

## SORPTION OF WATER VAPOUR BY POWDERED *CICER ARIETINUM*. HEAT OF SORPTION

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The sorption of water and toluene vapours on gram powder (*Cicer arietinum*) has been studied with a view to ascertaining the fate of the sorbed vapour. Three samples of powder (alkali-washed, toluene-washed and untreated) have been used. The isosteric heats of sorption have been determined. It appears that at least the first lots of water vapour taken up correspond to persorption rather than capillary or multi-layer condensation. Alkali-washed and toluene-washed samples show similar enhancement of sorption over the untreated powder. The heat of sorption decreases sharply from over 20,000 cal./mole at low values of sorption to about the latent heat of condensation of high values.

Makower ("Analytical Methods in Food Chemistry", American Chemical Society, 1950, p. 37) points out that "the moisture determination is perhaps one of the most widely used analytical measurements in processing and testing food products..... moisture content is frequently an index of stability and quality of food". However, he discusses in detail that moisture determination in vegetables and fruits is a difficult matter. The difficulties are much lessened with corn and perhaps other grains. Sair and Fetzer (*Cereal Chem.*, 1942, 19, 633) found that corn might be heated to 110° in contact with boiling toluene without decomposition, while vegetables started decomposing around 70°.

Makower doubts the utility of using moisture content of the whole food as a critical variable, because the moisture is not uniformly distributed among the various constituents. Thus, for example, the moisture content may be a sum of the constituent starch, protein, sugar and cellulose. Each of these is determined by the relative humidity and is described by an isotherm for the component. The overall moisture is therefore of little significance since the water content of the most sensitive component will determine deterioration. Hence, Makower and Miss Myers (*Proc. Inst. Food Technol.*, 1943, 156) have suggested the equilibrium pressure of water vapour as an index of moisture. They, however, remark that "At the present time very few vapour pressure data are available for foods".

It is partly to provide data of this kind as well as make an attempt to ascertain how the water exists in the grain that the present work has been undertaken. It might appear at first sight that any theoretical approach from the point of view of sorption will be futile considering the chemically heterogeneous character of the material. However, it is difficult to think of a solid adsorbent which is chemically homogeneous (not excluding adsorbent silica or alumina). A chemically homogeneous solid may yet be physically inhomogeneous, as has been discussed by the author in two earlier papers (*J. Phys. Chem.*, 1945, 49, 442; *J. Phys. Coll. Chem.*, 1949, 53, 1091). The capillary condensation theory in any case completely ignores the chemical nature of the adsorbing material (as long as it is wetted by water). It appears that for most theoretical purposes gram powder is as good an adsorbent as any other powdered solid.

*Cicer arietinum* is a common Indian gram with a large protein content, albuminoids 21.7%, water 11.5%, starch 59%, oil 4.2%, fibre 1%, ash 2.6% including phosphoric acid 1.1%, for husked seeds (Church, "Food Grains of India," cited by Watt, "Economic Products of India," Vol. 2, p. 210, Calcutta, 1889). The composition is, of course, variable as will appear from another typical analysis: moisture 9.8%, protein 17.1%, fats (ether extract) 5.3%, minerals 2.7%, fibre 3.9%, carbohydrates 61.2%, calcium 0.19% and phosphorus 0.24% for the whole grain ("Wealth of India", Vol. 2, p. 154, New Delhi, 1950).

### EXPERIMENTAL

The grains were split to remove the skin and powdered to 40-60 mesh. One portion was refluxed with dilute sodium hydroxide, washed thoroughly with distilled water and dried. Another portion was refluxed with excess of toluene and dried. A third portion was not subjected to any washing. It was evacuated at 55° before taking sorption measurements. It was then evacuated at 100° before another run. An excess of water was then added to the powder, the containing bulb maintained in boiling water for half an hour, and the sample then evacuated at 100° for fresh runs. Finally, it was evacuated at 250° for the last set of measurements. The sorption apparatus used has been previously described (this *Journal*, 1949, 28, 308). The sorption bulb was maintained at constant temperatures with the help of a Dewar flask containing suitable bath materials.

TABLE I

*Sorption on alkali-washed gram powder.*

$x/m$  = mg. water sorbed per g. of powder.  $p$  = pressure in mm. oil.  
(1 mm oil = 0.0714 mm. mercury).

		Temp. = 0°. Desorption.						Temp. = 0°. Adsorption.											
$p$	61	60	58	49	32	10	16	25	45	61									
$x/m$	488	387	302	210	164	100	72	99	169	279									
		Temp. = 10°. Desorption.																	
$p$	124	121	118	100	79	56	40	29	19	3									
$x/m$	403	350	334	201	166	133	111	97	81	52									
		Temp. = 20°. Desorption.																	
$p$	232	229	221	197	165	146	128	102	80	73	55	44	32	22	10				
$x/m$	322	274	238	195	171	152	139	121	108	103	85	79	71	59	44				
		Temp. = 30°. Desorption.						Temp. = 40°. Desorption.											
$p$	252	197	158	115	89	64	39	34	16	278	228	200	165	139	112	86	76	43	9
$x/m$	39	118	102	82	71	66	51	48	31	87	80	75	68	63	56	50	43	36	19

The sorption data for water and toluene are shown in Tables I-IV. Some of the isotherms are shown in Fig. 1 in which  $x/m = \text{mg. water vapour (or toluene) sorbed per g. of powder}$  is plotted against the equilibrium pressure in mm. oil (1 mm. oil = 0.0714 mm. mercury). As far as one can see all the isotherms belong to Type II, (Brunauer, "Adsorption of Gases and Vapors", p. 150, Princeton University Press, 1943), excepting the water isotherm for the powder evacuated at 250°. It appears from the sorption data that sorption hysteresis exists in all cases of water sorption excepting the last mentioned. The hysteresis commences at the lowest pressures. This unusual observation may not have been possible without the sensitive oil manometer.

TABLE II

*Sorption on toluene-washed gram powder.*

	Temp. = 0°. Desorption.						Temp. = 0°. Adsorption.								
$p$	62	62	58	45	32	9	25	35	44	62					
$x/m$	337	317	273	183	137	79	110	128	154	370					
	Temp. = 10°. Desorption.						Temp. = 20°. Desorption.								
$p$	130	127	116	86	52	19	232	210	162	96	51	12			
$x/m$	495	417	296	168	109	74	308	243	143	105	81	53			
	Temp. = 30°. Desorption.									Temp. = 30°. Adsorption.					
$p$	276	250	204	180	115	77	45	21	3	14	60	101	153	194	208
$x/m$	135	126	111	101	87	68	57	50	29	33	52	64	77	87	95
	Temp. = 40°. Desorption.														
$p$	287	282	235	203	151	125	103	80	77	67	18	6	small		
$x/m$	91	90	82	78	70	66	62	57	54	51	30	20	6		

TABLE III

*Sorption on untreated gram powder.*

Temp. = 0°. Powder evacuated at 55°-60° and flushed several times.

	Desorption.										
$p$	62	59	57	53	45	41	35	22	10	small	
$x/m$	178	160	147	125	102	89	77	64	47	26	
	Temp. = 35°. Desorption, on the same sample.										
$p$	234	218	190	173	147	126	102	88	67	51	34
$x/m$	41	39	37	35	33	32	28	26	22	20	15
	Temp. = 0°. Powder moistened with water and heated at 100° for $\frac{1}{2}$ hour, then evacuated at 100°.										
	Desorption.										
$p$	62	60	58	54	37	15					
$x/m$	256	219	165	119	81	55					
	Temp. = 0°. Powder evacuated for half an hour at 250°-270°. Desorption.										
$p$	62	39	31	26	21	11					
$x/m$	38	37	36	34	32	24					

TABLE IV

*Sorption of toluene on gram powder (desorption).*

$p$	Toluene-washed-powder.				Alkali-washed-powder.			
	96	41	15	small	92	87	14	13
$x/m$	22	6	5	3.2	44	8	2.2	1.8

TABLE V

*Heats of desorption from isosteres.* $Q$  (cal./mole) corresponding to amounts sorbed at 20°

$x/m$	Water on alkali-treated gram.				Water on untreated gram (Table III, first two runs)	
	40	50	80	100	30	40
$Q$	20150	16030	13930	11310	17640	14170

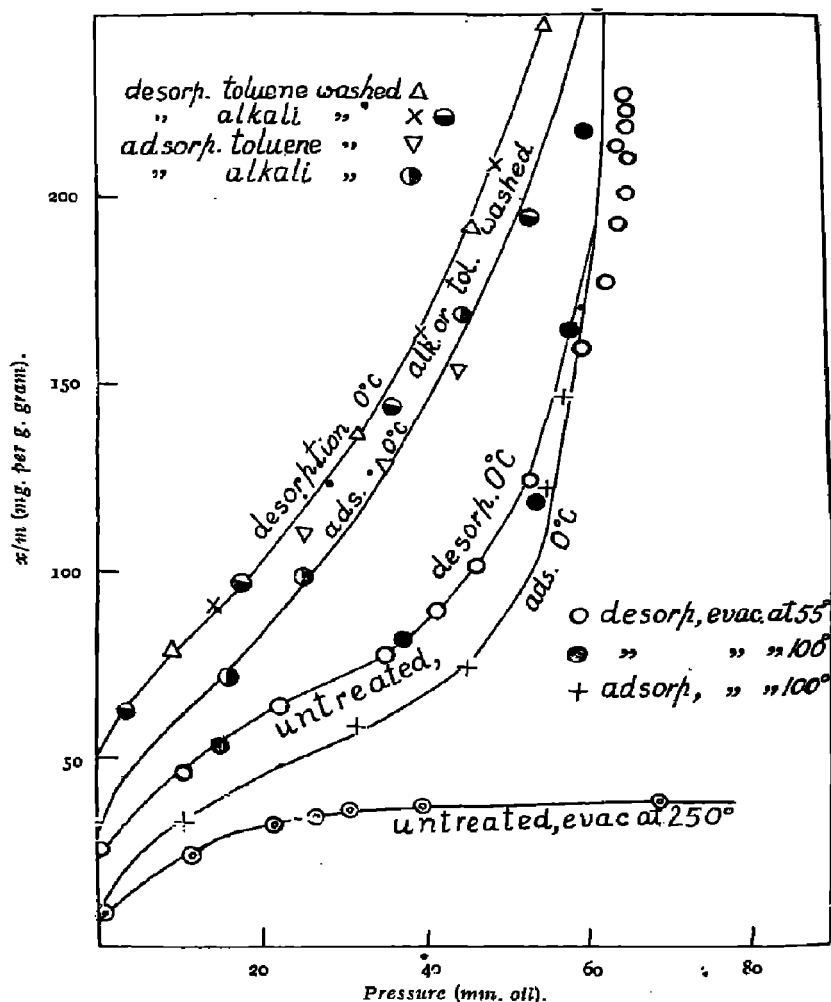
$x/m$	Water on toluene-washed gram.							
	40	60	80	100	120	140	180	220
$Q$	23640	18020	14090	12940	11340	10570	10100	10020

The amounts of sorption in these tables may be converted into c. c./g. powder. It would then appear that a far smaller volume of toluene is taken up than water under similar conditions. Even at saturation pressure, the volume of toluene sorbed is much less than that of water. Clearly therefore the principal process involved is not capillary condensation.

## DISCUSSION

Washing with alkali or toluene considerably enhances sorption for water. It is interesting that the increase is almost the same in each case. As a matter of fact the sorptions for the two samples are almost coincident at any temperature. However, in the sorption of toluene, the toluene-treated sample shows a larger capacity (Table IV). Solid circles on the desorption isotherm of untreated gram in Fig. 1 correspond to the sample which has been boiled in contact with water before evacuation. Boiling is likely to produce changes in the gram (e.g. bursting of cells), but strangely enough, the sorptive properties are not affected. Table III shows that evacuation at 55°-60° is not enough to remove all the water from the powder. The apparent  $x/m$  values are therefore smaller than those for the same sample evacuated at 100°.

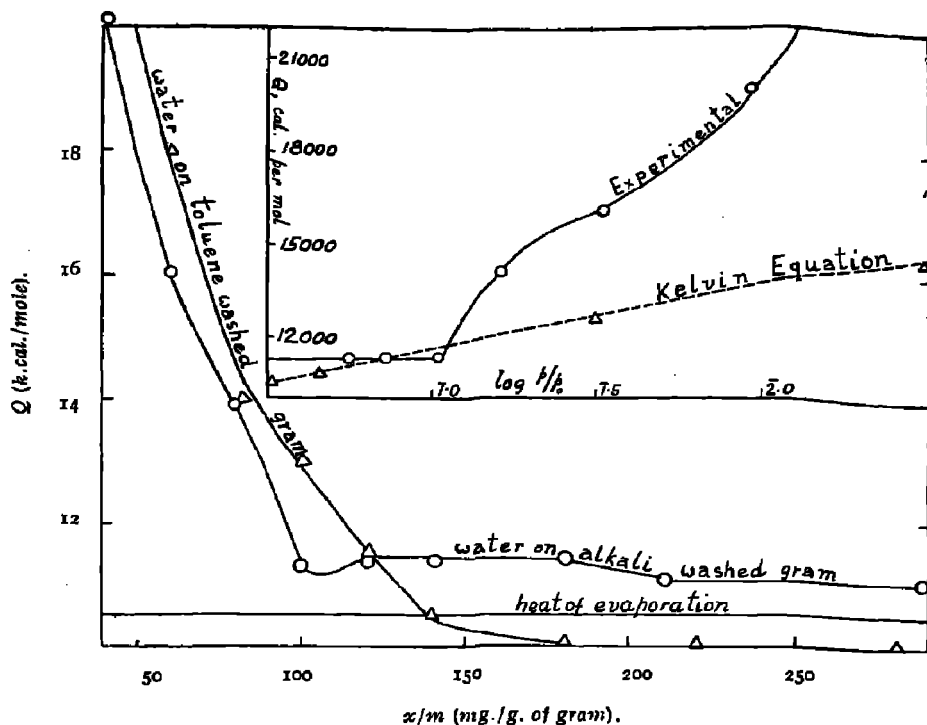
FIG. 1  
Sorpiion isotherm.



Most of these curious observations are easily understood if we consider that the main process concerned in these sorptions is a deep and highly disperse penetration of the sorbed molecules in the material of the adsorbent, a process akin to persorption rather than capillary or multi-layer condensation. This would explain the enhancement of sorption on washing with toluene or alkali (removal of fatty matter and opening up structures for penetration of water molecules), the much smaller sorption of toluene (hindrance to penetration due to large size of toluene molecules), and indifference towards boiling as far as water sorption is concerned, since the cell wall is already freely pervious to water molecules.

FIG. 2

FIG. 3



*Isosteric Heats of Sorption.*—The above view concerning the fate of sorbed water is further supported by calculations of isosteric heats of sorption. These heats ( $Q$ ) have been calculated from the desorption isotherms for water by the method discussed before (*this Journal*, 1949, 26, 345) and are shown in Table V.  $Q$  has been plotted against  $x/m$  in Fig. 2. In spite of the apparent similarity of the curves for the two samples (toluene-washed and alkali-washed), the  $Q$  values show differences. The toluene-treated sample shows larger values initially, but smaller ones finally. The curve becomes flat at  $x/m$  = about 100 for the alkali-washed gram, but only at a higher value, about 140, for the toluene washed-sample. In both cases  $Q$  tends to attain the value of latent heat of evaporation of water at high  $x/m$ . The widely variable  $Q$  is fundamentally opposed to the possibilities of the sorbed water being present as capillary condensed or multi-layer condensed water. The latter presumes a constant value for  $Q$ . The former does require a variation of  $Q$ , but of a smaller order. Proceeding from the Kelvin equation

$$RT \ln \frac{p}{p_0} = - \frac{\sigma V}{r} \quad \dots (i)$$

one can obtain the equation

$$Q = L + RT \ln \frac{p_0}{p} \left( 1 - \frac{d \ln \sigma}{d \ln T} \right) \quad \dots \quad \dots \quad (ii)$$

where  $L$  = molar latent heat of evaporation,  $V$  = molar volume,  $r$  = radius of meniscus of the capillary condensed liquid and  $\sigma$  = surface tension. Taking  $\sigma = 72.66$  at  $292^\circ \text{K}$  and  $72.73$  at  $294^\circ \text{K}$ , equation (ii) may be written as

$$Q = L + 2.303 \times 1.59 \log \frac{p_0}{p} \quad \dots \quad \dots \quad (iii)$$

For the simple capillary condensation one should expect a straight line graph between  $Q$  and  $\log p_0/p$  ( $p_0$  = saturation pressure and  $p$  = equilibrium pressure at the given temperature). The graph corresponding to equation (iii) and the experimental graph are shown in Fig. 3 (inset in Fig. 2). The two graphs are widely separated and the experimentally obtained  $Q$  values are generally much larger than those from (iii). It is clear that the adsorbent material is exerting a more specific effect on the sorbed water. It can hardly do so without coming in intimate contact with most of the sorbed water molecules, such as takes place in persorption. The structure of the material responsible for persorption is broken down perhaps near  $250^\circ$ , when the sorption falls down steeply, and the isotherm becomes indicative of simple surface adsorption (Type I isotherm).

We have stated above that gram ordinarily contains about 10% moisture ( $x/m = 100$ ). On the basis of the above study it appears reasonable to conclude that practically all of this water is intracellular. Dry gram contains little water condensed in the intercellular capillary spaces, if any.

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