

# HEAT OF VAPORIZATION FOR SHELLED CORN<sup>1</sup>

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## ABSTRACT

Heats of vaporization of shelled corn at various moisture contents were obtained from different analyses of the moisture equilibrium isotherms of the product. The Clausius-Clapeyron, the Othmer, and the Brunauer-Emmett-Teller (B.E.T.) equations were used for calculations of the values of the heats of vaporization.

Over the temperature range of 86° to 122°F. the heats of vaporization as calculated by the Clausius-Clapeyron equation were found to decrease from 700 cal./g. at a moisture content of 8% dry basis to a value of 602 cal./g. at 22% moisture content dry basis. The Othmer equation showed a similar trend, although the values were somewhat higher than obtained by the Clausius-Clapeyron equation. The B.E.T. equation only holds for moisture contents below 9%, which made comparison with the other two equations impossible over the 8 to 22% moisture content range.

This investigation has shown that the heats of vaporization of agricultural products at moisture contents below 9% dry basis can be obtained successfully by using one of three equations: the Clausius-Clapeyron, the Othmer, or the B.E.T. equation. Above a moisture content of 9% dry basis, the first two are applicable.

The energy relationships involved in a drying process are of great interest from the standpoint of economy and efficiency. It is a well-established fact that the heat required to remove 1 lb. of water from agricultural products such as grain can be substantially larger than that required for the vaporization of 1 lb. of free water. Little is known, however, as to the exact amounts of heat needed for drying the various kinds of materials at various moisture levels and at various temperatures. Notwithstanding a few noteworthy contributions along that line (1,4,8,10), there exists a great need for additional engineering data on the heat of vaporization of agricultural products. The purpose of this paper was to calculate the heat of vaporization for shelled corn at varying moisture contents using different well-known physicochemical relationships.

## Experimental

A series of desorption isotherms was constructed from experimen-

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tally determined equilibrium moisture content values for shelled corn. The isotherms have been presented in a previous article, where they were analyzed by means of Newton's equation (6,7). The isotherms are reproduced in Fig. 1. A static method was used for obtaining

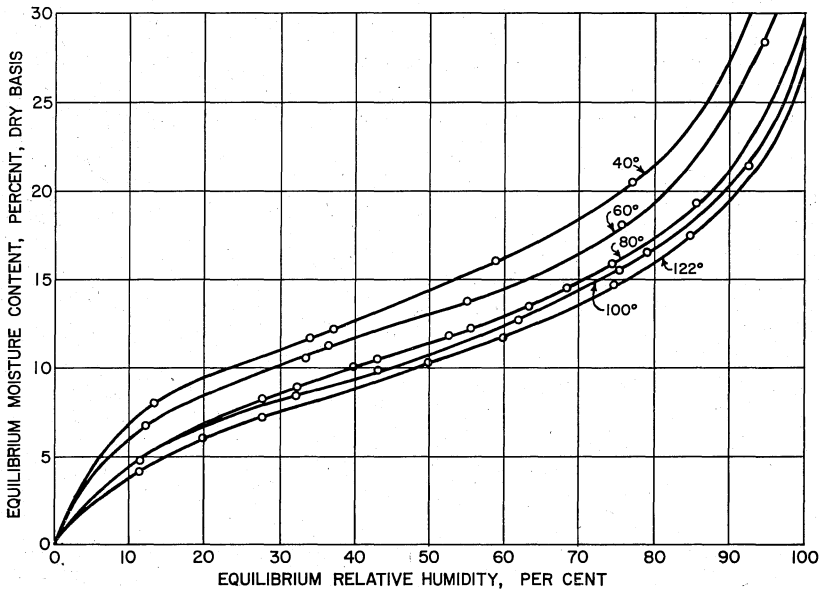


Fig. 1. Desorption isotherms for shelled corn.

moisture equilibrium data whereby thin layers of corn were placed above saturated aqueous solutions of chemically pure salts in small cabinets. The temperature in the cabinets was thermostatically controlled at 40°, 60°, 86°, 100°, or 122°F.

*Thermodynamic Observations on Adsorption.* When a gas or vapor is adsorbed by a solid, the adsorbed particles are either held rigidly to the surface, or they are free to move over the surface in two dimensions. Since prior to adsorption the gas molecules move freely in three dimensions, it follows that the adsorption process is always accompanied by a decrease in entropy.

The atoms or molecules constituting a given solid are held together by different forces. Whatever the nature of these forces, an atom located inside the body of the solid is subjected to equal forces in all directions, whereas for an atom in the plane of the surface, the inward pull is greater than the outward forces. The result is that a solid exhibits a surface tension, similar to that of liquids, even though of much greater magnitude (2). Upon adsorption of a vapor by the solid,

the atoms or molecules of the former saturate some of the unbalanced forces of the surface, thereby decreasing the surface tensions and hence also the free surface energy. Since any process that decreases the free surface energy occurs spontaneously, all adsorption phenomena are spontaneous in character. Thermodynamically, the adsorption equilibrium is attained when the change in free surface energy of the system becomes zero. The change in free surface energy during the adsorption process results in the evolution of heat by the adsorbing substance. The amount of heat liberated per unit weight is generally called the heat of adsorption. The magnitude of the heat of adsorption of a gas or vapor on a substance serves as a measure of the nature of the forces involved in the adsorption process and may assist in distinguishing between physical and chemical adsorption.

*Clausius-Clapeyron Equation.* For equilibrium systems the following thermodynamic relationship between vapor pressure and temperature can be developed from Maxwell's equation (5):

$$\frac{dP}{dT} = \frac{L}{T(V_g - V)}, \quad (1)$$

where  $P$  = vapor pressure

$T$  = absolute temperature

$L$  = latent heat of vaporization per mole

$V_g$  = vapor volume

$V$  = liquid volume

The above relationship is known as the Clapeyron equation. By neglecting the volume of water in the form of liquid and assuming ideal gas behavior for the water vapor, equation 1 reduces to the Clausius-Clapeyron equation (5):

$$\frac{dP}{dT} = \frac{LP}{RT^2} \quad (2)$$

where  $R$  = universal gas constant

Equation 2 can be integrated whenever  $L$  is known as a function of  $T$ . Assuming that  $L$  does not vary over a moderate range of temperatures, equation 2 becomes on integration

$$\ln P = -\frac{L}{RT} + \text{constant} \quad (3)$$

When  $\ln P$  versus  $1/T$  is plotted on semilogarithmic paper, the resulting straight lines will have a negative slope equal to  $L/R$  and an intercept on the  $1/T$ -axis equal to the constant. The straight lines are

isosteres since they are drawn through points which represent constant moisture equilibrium conditions.

Figure 2 shows the isosteres for shelled corn calculated with equa-

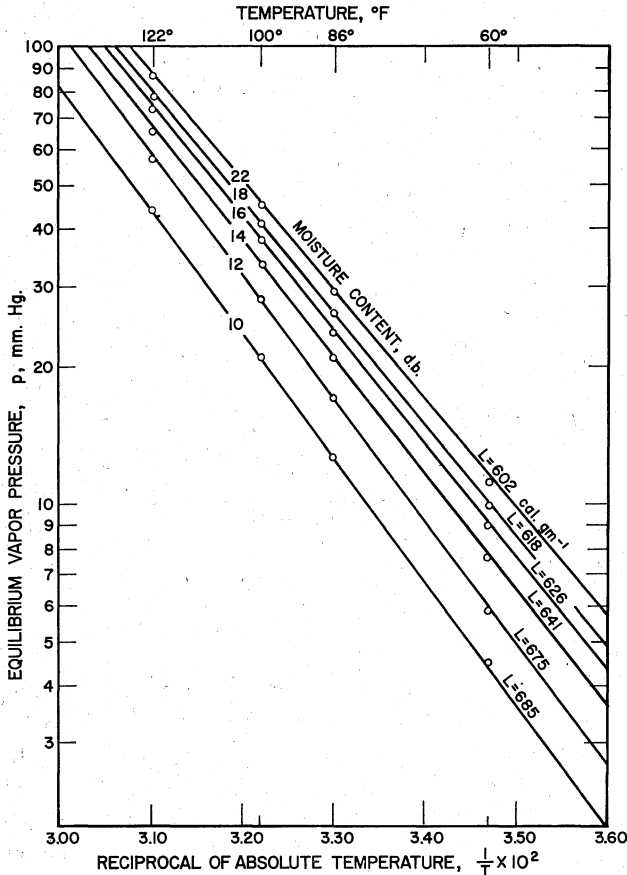


Fig. 2. Evaluation of latent heat of vaporization for shelled corn at various moisture levels using the Clausius-Clapeyron equation.

tion 3 for six different moisture contents from 10 to 22%, d.b., and in the temperature range from 60° to 122°F. The values of P, the equilibrium vapor pressures, for a particular temperature and moisture content were obtained by multiplying the equilibrium relative humidity as read from Fig. 1 by the saturation vapor pressure of water at the temperature under consideration. It is evident that very satisfactory straight lines are obtained in the 60° to 122°F. temperature range. Outside of this range appreciable deviations from linearity re-

sulted, as could have been expected in view of the simplifying assumptions used in deriving equation 3.

The values of  $L$ , the latent heats of vaporization, at different corn moisture contents were calculated by multiplying the values of the slope of the lines in Fig. 2 by  $R$ , the universal gas constant. The values are given in Table I as well as in Fig. 2.

TABLE I  
LATENT HEAT OF VAPORIZATION FOR SHELLED CORN OBTAINED BY  
DIFFERENT METHODS

MOISTURE CONTENT, D.B.	CLAUSIUS- CLAPEYRON (86°-122°F.)	OTHMER (100°F.)	B.E.T. (100°F.)
%	cal./g.	cal./g.	cal./g.
8	700	795	667
10	685	755	
12	675	708	
14	641	671	
16	626	648	
18	618	625	
22	602	620	

*Othmer Equation.* Another method sometimes employed in evaluating the latent heat of vaporization from moisture equilibrium isotherms is Othmer's graphical method. Using the Clapeyron equation, Othmer derived the following relationship (9):

$$\frac{\ln P}{\ln P'} = (L/L') + C, \quad (4)$$

where  $L$  is the latent heat of vaporization per mole of adsorbed material at a given temperature,  $L'$  the molar latent heat of vaporization of free water at the same temperature,  $P$  the equilibrium vapor pressure of the material,  $P'$  the saturation vapor pressure of free water, and  $C$  the constant of integration. Equation 4 will give a straight line on a plot of  $\ln P$  vs.  $\ln P'$  if the ratio  $L/L'$  remains constant throughout the temperature range.

Two of the three assumptions made in equations 2 and 4 are the same; namely, that the perfect gas law holds and that the liquid volume is insignificant compared to the vapor volume. However, the third assumption of equation 2, that  $L$  does not vary with temperature, is only true in a small temperature range. The third assumption of equation 4, that the term  $L/L'$  will be substantially unchanged, is true for a much wider temperature range, since the variation of both  $L$  and  $L'$  follows the same law, resulting in a virtually unchanged quotient. Thus, equation 4 can be applied with accuracy over a wider range than equation 2.

When the equilibrium vapor pressures of shelled corn at different moisture contents and in the temperature range from 40° to 100°F. were plotted on log-log paper against the saturation vapor pressures of free water at the same temperatures, straight lines were obtained (Fig. 3). To determine the latent heats of vaporization from the Othmer plots, the slopes of the straight lines in Fig. 3 were measured. Once the ratio  $L/L'$  is known,  $L$  can be calculated. The values of  $L$  for shelled corn at different moisture contents at 100° F., as obtained by Othmer's equation, are also given in Table I.

The latent heat of vaporization values based on Othmer's equation are slightly higher than those based on the Clausius-Clapeyron equations. Owing to the more realistic assumptions made in the derivation of the Othmer equation, the values obtained by this method are likely to be more accurate.

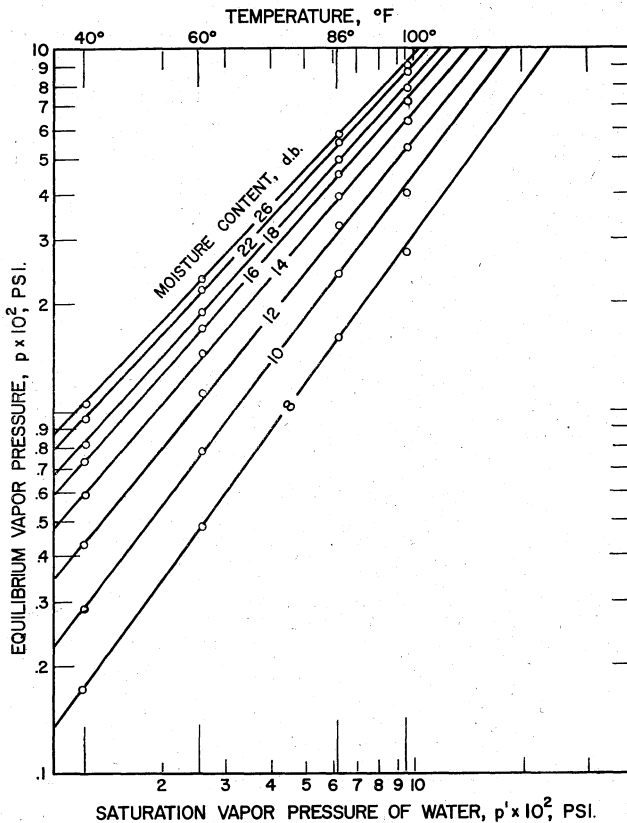


Fig. 3. Othmer plots of desorption data for shelled corn of various moisture levels.

*B.E.T. Equation.* An analysis of the experimental isotherms based on the theory of multimolecular adsorption on a free surface, developed by Brunauer, Emmett and Teller (2,3), affords another method for evaluating the magnitudes of the latent heats of vaporization.

The B.E.T. isotherm equation for a substance on which an infinite number of molecular layers has been adsorbed, can be written as:

$$\frac{P}{v(P' - P)} = \frac{1}{v_{m,c}} + \frac{c - 1}{v_{m,c}} \cdot \frac{P}{P'} \quad (5)$$

where  $v$  is the volume of the vapor adsorbed at pressure  $P$  and absolute temperature  $T$ ;  $P'$  the saturation vapor pressure of the adsorbate at temperature  $T$  of the experiment;  $v_m$  the vapor volume when the entire adsorbent surface is covered with a monomolecular layer; and  $c$  approximately equal to  $(L - L')/RT$ , with  $L$  representing the latent heat of adsorption of the first layer of molecules and  $L'$  the heat of evaporation of the adsorbate in liquid form.

If the theory of adsorption of an infinite number of molecular layers is correct, the plot of  $P/v(P' - P)$  versus  $P/P'$  should yield a straight line, according to equation 5. The straight line will have a slope of  $(c - 1)/v_{m,c}$  and an intercept of  $1/v_{m,c}$ . Thus one can obtain the two constants  $v_m$  and  $c$  from the experimental data.

Figure 4 shows that the experimental isotherms plotted according

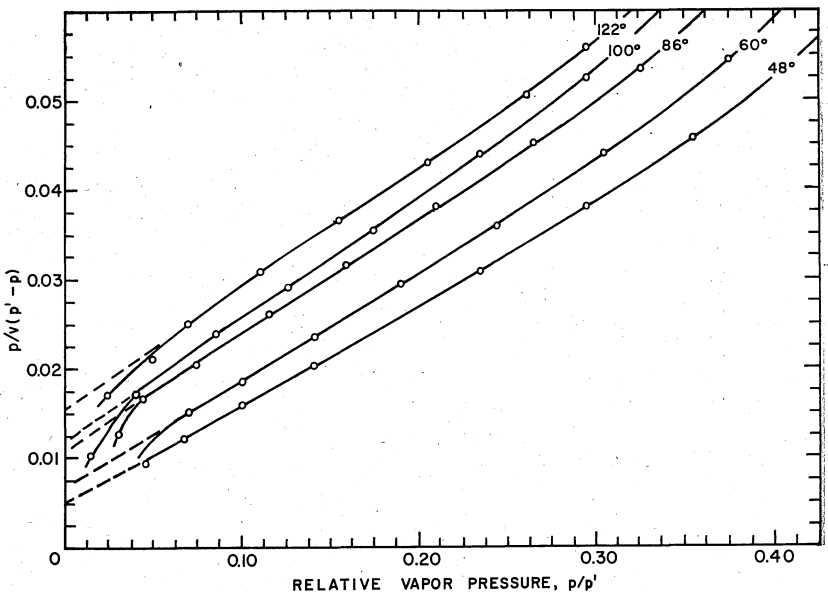


Fig. 4. B.E.T. plots of desorption isotherms for shelled corn.

to the B.E.T. equation 5 are straight lines between the relative vapor pressures of 0.05 and 0.35 (which is equivalent to moisture contents between 3 and 9%). The values  $v_m$  and  $c$  were evaluated from the slopes and intercepts of the respective straight lines. The magnitudes of  $(L - L')$  could then be calculated from the relationship  $c = \exp(L - L')/RT$ . The values of  $L$  could readily be obtained by adding the heat of liquefaction of water at the corresponding isotherm temperature to the net values previously calculated. For a moisture content of 8% and at 100°F., the B.E.T. method yielded a latent heat of vaporization for shelled corn 667 cal./g. as compared to 700 cal./g. by the Clausius-Clapeyron method. The close agreement between these two values is an indirect indication that multimolecular adsorption may indeed be the mechanism involved in the moisture-holding capacity of shelled corn.

#### Literature Cited

1. BECKER, H. A., and SALLANS, H. R. A study of the desorption isotherms of wheat at 25°C. and 50°C. *Cereal Chem.* **33**: 79-91 (1956).
2. BRUNAUER, S. The adsorption of gases and vapors, vol. I. Princeton University Press: Princeton, N.J. (1945).
3. BRUNAUER, S., EMMETT, P. H., and TELLER, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**: 309-319 (1938).
4. GALLAHER, G. L. A method of determining the latent heat of agricultural crops. *Agr. Eng.* **32**: 34-38 (1951).
5. GETMAN, F. G., and DANIELS, F. *Outlines of theoretical chemistry* (5th ed.). Wiley: New York (1931).
6. HALL, C. W., and RODRIGUEZ-ARIAS, J. H. Application of Newton's equation to moisture removal from shelled corn at 40-140°F. *J. Agr. Eng. Research* **3** (4): 275-280 (1958).
7. HALL, C. W., and RODRIGUEZ-ARIAS, J. H. Equilibrium moisture content of shelled corn. *Agr. Eng.* **39**: 466-470 (1958).
8. JOHNSON, H. K., and DALE, A. C. Heat required to vaporize moisture in wheat and shelled corn during the process of artificial drying. *Agr. Eng.* **35**: 705-709 (1954).
9. OTHMER, D. F. Correlating vapor pressure and latent heat data. *Ind. Eng. Chem.* **32**: 841-846 (1940).
10. THOMPSON, H. J., and SHEDD, C. K. Equilibrium moisture and heat of vaporization of shelled corn and wheat. *Agr. Eng.* **35**: 786-788 (1954).