in the upper bulb and the excess has to distil into the cooler lower bulb. In the latter case most of the liquid goes over in a few minutes, but a period of about 20 hours is allowed for equilibrium to be attained; thereupon the tube connecting the two bulbs is sealed off for weighing and analysis of contents. In the calculation of the results correction has to be made for the weight of the vapor in the bulbs, also for weighing in a vacuum and finally for the amount of air originally contained in the carbon and displaced by the liquid or during the evacuation. The first two corrections can if preferred be obtained from standard tables; the last requires a blank experiment; and for our sugar carbon the last correction was found to be 1.2% of the weight of the carbon, both for dry and wet surfaces.

Acetic acid ("Kahlbaum") was distilled from potassium permanganate and a middle portion taken; toluene obtained from Kahlbaum was similarly treated. Except where specially indicated, Kahlbaum's sugar carbon was employed. This had been heated in a vacuum in a silica flask by means of a blow-pipe flame for three hours, cooled in a vacuum and kept in a stoppered bottle in a desiccator.

Results for Pure Solvents

In Tables I and II the first column gives the temperature of the bulb containing the carbon, the second that of the lower bulb, the third and fourth

TABLE I

SORPTION OF TOLUENE VAPOR BY CARBON AT VARIOUS TEMPERATURES AND PRESSURES

REVERSE METHOD

Temperature		Pressure in mm. of Hg				
Upper °C.	Lower °C.	p_1	p_2	p_2/p_1	x/m	Mean
125	25.5	1170	30	0.0256	0.111	
					.111	0.111
125	50	1170	95	.0812	.110	
					.113	.112
125	75	1170	246	.2102	.119	
					.125	
					.127	.125
					.129	
					.125	
170	25.5	3240	30	.0093	.101	
					.100	.099
					.096	
180	90	3940	400	.1015	.121	.121
245	25.5	11780	30	.0025	.079	
					.080	.080
245	75	11780	246	.0209	.102	
					.103	.102
245	92	11780	433	.0368	.105	
					.116	.111

the vapor pressures obtaining, the fifth the ratio of these two pressures, and the last two columns the values of x/m, that is, the weight sorbed per gram of carbon.

In all of these experiments the apparatus was put in the electric thermostat one hour after the toluene had been pipetted into the upper bulb. In one experiment the apparatus was left for 24 hours at room temperature before it was put into the thermostat and in this case x/m was found to be 0.110 for 125° and 25.5°, proving that further time of contact of liquid with charcoal had no appreciable effect on the final equilibrium. A "direct" experiment (starting with the liquid in the lower bulb) at 125° and 53° gave $x/m = 0.111$ in four days, showing that equilibrium was attained from both sides.

Table II

Sorption of Acetic Acid Vapor by Carbon at Various Temperatures and Pressures

"Reverse" Method

Temperature, °C.		Pressure	Mm. of Hg			
Upper	Lower	p_1	p_2	p_2/p_1	x/m	Mean
71	25.5	76.6	16	0.2088	0.166	
					.173	0.169
100	75	417.1	168.5	.4040	.175	
					.180	.177
125	25.5	930.8	16	.0172	.142	
					.138	.140
125	50	930.8	57	.0612	.149	
					.152	.150
125	75	930.8	168.5	.1810	.163	
					.167	.165
180	25.5	3833	16	.0042	.055	
					.047	.051
180	90	3833	294	.0767	.121	
					.112	.117
245	25.5	13683	16	.0012	.002	
					.013	.008

Zawidzki[3] investigated the equilibrium between double and single molecules of acetic acid at 69.94° and 80.05° and thus the equilibrium constant K can be calculated for all other temperatures. The heat of reaction Q was found to be 17,510 calories, that is, the dissociation is strongly endothermic and would be favored by rise of temperature. At 125° and 16-mm. pressure, the partial vapor pressure of the double molecules becomes only 0.7 mm., while at 180° and 16mm. pressure practically no double molecules exist.

The sugar carbon is wetted by water only as the air film is displaced. The weight of the water vapor sorbed was found to be but slightly greater than that of the air normally sorbed.

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[3] Zawidzki, *Z. physik. Chem.*, **34,** 138 (1900).

Results for Mixtures

Whereas in the preceding experiments 10 cc. of pure solvent was taken in each case, 1.69 cc. of solution was taken in order that the change in concentration brought about through sorption might be more accurately determined by analysis. In each case a blank experiment was carried out in the absence of charcoal in order to determine the weight and composition of the vapor in the upper bulb.

The results given in Tables III and IV were obtained in "reverse" experiments.

Table III

Sorption from Mixtures of Acetic Acid and Toluene at 25.5° by Carbon at 125°

Solution %HAc	Carbon *m*	Solution after	x/m HAc	x/m Toluene	%HAc in film	Total film[a] %
8.13	1.1697	5.76	0.037	0.094	29.0	97
	1.0865	5.88	.039	.091		
17.98	0.9894	16.41	.049	.076		
	1.0237	15.68	.058	.069	42.1	91
31.14	1.0739	29.41	.064	.068		
	1.0980	30.02	.070	.065	50.0	95
49.37	1.4235	46.72	.102	.054		
	1.1453	46.69	.093	.044	66.6	98
68.92	1.1947	66.85	.116	.021	79.1	90
	1.1480	68.29	.105	.036		

[a] For explanation see p. 2724.

Table IV

Sorption from Mixtures of Acetic Acid and Toluene at 75° by Carbon at 125°

Solution % HAc	Carbon *m*	Solution after	x/m HAc	x/m Toluene	%HAc in film	Total film[a] %
8.13	1.0376	6.59	0.030	0.116	..	...
	1.1616	6.83	.025	.122	19	112
17.98	1.0976	16.85	.042	.108	..	...
	0.9839	17.02	.040	.105	2	110

[a] For explanation see p. 2724.

The animal charcoal used in the first two experiments of Table V was extracted with concd. hydrochloric acid for four days, then washed until washings gave no precipitate with silver nitrate and finally heated to redness.

For the last two experiments the charcoal was re-extracted with aqua regia for 24 hours and then treated as before.

Table V

Sorption from Mixtures of Acetic Acid and Toluene at 25.5° by Animal Charcoal at 125°

Solution % HAc	Carbon *m*	x/m HAc	x/m Toluene	% HAc in film
54.63	1.3164	0.076	0.014	
	1.2000	.074	.008	87
54.63	1.2738	.082	.010	
		.073	.013	86

Results for Ordinary Sorption Experiments at Room Temperature

These were carried out by weighing in about 100 cc. of the solution into a tube containing a weighed amount of charcoal. After one hour a weighed sample of the equilibrium solution was titrated to ascertain the final concentration.

In the following table c_1 denotes the initial concentration of acetic acid in grams per gram of solution; c_2 denotes the final (equilibrium) concentration of acetic acid in grams per gram of solution; m denotes the weight of charcoal (air-free); x^1/m denotes the acetic acid apparently adsorbed per gram of charcoal and is in fact $\frac{g}{m} \cdot \frac{c_1 - c_2}{1 - c_2}$ where g is the weight of 10 cc. of the original solution.

TABLE VI

SORPTION BY CARBON IMMERSED IN LIQUID MIXTURES OF ACETIC ACID AND TOLUENE

c_1	c_2	m	x^1/m
0.8590	0.8553	1.039	0.250
	.8567	1.035	.158
.8593	.8533	1.030	.404
	.8569	1.041	.164
.7132	.7057	1.010	.248
	.7068	1.012	.211
.5110	.5051	1.040	.094
	.5060	1.036	.092
.3269	.3198	1.018	.094
	.3196	1.023	.096
	.3195	1.022	.097[a]
.2326	.2288	1.047	.042
	.2284	1.040	.047

[a] At 90°.

Discussion

A. Pure Solvents.—It is evident that we possess a particularly convenient method[4] for the study of the sorption of vapors over a wide range of temperature and pressure.

Considering first the result for toluene, we notice that at each temperature with increasing pressure of vapor in the apparatus, a maximum value of sorption is readily attained. Further, this saturation value, 1 g. of toluene to 8 g. of carbon, is nearly independent of the temperature of the carbon, being only slightly less at 245° than at 125°.

The chief difference in behavior observed is that the higher the temperature of the carbon, the greater is the pressure of toluene vapor required to attain the saturation value.

It is not so much the absolute magnitude of the vapor pressure or the

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[4] A further important improvement and simplification making the method very suitable for general adoption will be described in a subsequent communication. A coiled spring of fused silica is employed as "sorption balance" permitting the complete study of sorption isotherms at all pressures and temperatures to be carried out without opening the apparatus.

difference in vapor pressure of the liquid at the temperatures of the lower and upper bulbs, as rather the ratio of the vapor pressures at the two temperatures that defines the minimum pressure for the attainment of the saturation value. This would be approximately reflected in a constant difference of temperature between the upper and lower bulbs to obtain the same degree of sorption nearly independent of the absolute temperature.

The question at once arises as to whether this saturation value is to be regarded as a monomolecular film upon the surface of the carbon, which would explain independence of the temperature.

Langmuir considers that the porosity of charcoal obtained from cellulose extends to atomic dimensions, and that there is no definite surface which can be covered by a layer one molecule deep. Among the spaces between the atoms of carbon there must be some in which a molecule would be nearly surrounded by carbon atoms on all sides, whereas in others a molecule would be able to hold to a single carbon atom. There would, however, be a fairly sharp limit to the number of molecules which would come into intimate contact with carbon atoms. This saturated state would correspond to the monomolecular film observed on plain non-porous surfaces of mica, glass and platinum as studied by Sweetser. Similar considerations would probably apply to our sugar carbon. They also would explain the fact that the saturation value was not quite sharp, but that it was distinctly higher when the vapor pressure is further increased for any one temperature. It is impossible to study this effect very closely, since if the temperature of the two bulbs is brought too close together, condensation of liquid undoubtedly commences in the finer pores.

The behavior of acetic acid is in the main similar to that of toluene; and once more there is a saturation value which is nearly independent of the temperature of the carbon, 1 g. of acetic acid to 6 g. of carbon. If we are to regard these saturation values as the equivalent of monomolecular films, they must be proportional to the molecular weights of the adsorbed substances. This is found to be the case if we assume that acetic acid exists on the surface in the form of double molecules only. Thus, if the weight of a film of toluene is 12.5% that of the carbon, that of an equivalent film of double molecules of acetic would be 0.163 in agreement with the values 0.165 to 0.169 observed. However, this is not decisive since the volumes of these amounts of toluene and acetic acid are very similar in the form of liquid.

The big difference between toluene and acetic acid is that the latter is sorbed with much more difficulty at high temperatures. Indeed, at 245° (with liquid at 25°) the adsorbed acetic acid film has practically disappeared, while 64% of the toluene film is retained. This is what was to have been expected from the known effect of increase of temperature in rapidly eliminating the double molecules.

From these results for the pure solvents it is seen that the sorption of acetic acid is comparable with that of toluene at lower temperatures, whereas at higher temperatures it is very much less. From this we should predict that in mixtures of acetic acid in toluene in ordinary sorption experiments, positive sorption of acetic acid would be observed at low temperatures and apparent negative sorption at high temperatures.

B. Mixtures of Acetic Acid and Toluene.—In Tables III and IV we have the data for the sorption from mixtures of acetic acid and toluene at 25° and 75° with carbon at 125°. The first test to apply is to see whether the value of the sorption in each case corresponds to a complete monomolecular film in which a proportion of single toluene molecules are replaced by double molecules of acetic acid. This is done in the final column by assuming that the values for the saturated film for toluene and acetic acid separately would have been 0.125 and 0.165, respectively and by adding the proportions of these two values actually sorbed for each of the components of the mixture. The result in Table III is to show a film which is 90 to 98% complete and in Table IV for 75°, 110% and 112%, values which agree within the experimental error.

Comparison of the first and sixth columns of these tables shows that in each case the proportion of the acetic acid in the film is greater than in the original liquid; in other words what is called positive sorption has taken place. This is in accordance with the ordinary sorption experiments recorded in Table VI. The greater relative sorption of acetic acid is that from the 18% solution at 25°. On the other hand, the true sorption of acetic acid increases steadily with increase in its concentration. This brings out clearly the distinction between the present absolute results and those of the ordinary relative method.

The relative sorption of acetic acid is less when the liquid is heated to 75°, a fact which is doubtless in accordance with the effect of rise of temperature upon the concentration of double molecules in the vapor, although this is difficult to calculate with accuracy. It also goes parallel with the difference between the partial pressures of acetic acid and toluene at the two temperatures.

C. Ordinary Sorption Experiments.—The experiments in Table VI are not perfectly comparable with those of the other tables, but they serve to confirm the occurrence of positive sorption in every case. Schmidt-Walter[5] observed this also in the case of sugar carbon. The absolute amount of acetic acid sorbed is, however, greater than that expected from the hypothesis here employed.

Our thanks are due to the Colston Research Society of the University of Bristol for a grant for materials.

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[5] Schmidt-Walter, *Kolloid Z.*, **14**, 249 (1914).

Summary

1. The sorption of vapors of toluene and acetic acid by sugar carbon affords saturation values nearly independent of the absolute temperature.
2. Determination of the true sorption of both solvent and solute is in accordance with the conception that toluene and acetic acid can replace each other in the adsorbed film.
3. These absolute determinations of sorption agree with the ordinary relative determinations which exhibit "positive sorption" of acetic acid.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ELECTROMETRIC TITRATION OF ANTIMONY AND TIN BY POTASSIUM DICHROMATE

BY MAURICE H. FLEYSHER

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The quantitative oxidation of antimony in a hydrochloric acid solution from the trivalent to the pentavalent state by a standard solution of potassium dichromate has been observed by Kessler[1] and that of tin from the bivalent to the quadrivalent condition by Steng.[2] In each of these methods difficulty was experienced in observing the end-point of the titration. Recently an oxidimetric study of antimony has been made by Knop.[3] Since the work of Hildebrand[4] a large amount of investigation has been made in the application of the electrometric indicator in volumetric analysis. In the present study the estimations of antimony and tin have been made using an oxidation-reduction electrode. Antimonous and stannous chlorides were titrated in a hydrochloric acid solution singly and in mixtures by potassium dichromate. By adding an excess of mercuric chloride to a mixture of the two before titration, the tin is oxidized and the antimony content is accurately determined in the presence of the tin. The mercurous and mercuric chlorides present in the cell exert no influence on the character of the titration.

Apparatus and Materials

The apparatus used was the same as that described by Hildebrand[4] except that the hydrogen electrode was replaced by one of platinum foil and the mercury electrometer by a Leeds and Northrup portable galvanometer. A normal calomel electrode served as the constant half of the cell, the other half of which was a 200cc. beaker containing the solution to be titrated and into which dipped the platinum electrode.

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[1] Kessler, *Pogg. Ann.*, **118**, 17 (1863).

[2] Steng, *ibid.*, **92**, 57 (1854).

[3] Knop, *Z. anal. Chem.*, **63**, 81 (1923).

[4] Hildebrand, THIS JOURNAL, **35**, 869 (1913).