

Equilibrium Desorption of Water Vapor on Tobacco

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The equilibrium desorption moisture contents of air-cured (burley and Maryland), heat-cured (bright), and sun-cured (Turkish) tobaccos have been determined over a temperature range of 80° to 140° C. and a relative humidity range of 10 to 80%. The isosteric net heats of desorption varied from about 9000 to 16,000 B.t.u. per pound-mole in the region of 1% moisture to about 700 to 1800 B.t.u. per pound-mole in the 20% moisture region, depending on the type of tobacco. Apparatus and procedure are described which permit rapid isosteric (constant moisture content) determination on materials, such as tobacco, which are easily damaged by prolonged contact with excessive moisture or heat.

THE DRYING OF LEAF TOBACCO is of great importance to the tobacco industry. The moisture content of tobacco changes rapidly with changes in relative humidity, and the effect of temperature is also pronounced. In the storage, handling, and processing of tobacco, the moisture content must be held within close limits. If it is too low during drying of the leaf prior to storage, the tobacco will break badly during the handling operations, resulting in undue waste. If it is too high, the tobacco will decay during storage.

In order to study and evaluate tobacco dryer operations and performance properly, it was necessary to obtain data on the equilibrium moisture contents of the various types of tobaccos over a range of temperature normally encountered in drying operations. It was also desirable to obtain data on net heats of desorption over a wide range of moisture contents. This paper describes the apparatus and procedure used in obtaining these data and presents the results.

Method Used

An isosteric (constant moisture content) method in the absence of air was used to determine equilibrium moisture contents and isosteric net heats of desorption. This method has the following advantages over the frequently used isothermal procedure: It is rapid, because the resistance to diffusion offered by the inert gas barrier is eliminated, and the amount of mass transfer involved is relatively small; the heats of desorption may be determined directly from the data; and the method greatly reduces the danger of mold formation or hydrolysis of the tobacco during the determination.

The data were evaluated by means of the Clausius-Clapeyron equation, which may be written:

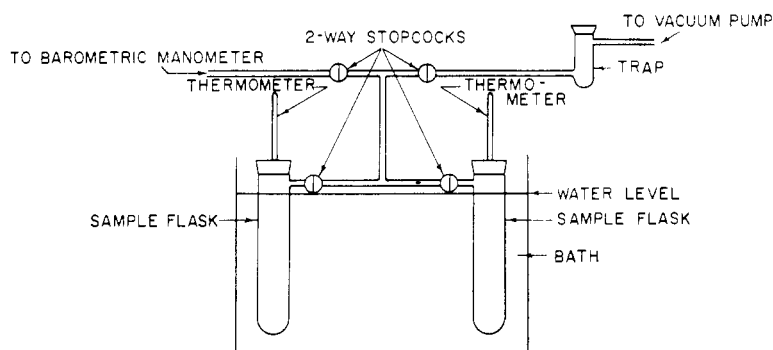


Figure 1. Apparatus for determining equilibrium moisture content

$$\frac{\partial \ln p}{\partial \left(\frac{1}{T}\right)} = -\frac{\lambda_T}{R} \quad (1)$$

A plot of $\ln p$ vs. $1/T$ will be linear, having a slope λ_T/R , provided λ_T is substantially independent of T .

The equation may also be written:

$$\frac{\partial \ln (p/P_0)}{\partial \left(\frac{1}{T}\right)} = -\frac{\lambda_N}{R} = \frac{\partial \ln x}{\partial \left(\frac{1}{T}\right)} \quad (2)$$

An apparatus was constructed to determine the vapor pressure of water on tobaccos at various temperatures and relative humidities. The net and total heats of desorption were determined by the use of Equations 1 and 2.

Apparatus and Procedure

The basic apparatus used in the determinations (Figure 1) consists of two sample flasks immersed in a constant-temperature bath and connected to a high vacuum pump and a barometric manometer. The flasks are equipped with calibrated thermometers graduated to 0.1° C. The flasks are immersed as deeply as possible in the bath, and the exposed tubing and parts are heated by infrared lamps to a temperature slightly

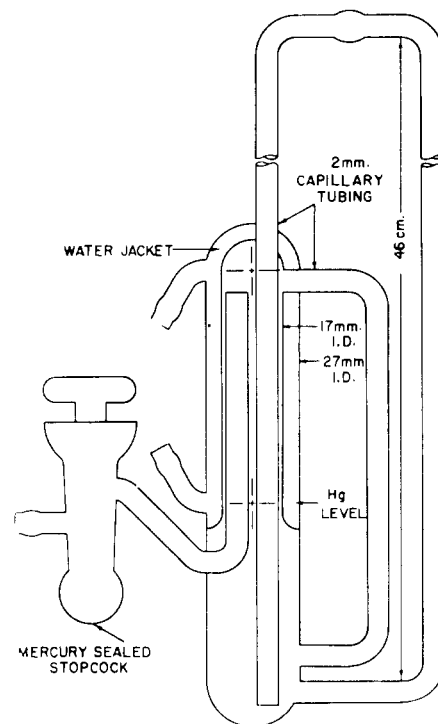


Figure 2. Construction of barometric manometer used to determine vapor pressures

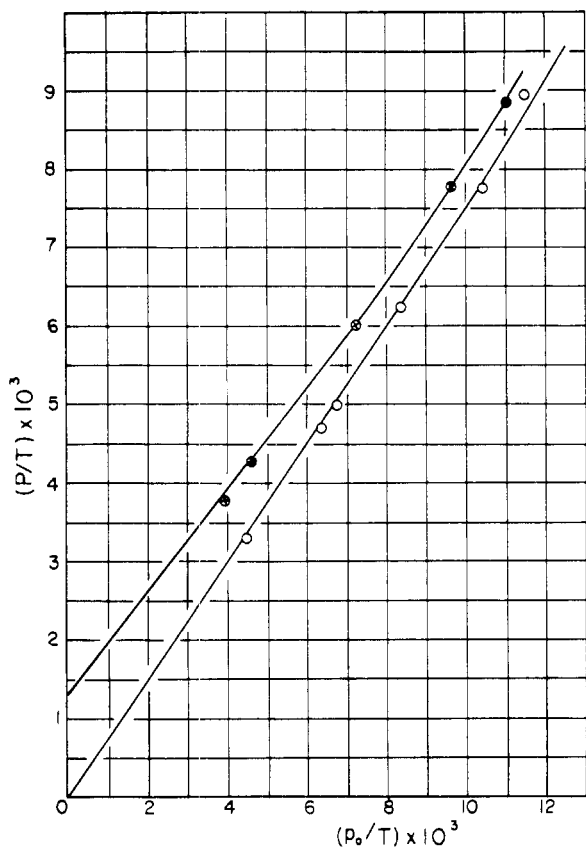


Figure 3. Sample plot of data taken on bright strip tobacco, illustrating method of detecting permanent gases

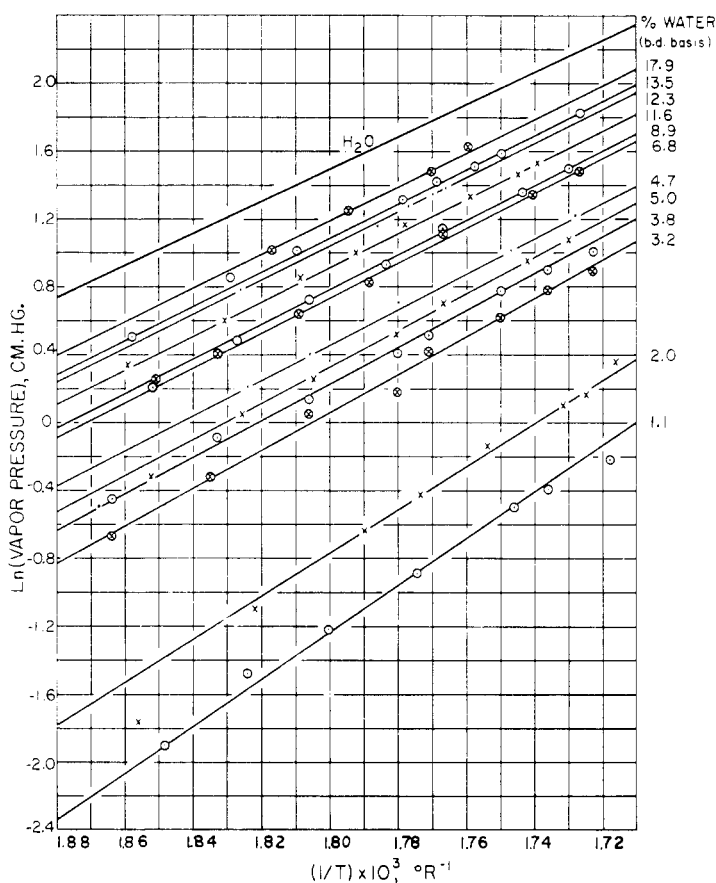


Figure 4. Isothermic plots of data for bright strip tobacco

higher than the saturation vapor pressure of the water, to avoid condensation in the lines.

The construction of the barometric manometer is shown in Figure 2. The manometer has two legs: a pressure or outer leg and a reference or inner leg. The pressure leg extends from the bottom of the manometer or mercury reservoir. This complete loop permits the expulsion of any gas or vapor that may be trapped in the top of the pressure leg by simply tilting the manometer. The gas chamber of the manometer is enclosed by a constant-temperature water jacket. The vapor is admitted through a mercury seal stopcock which has an entrance below the mercury level and then extends upward into the gas chamber. The difference in heights of the two mercury columns was read with a cathetometer.

Two samples of a given tobacco were allowed to attain a moisture content approximately that at which it was desired to determine the vapor pressure as a function of temperature. The flasks were then filled with the samples, and the air was rapidly pumped from the flasks.

After the tobacco and water vapor in the flasks reached equilibrium, as indicated by constant pressure and tobacco temperature, the pressures in the flasks were measured, and the temperatures of

the tobacco, bath, and manometer were recorded. Then the temperature of the bath was increased, and the procedure was repeated.

To determine the moisture content of the tobacco at the end of the run, the flask and tobacco were weighed and placed in a water bath at 140° F. A vacuum was applied to the flask until the per cent relative humidity of the water vapor over the tobacco was reduced to below 0.5 (about 16 hours). The tobacco and flask were reweighed, and the net weight of the flask was determined. The percentage of water on the tobacco was then calculated on a dry weight basis.

In all the work it was assumed that the loss of volatiles other than water was negligible. Undoubtedly, the presence of small amounts of volatiles was responsible for some of the scattering of the data, particularly in the region of low moisture content.

The procedure was repeated for each type of tobacco over a wide range of moisture contents.

The measured equilibrium vapor pressures will be in error if a permanent gas is present in the system or if the system has not reached equilibrium. The permanent gases could be removed by severe heating, but this would damage the sample.

In order to determine if permanent gases were present during a series of determinations, the following procedure was used.

In a system of constant volume composed of a mixture of permanent gases and water vapor, it may easily be shown by the use of the ideal gas laws that:

$$\frac{P}{T} = .1 + (x) \left(\frac{P_0}{T} \right) \quad (3)$$

Therefore a plot of P/T vs. P_0/T should give a curve of relatively slight curvature (x is relatively insensitive to temperature), which uniformly approaches the zero origin. Each set of data was tested by means of such curves, and its extrapolation to the zero origin was used as a criterion of acceptability of the data. Figure 3 shows such a sample plot of two sets of data. The upper curve shows that this set of data was unacceptable.

Figure 4 shows a sample plot of a set of data obtained on bright tobacco in the form of strips, using the Clausius-Clapeyron equation. Within the limits of experimental error, straight lines were obtained in every instance when $\ln p$ was plotted against $1/T$ at constant moisture content. As the per cent error in the determinations is greater in the region of very low moisture content, somewhat greater weight was given to

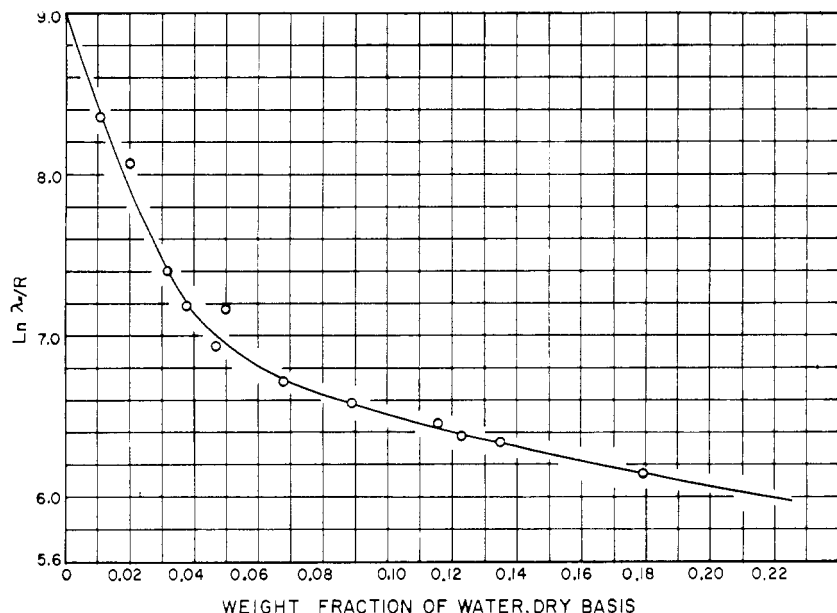


Figure 5. Plot of $\ln \frac{\lambda_N}{R}$ vs. weight fraction of water for bright strip tobacco

Table I. Isosteric Net Heats of Desorption

(B.t.u./lb. mole)

Moisture, % (Dry Basis)	Bright Strip	Turkish	Burley Strip	Maryland Strip	Bright Stems	Burley Stems
1	9,200	12,400	(15,800)	(15,800)	(12,000)	(14,400)
2	5,600	9,900	(14,400)	(14,800)	9,000	12,600
5	2,000	4,500	7,200	9,500	4,300	3,400
10	1,400	2,000	2,500	2,500	2,200	1,300
15	1,100	1,400	2,000	1,600	1,600	...
20	720	(1,300)	1,800	1,300	1,400	...

the points falling in the region of higher moisture content.

Isosteric net heats of desorption were calculated from such plots as Figure 4, using the form of the Clausius-Clapeyron equation given as Equation 2. Isosteric net heats of desorption data were interpolated and extrapolated by plotting $\ln \lambda_N/R$ against the weight fraction of water. The $\ln \lambda_N/R$ was used to remove some of the steepness from the curve and thus facilitate plotting. A typical plot is shown in Figure 5.

Because a small error in the slope of the lines of the isosteric plots could introduce relatively large errors in the derived isotherms, the data were smoothed and made self-consistent by the following procedure.

If x^* is the relative humidity at some reference temperature, T^* , by means of Equation 2 the following relationship may be obtained:

$$x = x^* e^{\lambda_N/R(1/T^* - 1/T)} \quad (4)$$

As a reference point, $1/T^*$ was chosen to be $1.80 \times 10^{-3} \text{ }^\circ\text{R}^{-1}$, which was in the middle of the range of temperatures investigated. From the isosteric plots, plots of weight fraction of water vs. relative humidity, x^* , at $1/T = 1.80 \times 10^{-3} \text{ }^\circ\text{R}^{-1}$ were made for each set of data and a smooth curve was drawn through the points. Figure 6 is an example of such a plot for bright strips. Values read from such curves and values of λ_N/R read from plots such as Figure 5

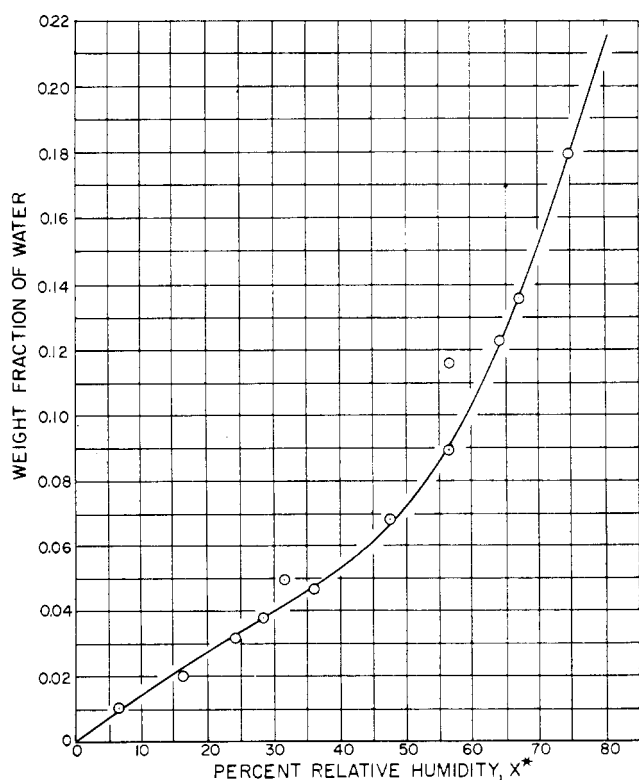


Figure 6. Plot of wt. fraction of water vs. relative humidity at $\frac{1}{T} = 1.80 \times 10^{-3} \text{ }^\circ\text{R}^{-1}$ for bright strips
Illustrating step in derivation of isotherms

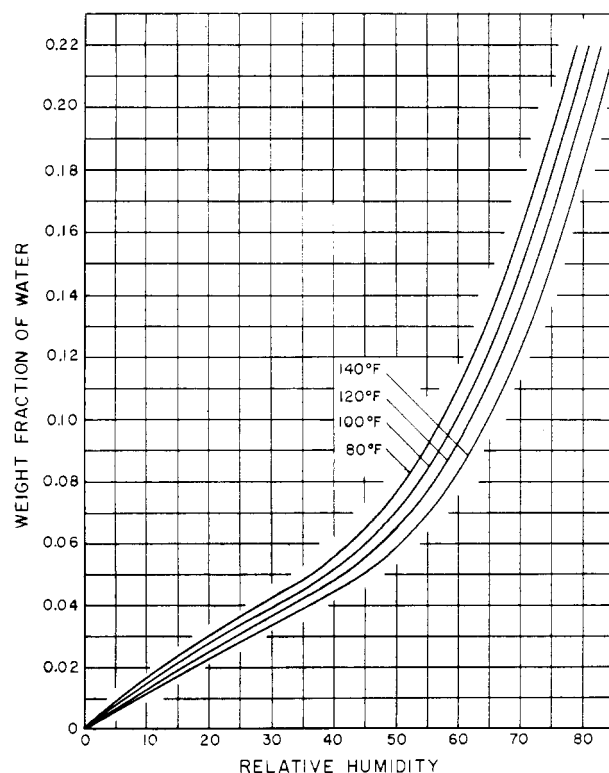


Figure 7. Desorption isotherms for bright strips derived from isosteric plots

Table II. Equilibrium Desorption Data

(Figures are wt. fraction of water, dry basis)

Temp., ° F.	Per Cent Relative Humidity							
	10	20	30	40	50	60	70	80
Bright Strip								
80	0.017	0.030	0.042	0.055	0.077	0.110	0.161	...
100	0.015	0.028	0.039	0.051	0.070	0.101	0.149	0.213
120	0.013	0.025	0.036	0.048	0.064	0.092	0.136	0.199
140	0.011	0.022	0.033	0.044	0.059	0.083	0.124	0.183
Turkish								
80	0.026	0.036	0.048	0.066	0.090	0.123	0.178	...
100	0.022	0.032	0.042	0.057	0.080	0.111	0.159	...
120	0.019	0.028	0.035	0.047	0.068	0.098	0.140	0.216
140	0.016	0.023	0.029	0.038	0.057	0.086	0.123	0.188
Burley Strip								
80	0.035	0.052	0.059	0.067	0.080	0.105	0.154	...
100	0.027	0.045	0.055	0.063	0.077	0.091	0.129	0.197
120	0.019	0.036	0.049	0.058	0.066	0.079	0.106	0.160
140	0.013	0.028	0.043	0.054	0.063	0.073	0.093	0.135
Maryland Strip								
80	0.042	0.056	0.064	0.075	0.092	0.120	0.163	0.222
100	0.035	0.050	0.059	0.068	0.083	0.107	0.146	0.202
120	0.026	0.043	0.053	0.062	0.074	0.095	0.129	0.181
140	0.017	0.032	0.044	0.053	0.064	0.081	0.111	0.161
Bright Stems								
80	0.022	0.037	0.056	0.068	0.090	0.124	0.176	...
100	0.017	0.031	0.045	0.061	0.080	0.110	0.157	...
120	0.013	0.025	0.038	0.053	0.071	0.097	0.139	0.197
140	0.010	0.020	0.031	0.044	0.061	0.085	0.121	0.175
Burley Stems								
80	0.033	0.041	0.048	0.058	0.075	0.103
100	0.029	0.039	0.045	0.053	0.069	0.096
120	0.026	0.037	0.043	0.050	0.062	0.086
140	0.021	0.034	0.040	0.046	0.056	0.077	0.119	...

were substituted back into Equation 4 to construct the isotherms. Typical sets of isotherms are shown in Figures 7 and 8 for bright and burley tobaccos.

Results and Discussion

Isosteric Net Heats of Desorption.

Table I shows the isosteric net heats of desorption, in British thermal units per pound-mole, at various moisture contents for the various tobaccos investigated. The values in parentheses were obtained by extrapolation slightly outside the range of the experimental data. As is to be expected, the isosteric net heats of desorption increase rapidly at lower moisture contents because of the predominance of low energy sites.

An examination of the magnitudes of the isosteric net heats of desorption and the general shapes of the heat of desorption curves reveals that the tobaccos fall into three natural groups which are known in the tobacco industry to be similar in many other respects; one group is represented by bright tobacco, one by Turkish tobacco, and the other group is composed of burley tobacco and Maryland tobacco. The differences between groups are less marked at the higher moisture contents, as the low energy sites are nearly all occupied by water molecules.

The isosteric heats of desorption differ by the factor *RT* from the differential heats of desorption (7). The calorimetric heats of desorption lie somewhere between the differential and isosteric heats of desorption.

Equilibrium Moisture Contents.

Table II contains the data read from the derived isotherms, and shows the relationship among weight fraction of water, temperature, and relative humidity. The differences between bright tobacco, Turkish tobacco, and between burley tobacco and Maryland tobacco are apparent. The effect of temperature on equilibrium moisture contents is pronounced.

The burley-type tobaccos exhibit a greater "knee" in the equilibrium desorption curves (see Figures 7 and 8), which is caused by a sharper change in the net heats of desorption due to a larger number of low energy sites.

Conclusions

A rapid method for the determination of equilibrium moisture contents of plant tissues reduces the danger of mold formation and hydrolysis. As long as the presence of permanent gases is guarded against or a suitable correction factor applied, the method gives reliable results.

The equilibrium moisture contents and isosteric net heats of desorption of bright leaf, burley leaf, Maryland tobacco, and Turkish tobacco indicate

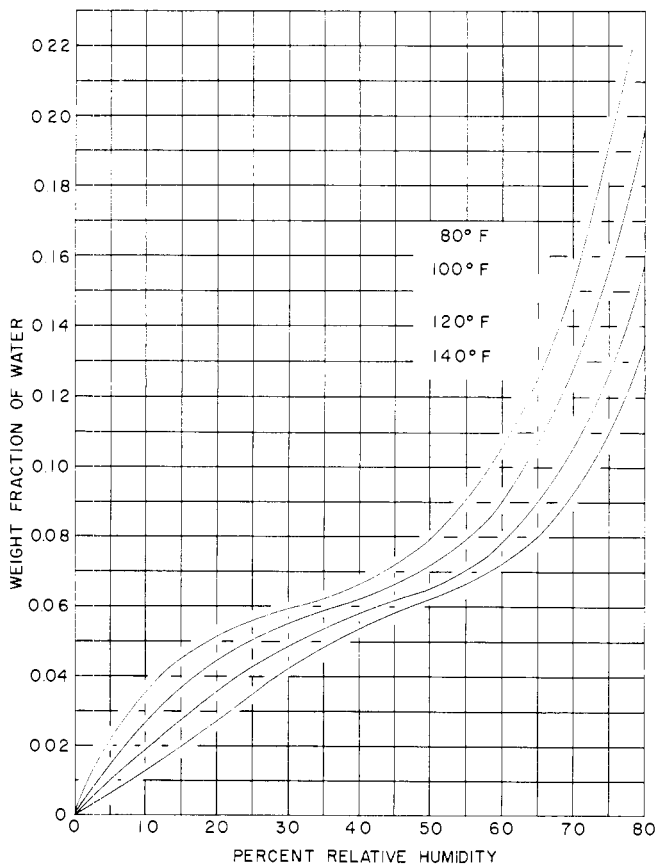


Figure 8. Desorption isotherms for burley strips derived from isosteric plots

that the air-cured, heat-cured, and sun-cured tobaccos fall into natural groups with respect to these physical properties. The range of isosteric net heats of desorption is from about 700 to about 16,000 B.t.u. per pound mole, depending on the type of tobacco and its moisture content.

The isosteric net heats of desorption of bright stems are higher than the leaf, whereas those of burley stems are somewhat lower than the leaf.

The effect of temperature on equilibrium moisture content for a given relative humidity is pronounced, and may

amount to as much as 0.06 weight fraction of water for a 60° F. increase in temperature in the region of 70% relative humidity.

Nomenclature

A = a constant
 P = total pressure, cm. of mercury
 p = vapor pressure, cm. of mercury
 P_0 = saturation vapor pressure of water, cm. mercury
 $^{\circ}R$ = degrees Rankine
 R = gas constant, B.t.u./lb. mole/ $^{\circ}R$
 T = absolute temperature, $^{\circ}R$
 T^* = absolute reference temperature, $^{\circ}R$

x = relative humidity, %
 x^* = relative humidity at temperature T^* , %
 λ_T = total heat of desorption, B.t.u./lb. mole
 λ_V = isosteric net heat of desorption, B.t.u./lb. mole

Literature Cited

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BEER ANALYSIS

Chromatographic Determination of Trace Amounts of Sucrose in Beer

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In a study of the useful limits of the paper chromatographic method as applied to materials of biological origin, beer was examined for sucrose. Sucrose could not be found in a sample of bottled beer, but it occurred in draft beer to the extent of about 20 p.p.m. Suggestions for the occurrence of sucrose in draft beer are made. Recovery experiments show that 5 p.p.m. of sucrose in beer is detectable. In attempts to lower this limit, difficulties were encountered as a result of interference of materials present in the filter paper.

A METHOD OF ISOLATING AND DETERMINING TRACES of sucrose would be of general application to the determination of traces of other sugars. Sucrose offers certain analytical difficulties, as it is harder to detect than most sugars. It does not react with the very sensitive reagents that are available for detecting the reducing sugars. Furthermore, sucrose decomposes comparatively easily, and this can impose certain limitations on the methods used to isolate it.

The brewing industry determines "residual fermentable extract" by a method in which a large amount of yeast is added to the beer and the extent of further fermentation measured by changes in the "real extract" or in the copper-reducing substances. This value has been taken to indicate the residual sugar

content of the beer, although the possibility of large inaccuracies in these methods has been recently pointed out (20, 23). It was of interest, therefore, to see whether sucrose contributed to this value. McFarlane and Held (11) found sucrose in some American and Canadian bottled ales and beers. British beers are known to contain considerable amounts of added sucrose.

In recent years, paper chromatography has had successful application in studies of the fate of sugars in the brewing of beer (1, 2, 4, 5, 8, 11, 13-18), in dough and bread making (7, 10), and in investigations of the sugars present in various plant materials (13-18, 25). These studies, for the most part, have not attempted to measure sugars in extreme dilutions, and the lower level of

most determinations has not been less than 0.01% and is usually much higher.

The paper chromatographic studies cited have shown that, with a few exceptions, the simple sugars present in wort are assimilated rapidly on fermentation. In one study (1, 8) of top fermentation, glucose and fructose could not be found after 24 hours nor sucrose after only 9 hours. The corresponding times for bottom fermentation were roughly doubled. Obviously, these sugars might have been found if the sensitivity of the method had been greater. The present study was undertaken in an effort to increase the sensitivity from the usual 100 to 1000-p.p.m. range to 1 p.p.m. so that there could be a corresponding increase in the certitude of negative findings.