Change of Moisture Content of Cottonseed Products With Respect to Atmospheric Conditions

By EGBERT FREYER
South Texas Cotton Oil Company

THE writer's interest in this subject originated with the determination of the data presented in Table I. His laboratory, newly built and equipped with protein apparatus of somewhat original design and of local construction, started the 1931-32 season without receiving Smalley Foundation check meal samples. With the purpose of securing additional checks on the accuracy of the work being done, the remaining portions of eight of the check meal samples were obtained from a neighboring member laboratory and ammonia determinations made on them at intervals. In the results is to be found a rather interesting lesson: namely, that any laboratory desiring to receive the benefits of cooperative analytical work on meal samples, had best join the Smalley Foundation, and not borrow the remnants of its samples.

The ammonia values found are seen to be irregularly lower than the accepted average values. It was suspected that, due to repeated openings of the sample containers, their moisture contents had increased to an extent sufficient to account for the low values. Moisture determinations were therefore made, with the results shown in Columns 4, 5 and 6. The corrected ammonia values are high. Now when it was considered that the moisture determinations were made after the ammonias were run, and especially after the volume of the samples had been reduced; so that the specific surface (surface/volume) had increased, facilitating moisture absorption, it appeared likely that a fair proportion of the moisture absorption of the samples occurred between the two determinations.

Accordingly, the ammonia values were again corrected, using one-half of the moisture differences. The new values shown in Column 7, while they individually vary fairly widely from the accepted values, are, on the average, in very close agreement with them. In view of circumstances under which these samples were received and analyzed (less than five grams were left for moisture tests, so that duplicates could not be run), the large variations of 0.08 per cent and 0.09 per cent are not surprising.

In order to examine more closely the change of moisture content of meal, two samples of extreme moisture content were exposed to a warm humid atmosphere. Sample A-Table II had been stored for several months in the carboard mailing case in which it was received, at which time the moisture content was reported as 8.07 per cent. Over three per cent was absorbed, until at 11.35 per cent moisture content it was in equilibrium with the humid atmosphere. Under the same conditions, Sample B, which had been partially dried, absorbed moisture at the rate of 0.1 per cent per three minute exposure.

TABLE II—EFFECT OF EXPOSURE TO ATMOSPHERE ON THE MOISTURE CONTENT OF COTTONSEED MEAL

A—High Moisture Content			B—Low Moisture Content	
Time Exposed			Time Exposed	
Min.	Sec.	% H_2O	Min.	% H_2O
1	21	11.35	1½	4.01
3	26	11.34	3	4.07
8	41	11.34	17½	4.24
11	26	11.41	19	4.34
13	56	11.34	21	4.43
16	11	11.27	22½	4.49
17	56	11.41	24½	4.61
			26	4.54
			28	4.71
			29½	4.77
			31½	4.85
			33	4.97

Next, a number of samples representing car shipments were taken at random from the storage shelves and the moistures were rerun on them. The moisture contents were then compared with the values originally reported, and the gain was found to be inversely proportional to the original moisture content and independent of the length of the storage period in the range of 1 to 144 days. Humid conditions prevailed, in general, during the period of storage. The data are given in Table III and plotted in Figure I.

Such, then, are the observations that led to the formation of this committee.

TABLE III—MOISTURE CHANGE IN MEAL SAMPLES STORED IN CARDBOARD MAILING CASES

Sample Date	Elapsed Time Days	Reported Moisture %	Moisture %	Gain % H_2O
4- 2-32	144	7.55	8.40	0.85
5-30-32	86	8.26	8.61	0.35
7-16-32	39	6.65	8.71	1.52
8- 5-32	19	6.74	8.14	1.40
8-23-32	1	6.92	8.25	1.33

MOISTURE CHANGE (IN 24 HOURS) OF TWO STORED SAMPLES

Date	Humidity °	Temperature ° F.	Vap. Pres.	Moisture %	Gain %
8-24-32	68	92	1.02	8.44	....
8-25-32	72	90	1.01	8.65	0.21
8-24-32	68	92	1.02	6.76	....
8-25-32	72	90	1.01	7.25	0.49

TABLE I
Effect of Change in Moisture Content on Analysis of Check Samples of Cottonseed Meal.

Accepted Ammonia	Ammonia Found	Difference	Accepted Moisture=Ma	Moisture Found=Mf	(Mf—Ma)	Ammonia, Corrected for Full Moisture Difference	Difference	Ammonia, Corrected for ½ Moisture Difference	Difference
7.27	7.26	—0.01	7.55	9.83	2.28	7.44	+0.17	7.33	+0.06
6.43	6.37	—0.06	7.45	8.68	1.23	6.46	+0.03	6.41	—0.02
7.20	7.15	—0.05	8.29	...	...	...	...	...	...
7.14	7.16	0.02	8.00	9.55	1.55	7.28	+0.14	7.22	+0.08
8.12	7.96	—0.16	6.14	9.60	3.46	8.27	+0.15	8.11	—0.01
6.67	6.63	—0.04	7.51	9.86	2.35	6.80	+0.13	6.71	+0.04
4.94	4.87	—0.07	4.42	7.90	3 48	5.05	+0.11	4.96	+0.02
7.79	7.67	—0.12	6.79	7.50	0.71	7.72	—0.07	7.70	—0.09
Avg. Difference ...		—0.064	...	...	...	...	+0.0943	...	+0.0113

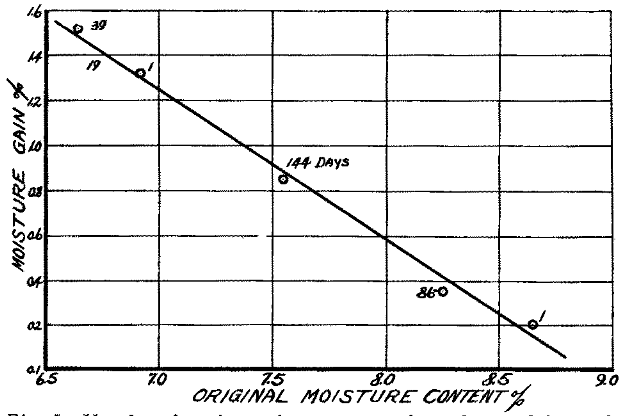

Fig. I—Uptake of moisture by cottonwood meal stored in cardboard mailing cases

That cottonseed meal absorbs and loses moisture is common knowledge to any observing person who has handled it in the laboratory. That such changes may have serious bearing on the protetin and fat analysis of this product is probably not appreciated generally. But that, in settlement analysis, a price difference as large as $20.00 per car of cake may result from possible variations in moisture content is a circumstance that makes this problem worthy of some attention.

Experiments Involving Known But Random Humidities

In the main, three conditions govern the transfer of moisture between a material like cottonseed meal and the atmosphere. These are (1) the aqueous vapor pressure of the meal, (2) the vapor pressure of the atmosphere, and (3) the contact area, or the character of exposure.

In this work only a few different samples of 43 per cent meal were used and no effort was made to ascertain how the vapor pressure from different meal samples might vary under the same conditions. It is probable that variations in the hull and oil contents, as well as in other constituents of meal, cause variations in its vapor pressure.

The vapor pressure of the atmosphere is a measure of the absolute humidity and is expressed in this paper in inches of mercury, in accordance with the practice of the U. S. Weather Bureau. At a given temperature the vapor pressure depends on the relative humidity and may be found by multiplying the vapor pressure of water for that temperature by the relative humidity. It shall be seen that the moisture content of meal depends more upon the relative humidity than upon the vapor pressure. The surface contact between the meal and the atmosphere governs the rate of moisture exchange, and theoretically has no bearing on the final or equilibrium value of the moisture content; although this may have two values depending upon whether it is approached from the dry or the wet side.

The first experiment of this series (Table IV) shows that under humid conditions, a sample of relatively high moisture content may lose about 0.3 per cent of moisture as it is ground in a mill, while one of low moisture content may gain an equal amount under the same conditions. Experiment (2) shows that the former sample appears to be in equilibrium with approximately the same atmosphere when exposed in bulk, whereas the low moisture meal gains considerable water under the same conditions. More prolonged exposures in beakers, however, results in continued, but diminishing uptake in both cases, as shown in the third series of measurements. The last series indicates the behavior of high and low moisture meals in an average atmosphere, one losing, the other gaining, both approaching the value of 7.9 per cent. In view of its bearing on the analysis of cottonseed, it was considered important to determine the extent of moisture exchange between this product and the atmosphere during cleaning, in which treatment it is considerably exposed; especially as the Official Method requires the sample for moisture determination to be taken *after* the seed is cleaned.

For several days the seed received by this laboratory were handled as follows: Samples for moisture were taken before and after cleaning; the time of cleaning was noted; and the humidity was determined by taking wet and dry bulb temperature readings. The data are given in Table V. In the last two series represented, samples of definite moisture content were selected and the atmosphere was artificially heated and humidified. A slight loss is indicated in the first series when the atmosphere may be said to have been cool and dry.

Almost the same conditions obtained in the second series, and the uptake is very slight.

In the third, for reasons that will appear later, loss of moisture due to low humidity was prevented by the effect of the low dry bulb temperature.

In the fourth, dry bulb temperature, humidity, and vapor pressure were moderately high and the samples gained moisture.

In the fifth, the tendency towards gain due to the higher vapor pressure was more than counterbalanced by the opposite effect of the higher temperature.

In the sixth series, the conditions are fairly extreme, but such are not unusual in the coastal belts. Considerable gain of moisture occurred, both in the case of high and low moisture seed.

The last represents a condition common in the South until as late as October. The loss is roughly proportional to the moisture content.

The changes thus noticed are of a sufficient magnitude to account in part for the wide discrepancies in the

TABLE IV—EFFECT OF GRINDING MEAL IN BAUER MILL ON MOISTURE CONTENT

Dry Bulb Temp. °F.	Humidity Rel., %	V. Pres.	Moisture Content Before %	After %	Gain ( ) Loss (—)
87	80	1.02-In.	8.81	8.47	—0.34
90	74	1.04	8.85	8.69	—0.16
86	77	0.96	8.77	8.84	0.07
83	45	0.50	8.80	8.59	—0.31
87	80	1.02	6.58	6.50	—0.08
90	74	1.04	6.54	6.84	0.30
86	77	0.96	6.17	6.58	0.41
83	45	0.50	6.20	6.40	0.20
Following were exposed to air four hours in 100 cc. beakers:					
°F.	%				
91	64	0.96	8.77	8.77	0.00
91	64	0.96	6.17	6.82	0.65
Following were exposed overnight, humidity being given for time of weighing:					
°F.	%				
86	77	0.96	8.77	9.34	0.57
87	84	1.07	9.34	9.46	0.12
85	80	0.96	9.46	9.55	0.09
86	77	0.96	6.82	7.86	1.04
87	84	1.07	7.86	8.88	1.02
85	80	0.96	8.88	9.00	0.12

CHANGE OF MOISTURE CONTENT ON EXPOSING MEAL TO AIR FOR EXTENDED PERIODS

Date	Time Expd., Hrs.	H_2O	H_2O	Humidity Condition 9:00 A. M.	12 Noon	4:00 P. M.
9- 7-32	 0	8.8	6.2	°F.	°F.	°F.
9- 7-32	 6	8.59	6.48	79	88	91
9- 8-32	24	8.24	6.76	55%	45%	42%
9- 9-32	48	7.40	6.69	0.55-in.	0.59-in.	0.63-in.
9-10-32	72	7.03	6.74			

TABLE V — CHANGE IN MOISTURE CONTENT OF SEED DURING CLEANING

Temperature Wet Bulb °F.	Dry Bulb °F.	Relative Humidity %	Vapor Pres. (In Hg.)	Time of Cleaning Min.	Moisture Content Before %	After %	Difference
55	66	48	.306	15	11.5	10.8	—0.7
55	66	48	.306	5	9.9	9.8	—0.1
55	66	48	.306	5	8.6	8.5	—0.1
55	67	45	.297	3	10.4	10.0	—0.4
55	67	45	.297	6	10.0	10.0	0.0
55	65	52	.320	4	8.7	8.6	—0.1
55	65	52	.320	6	9.8	10.2	+0.4
54	66	45	.287	5	8.8	8.8	0.0
54	66	45	.287	4	9.2	9.3	—0.1
56	70	40	.293	4	9.0	9.2	+0.2
56	70	40	.293	4	8.8	8.7	—0.1
56	70	40	.293	6	8.7	8.9	+0.2
56	69	43	.304	3	9.1	9.2	+0.1
55	69	39	.276	15	10.8	10.9	+0.1
55	69	39	.276	3	10.4	10.5	+0.1
56	69	43	.304	3	8.3	8.3	0.0
48	60	39	.202	4	9.8	9.8	0.0
48	60	39	.202	9	10.0	10.0	0.0
62	70	64	.468	11	9.3	9.0	—0.3
62	70	64	.468	5	8.5	8.5	0.0
62	70	64	.468	9	8.3	8.3	0.0
62	70	64	.468	4	9.1	9.2	+0.1
62	70	64	.468	13	9.3	9.9	+0.6
62	70	64	.468	4	9.3	9.3	0.0
64	72	65	.510	11	8.8	9.0	+0.2
64	72	65	.510	4	9.6	10.3	+0.7
64	72	65	.510	5	8.9	9.2	+0.3
64	72	65	.510	4	9.8	9.5	—0.3
63	71	64	.49	2	8.6	9.1	+0.5
63	71	64	.49	4	9.2	9.9	+0.7
63	71	64	.49	3	8.5	8.9	+0.4
70	80	61	.63	4	9.1	9.1	0.0
71	80	64	.67	8	10.0	10.1	+0.1
70	80	61	.63	3	9.9	9.9	0.0
68	77	63	.59	3	9.0	9.0	0.0
68	76	66	.60	4	8.6	8.6	0.0
69	77	67	.62	7	9.8	9.7	—0.1
68	77	63	.59	7	10.5	10.6	+0.1
68	77	63	.59	6	9.0	9.0	0.0
69	78	63	.61	13	10.0	9.9	—0.1
69	79	61	.61	4	9.8	9.5	—0.3
69	79	61	.61	5	10.6	10.1	—0.5
71	80	64	.67	5	11.4	11.5	+0.1
66	68.5	88	.62	10	14.0	14.7	+0.7
66	68.5	88	.62	10	12.3	12.7	+0.4
66	68.5	88	.62	10	7.4	7.8	+0.4
66	68.5	88	.62	10	7.4	7.8	+0.4
76	90	52	.73	10	7.8	7.7	—0.1
76	90	52	.73	10	10.15	10.0	—0.15
76	90	52	.73	10	14.7	14.15	—0.55

moisture content of seed as reported by various laboratories in the cooperative series. While for ordinary atmospheric conditions, they are not great enough to seriously affect the oil and ammonia analyses, yet under abnormal conditions such as occur often, and sometimes for protracted periods, in parts of the Cotton Belt, the loss or gain of moisture may be so marked as to cause a difference of 0.5—1.0 unit in the grade. The error from this source may be avoided by taking the portion of the sample for the moisture determination before the seed is cleaned. By such procedure two other sources of error are introduced: (1) error due to the including of foreign matter of moisture content different from that of the seed and (2) the possibility of not getting a portion representative of the whole sample. This latter could of course be avoided by mixing the sample before taking out the part for the moisture test and before cleaning. The effect of any unconscious segregation of seed during the cleaning could be corrected for by giving the sample an additional turn or two in the mixer *after* cleaning. The first error would be negligible except in the case of high percentages of such foreign matter as sand or pebbles.

Determination of Hygroscopic Moisture Under Controlled Conditions.

It seemed desirable while this investigation was in progress to ascertain how a meal sample would behave under all hygrometric conditions of the atmosphere as far as they are likely to be encountered in the Cotton Belt. Two meal samples were used, one of high, the other of low moisture content. Their analysis are as follows:

H_2O	Oil	Protein
7.1%	5.74%	43.8%
9.2	5.66	42.1
or, calculated to 8% moisture basis,		
8.0	5.68	43.4
8.0	5.73	42.6

Five humidities and five temperatures were chosen, giving twenty-five conditions, covering the ranges 20—100 per cent relative humidity and 6—35° C. (42.8—94° F.). Five-gram portions of meal were placed in official moisture dishes and exposed to the chosen hygrometric conditions in the following way. About 100 cc. of a sulphuric acid solution in water giving the desired humidity was placed in a pint jar; a small mayonnaise jar weighted with a few shot was placed in the acid, and on this, well above the acid was placed the moisture dish.

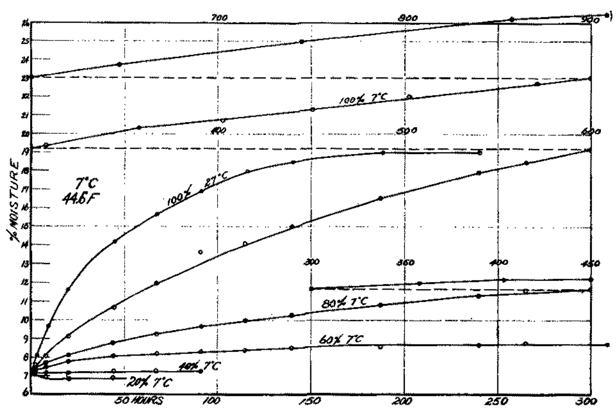

Fig. II

Then the airtight cap was screwed on and the whole placed in a water bath of the proper temperature (plus or minus 1° C.) The writer's laboratory is equipped with a well insulated closet, 43 ins. by 33 ins. having a drained space on the floor for 300 pounds of ice and a protected enclosure for samples to be kept at the minimum temperature. At the top is a heating lamp and thermoregulator set for the highest temperature desired. Between the lamp at the top and the ice at the bottom any intermediate temperatures are available, and adjust-

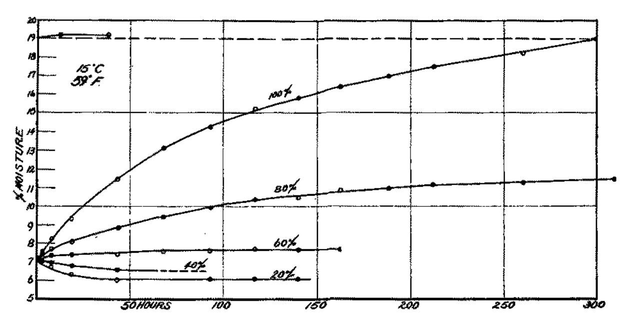

Fig. III

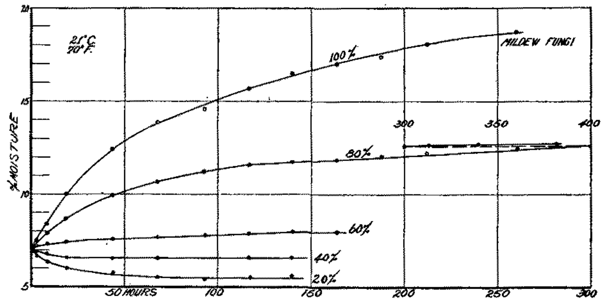

Fig. IV

able shelves, provided with thermometers, are placed at intervals. This arrangement was provided originally for storing shortening samples at various temperatures, but has proved useful in many ways. The ice consumption is about 50-150 lbs, per day, depending on the season.

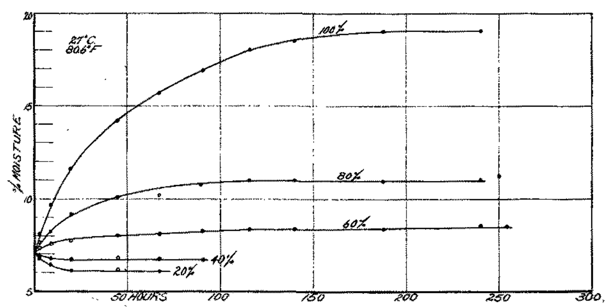

Fig. V

The meal samples thus exposed were weighed at various intervals of time, depending upon the rate of change, until the sample had come to equilibrium with its atmosphere, as indicated by the attainment of a constant weight. In the case of two of the samples kept under

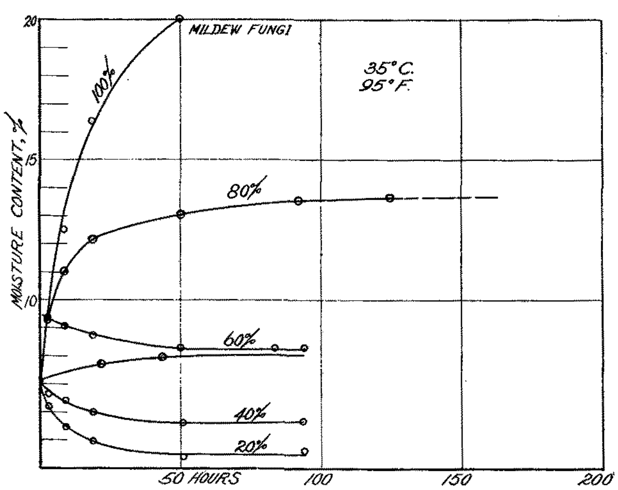

Fig. VI

100 per cent humidity, mildew fungi appeared and obviously terminated the test for those samples; and for the two conditions represented, we have only roughly estimated values of the equilibrium moisture content. The results of these tests are plotted in Figures 2-7.

DISCUSSION:

As would be expected, the greater the difference between the initial and equilibrium moisture contents, the

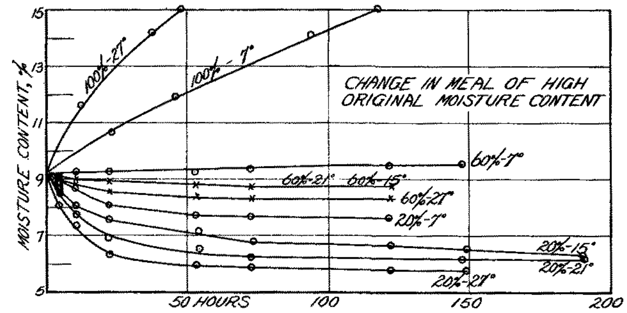

Fig. VII

longer is the time required to reach equilibrium. In Figure 5 it is seen that for 100 per cent humidity, increasing the temperature causes an increase in the rate of moisture absorption, but the final value is decreased. Figure 8 shows at A and B the variation of the equilibrium moisture content for different temperatures with (A), vapor pressure and (B), relative humidity. The effect of the aqueous vapor pressure of the sample is strikingly shown in A; for considering an external vapor pressure of 0.2 inches of mercury, the meal, which at 27° C. contains only 6.2 per cent moisture, will absorb at 7° C. until it contains 11 per cent. Or, for the sample to hold 19 per cent moisture, 1.00 in. of mercury vapor pressure is required at 27°, whereas only 0.25 inches are necessary at 7°, due to the decreased vapor pressure from the meal. At B we see that, except above 90 per cent humidity, the moisture content varies only slightly with temperature when plotted against the relative humidity; or in other words, the relative humidity is the chief factor governing exchange of moisture between meal and the atmosphere.

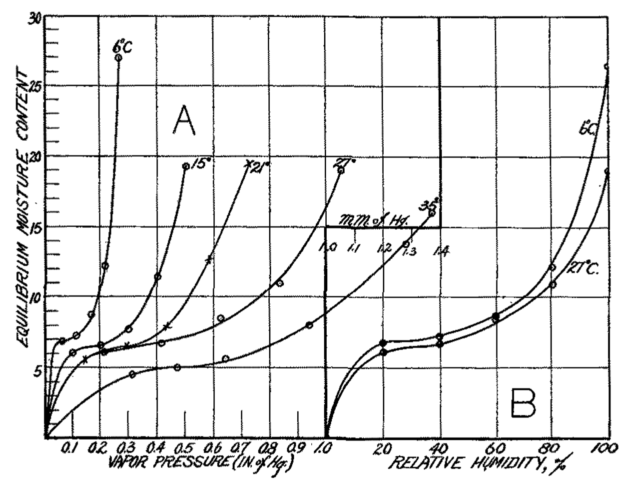

Fig. VIII

Since at equilibrium, the vapor pressure from the meal is equal to the vapor pressure of the atmosphere, we may construct vapor pressure curves for meals of various moisture contents by taking data from (A) Figure 8. This has been done in Figure 9, where the curve for water is given for comparison. In Figure 10 the changes in equilibrium moisture content are plotted against temperature for different relative humidities. In most of the curves there is a maximum and minimum. The curves marked by crosses are for meals losing moisture. This peculiar behavior may be explained by considering the course of the vapor-pressure-temperature curve of

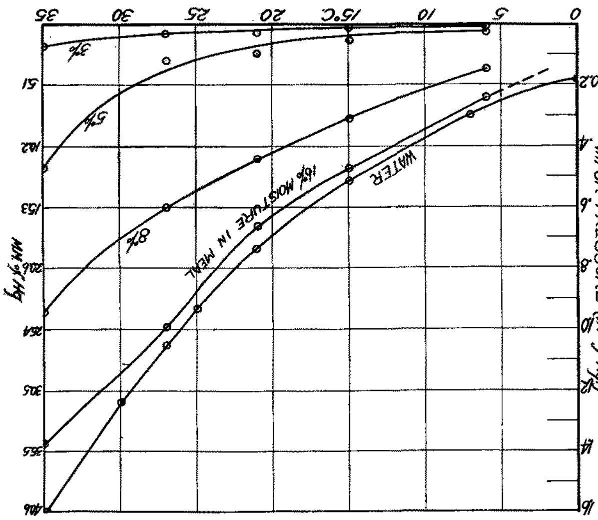

Fig. IX

meal and its relation to the corresponding curve for water vapor. Thus, at the lower temperatures, we would expect a decrease of equilibrium moisture content with increasing temperature, as shown by the curves, if the vapor pressure of the meal increases at a greater rate than that of water vapor. When the minima occur, the slopes of the vapor pressure curves should be the same; that is, the rates of vapor pressure increase should be equal. Corresponding to the upward trend of the curves, the slope of the vapor pressure curve of meal becomes greater than that of water until at the maxima they are again equal, after which the original relation is assumed. In other words, the vapor pressure curves of meal appear to be irregular. The explanation of this involves consideration of the mode or modes in which water is bound in meal; for example, we may postulate that part of the water is intimately associated in a colloidal state with the meal structure, the rest only loosely bound, the "hygroscopic moisture." There may be intermediate states. Between these various states there would exist equilibria, as well as between the hygroscopic and atmospheric moisture forms. Now as these would have different equilibrium constants which would themselves also have different temperature coefficients, we may regard the conditions as thus considered to be sufficiently complex to account for slight irregularities in the vapor pressure-temperature curve. In this connection, it is appropriate to consider the states of moisture in cottonseed. Here we clearly have a case of the existence of water in two different conditions: on the one hand, the "colloidal moisture" of the meat, on the other, the "hygroscopic moisture" of the hull and lint. It therefore seems reasonable to assume, as we have done above, that a similar, though less distinct, difference exists in the states in which water occurs in cottonseed meal.

Finally, attention is again directed to the fact that substances like cotton-seed meal have two apparent equilibrium moisture contents, depending upon whether equilibrium is approached by loss or by gain of water. This would indicate that one or both of these are false equilibria. It certainly means that meal may have two dif-

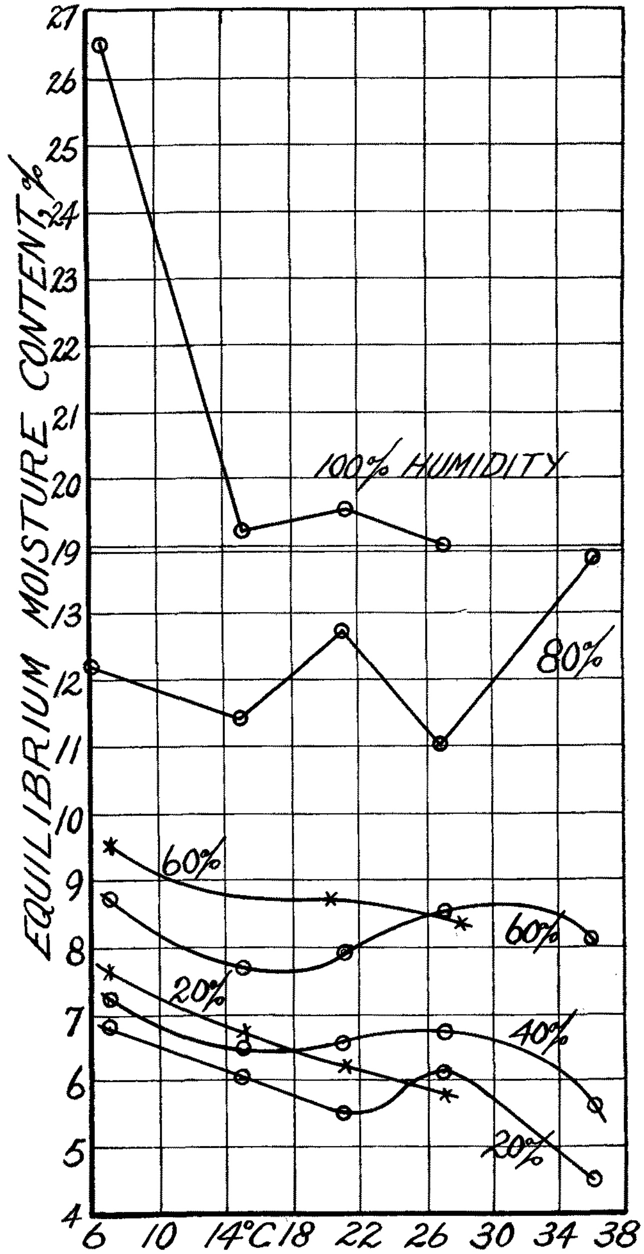

Fig. X

ferent vapor pressures at the same temperature, the higher being observed when the water is predominantly in the loosely bound state, the lower when the equilibria have shifted in the direction of the colloidal state.

Notice of Application—(First Publication)

The following have applied for Referee Chemist Certificates of the American Oil Chemists' Society:

Thos. B. Caldwell, Law & Company, Wilmington, N. C.

G. C. Henry, Law & Company, Cordele, Ga.

John D. Evans, Law & Company, Atlanta, Ga.

Notice of Application—(Second Publication)

Robert M. Simpson of Chas. W. Rice & Co., Columbia, S. C., has applied for a Referee Chemist Certificate of the American Oil Chemists' Society.