The Fatty Acid Content of Waxy Maize Starch.—It is interesting to note that waxy maize starch, containing essentially pure amylopectin, contains about one-seventh as much "fat-by-hydrolysis" as ordinary corn starch.[15] Since this difference is not due to the amount of fat available in the respective types of corn kernels, it probably can be attributed to the inability of amylopectin to combine readily with fatty acids.

Summary

X-Ray and optical investigation of the complex between amylose and fatty acid reveal it to have its own particular crystalline form. Amylose with a helical chain configuration will bind fatty acid, while amylose with an extended chain configuration will not, independent of relative particle size of the two materials. These points are interpreted to mean that a molecular complex, rather than surface adsorption, is involved.

Structurally, the fatty acid complex resembles closely the iodine complex, consisting of the close-packing of helical amylose tubes. The packing of the amylose is not materially influenced by the complexing agents, indicating that the complexing agents are contained in holes in the structure. Chemical evidence is presented that the holes occupied by iodine and fatty acid are the same. A number of reasons are presented for believing the holes in the center of the helices, rather than the holes between helices, are involved.

The above structure of the complex explains quantitatively the fatty acid content of the complex, the effect of previous fat content on the binding power of defatted granules, the low fat content of waxy starches, the differences between many solvents in fat extraction, the inability of amylopectin to bind fatty acid, etc. It is shown that surface adsorption and hydrogen bond formation and the placing of amylose between helices leave most of these points unexplained.

The force between amylose and complexing agent is explained in terms of dipolar interactions, adapting the mechanism suggested for the iodine complex. It is pointed out that hydrogen bonding as a force will not explain the great similarity between fatty acid and iodine complexes.

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[15] T. Schoch, THIS JOURNAL, **64**, 2957 (1942).

[16] Original received May 21, 1945.

An Equation for the Line of Saturation of Liquids and Vapors

BY JOHN E. HAGGENMACHER

No single mathematical relationship comprising all four variables of saturated fluids has been published. In the following a simple expression between vapor–volume, liquid–volume, pressure and temperature is established.

Consider the behavior of a system of saturated liquid and vapor reported on rectangular p, v,T-coördinates. It is a particularity of this state that corresponding volumes of liquid and vapor lie on parallels to the v-axis. The system is determined by one variable. The loci of all possible values of p,v,T, constitute the line of saturation. Geometrically the line is a skew curve, quadratic with respect to v, and situated on a ruled surface parallel to the v-axis.

The equation of such a three-dimensional curve may be put in the form

$$v = \frac{v_g + v_L}{2} \pm \frac{v_g - v_L}{2} \tag{1}$$

where v_g and v_L are the roots of a quadratic p,v,T-function. Therefore, if a rectangular equation of reasonable accuracy can be found for the line of saturation, it is, by purely mathematical means, possible to obtain expressions for $v_g + v_l$ and $v_g - v_l$, which may be simpler of construction than the original function. Both expressions are useful for thermodynamic considerations of saturated fluids.

The following relationship between pressure, volumes and temperature of saturated fluids was chosen for its good all around accuracy and simplicity.

TABLE I

COMPARISON BETWEEN EQUATION (2) AND VAN DER WAALS' FOR WATER[3] (SATURATED CONDITIONS)

$$p = \frac{CT}{v + B} - \frac{A}{T(v + B)^2} \tag{2}$$

$$C = 0.0045548 \quad A = 6.4469 \quad B = 0.0035593$$

$$p = \frac{CT}{v - b} - \frac{a}{v^2}$$

$$C = 0.0045548 \quad a = 0.016808 \quad b = 0.0016892$$

Temp., °C.	van der Waals	p atm. Eq. (2)	Lit.	% difference from lit. van der Waals	% difference from lit. Eq. (2)
0	0.0060316	0.0060303	0.0060273	+ 0.07	+0.05
40	0.072951	0.072820	0.072748	+ 0.28	+0.10
80	0.47092	0.46977	0.46740	+ 0.75	+0.51
120	1.9911	1.9799	1.9595	+ 1.61	+1.04
160	6.2887	6.2032	6.1032	+ 3.04	+1.64
200	16.135	15.687	15.332	+ 5.22	+2.32
240	35.585	33.818	33.044	+ 7.69	+2.34
280	70.090	64.533	63.343	+10.6	+1.88
320	125.99	112.11	111.40	+13.1	+0.64
360	200.24	182.30	184.26	+ 8.67	−1.07
374.11	310.7	(218.167)	218.167	+42.4	0.0

The general behavior of equation (2) in comparison with van der Waals' may be judged from the summary in Table II. The saturation pressures were calculated for the two equations and compared with experimental values.

TABLE II

COMPARISON BETWEEN EQUATION (2) AND VAN DER WAALS' (SATURATED CONDITIONS)

	Temp. range, °C.		% difference from exp. value			
			v. d. W.		Eq. (2)	
			min.	max.	min.	max.
Acetic acid	118.5	321.6	44.7	174	0	64
Acetone	56.1	235	0	51	0	13
Acetylene	− 30	+ 36.0	6	12	0	3.3
Ammonia	− 76	+132.9	1	23	0	2.5
Benzene	90	288.5	1	10.6	0	2.3
Bromobenzene	160	397	3.5	15.0	0	2.3
n-Butane	−177.8	+153	.6	13.3	0	6.8
Carbon dioxide	− 30	+ 31.1	1.3	11.2	0	3.0
Carbon monoxide	−192	+140.21	0	3.1	0	6.8
Carbon tetrachloride	80	283.15	1.9	41.4	0	3.9
Chlorine	0	144	6.2	11.5	0	6.7
Chlorobenzene	140	359.2	2.3	13.4	0	1.1
Cyclohexane	80.75	281	2.0	8.8	0	3.1
Dichlorodifluoromethane	− 40	+115.1	0.6	6.5	0	5.9
Diethylamine	55.4	223.5	3.3	13.5	0	9.8
Di-isobutyl	110	276.8	1.0	14.6	0	2.6
Ethane	− 88.62	+ 32.1	1.7	12.7	0	2.3
Ethyl acetate	77.15	250.1	3.2	31.6	0	2.0
Ethyl alcohol	78.3	243.1	2.2	25.9	0	1.8
Ethyl chloride	12.2	187	1.7	18.4	0	5.9
Ethylene	−103.8	+ 9.6	1.9	6.7	0	6.1
Ethyl ether	34.6	194.6	5.2	14.3	0	3.9
Ethyl formate	54.35	235.3	1.4	19.5	0	2.4
Ethyl propionate	99.0	272.9	2.1	18.8	0	2.5
Fluorobenzene	90	286.5	0.8	14.1	0	2.4
n-Heptane	100	266.85	0.3	7.9	0	2.0
n-Hexane	80	234.8	4.5	10	0	2.4
Hydrochloric acid	− 85.03	+ 51.5	4.4	14.6	0	6.7
Iodobenzene	190	448	3.2	13.2	0	2.0
Iso-pentane	30	187.8	6.5	13.5	0	9
Methane	−161.5	− 82.1	0.1	6.5	0	7.4
Methyl acetate	57.15	233.7	1.8	20.0	0	2.0
Methyl alcohol	64.7	240	4.7	81	0	5.7
Methyl butyrate	102.75	281.3	6.2	40	0	4.7
Methyl chloride	− 24	+143.2	1.7	12.8	0	1.8
Methyl ether	− 23.7	+126.9	3.2	21.1	0	3.6
Methyl formate	31.9	214.0	1.3	20.8	0	1.8
Methyl isobutyrate	92.3	267.55	3.7	18.3	0	2.4
Methyl propionate	79.7	257.4	2.2	24.7	0	1.9
Nitrous oxide	− 89.5	+ 36.5	4.6	8.9	0	3.7
n-Octane	130	296.2	2.6	17.7	0	2.5
n-Pentane	40	197.2	2.4	13.0	0	1.3
Phosgene	7.95	182	0.6	14.4	0	13.2
Propyl acetate	101.55	276.2	2.8	25.1	0	1.2
n-Propyl alcohol	97.4	263.7	1.3	25.7	0	2.9
Propyl formate	80.9	264.85	1.3	17.5	0	2.2
Sulfur dioxide	8	157.2	7.4	15.1	0	10.8
Sulfur trioxide	44.6	218.3	6.2	136	0	3.8
Tin tetrachloride	114.1	318.7	1.4	12.1	0	2.3
Water	0	374.11	0.1	42.4	0	2.3
Xenon	− 60	+ 16.6	1.7	9.4	0	4.2

For the gases argon, helium, hydrogen, neon, nitrogen, oxygen, a direct check with experimental data is not possible. Measurements in the saturated region of these gases are given as pressure temperature data and as volume temperature data, with the temperature hardly ever identical in the two sets. For this reason a comparison of van der Waals' and equation (2) with some vapor pressure equations was made. Naturally, values calculated from van der Waals' or from equation (2) depend on the excellence or the volume data, corresponding to the temperature chosen. This is true for the saturated region but neither for the liquid nor the gaseous region. Pressures, calculated from the various equations at temperatures up to the critical point, are listed in Table III.

TABLE III

PRESSURE CALCULATIONS FROM VARIOUS EQUATIONS

Argon

Equation	−161.23°C.	−135.51°	−125.17°	−122.14°
I. C. T.	7.430	28.367	43.280	48.006
v. d. W.	7.654	30.299	44.13	49.99
Eq. (2)	7.302	27.684	41.392	47.996[a]

Helium

Equation	3.30°K.	3.90°	4.71°	5.25°
I. C. T.	0.351	0.737	1.549	2.259
v. d. W.	0.363	0.653	1.525	2.290
S. K.[1]	0.367	0.734	1.514	2.240
Eq. (2)	0.336	0.653	1.417	2.261[a]

Hydrogen

Equation	−249.89°C.	−245.73°	−240.57°	−239.91°
I. C. T.	2.129	5.054	11.733	12.882
v. d. W.	2.170	5.180	11.877	13.066
Eq. (2)	2.051	4.792	11.343	12.80[a]

Neon

Equation	−247.92°C.	−237.04°	−230.07°	−228.71°
I. C. T.	0.573	7.706	22.009	26.18
v. d. W.	0.532	8.164	23.615	27.35
Eq. (2)	0.529	7.767	21.539	26.86[a]

Nitrogen

Equation	−173.73°C.	−161.20°	−153.65°	−147.13°
I. C. T.	7.332	16.080	24.216	33.408
v. d. W..	7.487	16.975	25.395	34.86
Eq. (2)	7.085	15.594	23.225	34.490[a]

Oxygen

Equation	−210.4°C.	−154.5°	−129.9°	−118.82°
Dodge.[2]	0.0153	9.404	31.470	47.643
v. d. W.	0.0139	10.040	32.665	51.70
Eq. (2)	0.0125	9.671	33.633	49.713[a]

[a] Accepted critical pressure (I. C. T.).

Throughout this paper the variables p,v,T, refer to saturated conditions only and are invalid for any other state.

In order to show the extent of accuracy of the arbitrarily chosen equation (2) it is compared with the van der Waals' equation for water under saturated conditions, from melting point to critical point. Water is the preferred testing substance since experimental data of the highest precision are available.

Solving equation (2) for v, gives

$$v = \frac{CT}{2p} - B \pm \sqrt{\left(\frac{CT}{2p}\right)^2 - \frac{A}{pT}} \qquad (3)$$

Inspection of equation (3) reveals that the terms before the plus-minus sign contain only the

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(1) Schmidt and Keesom equation, "Phenomena at the Temperature of Liquid Helium," Burton, Smith, Wilhelm, p. 54. Reinhold Publishing Corp., New York, N. Y., 1940.

(2) Dodge and Davis, THIS JOURNAL, 49, 610 (1927).

B-constant, while the term after the plus-minus sign contains only the A-constant. The choice of the original expression (2), thus leads to simple equations for $v_g + v_L$ and $v_g - v_L$, comprising but one constant besides the universal gas constant.

Comparison of equations (1) and (3) yields

$$v_g + v_L = \frac{CT}{p} - 2B \qquad (4)$$

and

$$v_g - v_L = \sqrt{\left(\frac{CT}{p}\right)^2 - \frac{4A}{pT}} \qquad (5)$$

Rearranging expression (4), we obtain as an equation for the line of saturation

$$p = \frac{CT}{v_g + v_L + 2B} \qquad (6)$$

that is, an equation connecting the volumes of saturated liquids and vapors with pressure and temperature. Its locus represents the region of a saturated liquid and its vapor in equilibrium.

The constants A and B may be evaluated by reason of two constraining equations which stand good at the critical point

$$v_g + v_L = 2v_c \qquad v_g - v_L = 0 \cdot \qquad (7)$$

Thus

$$A = \frac{C^2T_c^3}{4p_c} \qquad (8)$$

and

$$B = \frac{CT_c}{2p_c} - v_c \qquad (9)$$

Subscripts, c, indicate critical values.

In the numerical calculations to follow the values of the basic constants were taken as: the universal gas constant, R, 0.08206, for 1 atm. g-mole, °K.; molecular weights, m, based on atomic weights of 1942; ice-point, 273.16°K. The units of the variables in the equations are: pressure in atm. volumes in l. per g. and temperature in °K.

Table IV contains the constants of all the substances tested.

TABLE IV

CONSTANTS FOR SATURATED LIQUIDS AND VAPORS

Units: atm., l, g, °K.

Substance	A	$B \times 10^3$
Acetylene	1.1894	3.5485
Ammonia	3.4607	4.4286
Argon	0.07572	1.3481
Benzene	1.0208	2.8760
Bromobenzene	0.46075	1.8680
n-Butane	1.0714	3.9178
Carbon dioxide	0.33560	1.7340
Carbon monoxide	.14604	2.3179
Carbon tetrachloride	.27215	1.5038
Chlorine	.31935	1.4265
Chlorobenzene	.75328	2.4310
Cyclohexane	.99703	2.9595
Dichlorodifluoromethane	.16564	1.4974
Diethylamine	1.0651	3.6320
Diisobutyl	0.87460	3.8236
Ethane	1.0989	4.0858
Ethyl acetate	0.8220	3.1967
Ethyl alcohol	1.7295	3.6559
Ethyl chloride	0.76372	2.6503
Ethylene	.95583	3.4115
Ethyl ether	.85455	3.2818
Ethyl formate	.86446	2.9428
Ethyl propionate	.79563	3.2690
Ethyl sulfide	.91470	2.8967
Fluorobenzene	.71638	2.5327
Hydrogen	1.1896	20.631
Helium	0.0067237	9.3700
n-Heptane	.98371	3.9671
n-Hexane	1.0037	3.9034
Hydrochloric acid	0.53094	2.1183
Iodobenzene	.34006	1.5314
Isopentane	.96303	3.7013
Methane	.99616	4.4776
Methyl acetate	.86261	2.9871
Methyl alcohol	2.8165	4.6789
Methyl butyrate	0.80465	3.1840
Methyl chloride	.72436	2.4023
Methyl ether	.97673	3.1675
Methyl ethyl ether	.90169	3.1847
Methyl formate	.91245	2.7610
Methyl isobutyrate	.755666	3.1220
Methyl propionate	.82334	3.0797
Neon	.013513	1.2959
Nitrogen	.12820	2.2955
Nitrous oxide	.35985	1.8085
n-Octane	.96789	4.0146
Oxygen	.12158	1.6546
n-Pentane	1.0191	3.7904
Phosgene	0.28967	1.4480
Phosphine	.77489	2.7782
n-Propyl alcohol	1.4441	3.6807
Propyl acetate	0.81309	3.3244
Propyl formate	.84161	3.0104
Sulfur dioxide	4.2083	1.6170
Sulfur trioxide	0.37293	1.4255
Tin tetrachloride	.13898	1.1715
Water	6.4469	3.5593
Xenon	0.040806	0.68871

The pressures calculated by equation (6) from corresponding v_g, v_L and T-values for water have been published earlier.[4]

All substances show very much the same behavior, the differences between pressures calculated and experimental values depending, of course, also on the exactness of the experimental data.

The only substance found to show anomalous behavior is acetic acid. The presence of double molecules may be offered as an explanation for the discrepancies.

A further check upon the accuracy of equation (6) is furnished by verifying the relationship, $p(v_g + v_L + 2B)/CT = 1$. Inserting experimental values for p, v_g, v_L, and T, the results of the calculations are given for a few substances in Table VI. Similar conditions were obtained for all substances tested.

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(3) Calculated from critical data in "Int. Crit. Tables," Vol. III, 1928, p. 248.

(4) Haggenmacher, THIS JOURNAL, **66**, 313 (1944).

The behavior of gases and liquids is represented by a p,v,T-surface, the variations of a saturated liquid and its vapor in equilibrium by a p,v,T-line.

TABLE V

$p(v_g + v_L + 2B)/CT$ (FOR EXPERIMENTAL p, v, T-VALUES)

Water,[5] C = 0.0045548, B = 0.0035593

T, °C.		T, °C.		T, °C.	
0	0.9994	140	0.9794	280	0.9702
20	.9980	160	.9744	300	.9792
40	.9971	180	.9687	320	.9916
60	.9956	200	.9649	340	1.0074
80	.9930	220	.9621	350	1.0157
100	.9892	240	.9618	360	1.0203
120	.9846	260	.9641	374.11	(1.0000)

Dichlorodifluoromethane,[6] C = 0.00067861, B = 0.0014974

−40.00	0.9933	10.00	0.9945	60.00	1.0003
−23.33	.9920	26.67	1.0006	111.5	(1.0000)
− 6.67	.9912	43.33	1.0025		

Propyl acetate,[2] C = 0.00080349, B = 0.0033244

101.55	0.9766	180	0.9795	260	1.0360
120	.9788	200	0.9859	275	1.0221
140	.9730	220	0.9996	276.2	(1.0000)
160	.9763	240	1.0160		

This line of saturation is part of the p,v,T-surface, therefore, a direct comparison of the equations here presented and other equations of state is possible.

Summary

1. A relationship between the volumes, the pressure and the temperature of saturated fluids is derived which also affords a mathematical expression of the line of saturation.
2. Mathematical expressions for the sum and for the difference of the volumes of saturated liquids and vapors are deduced.
3. The relationship was tested on 58 substances and found to be more accurate in this region than 3-constant equations such as van der Waals' or Berthelot's.

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(5) Fales and Shapiro, THIS JOURNAL, **58**, 2418 (1936); Osborn and Meyers, *Bur. Standards J. Research*, **13**, 1 (1934); Smith, Keyes and Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 137, 139 (1934).

(6) Perry's "Chem. Eng. Handbook," 2nd ed., p. 2574 (1941).

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The Entrainment of Cobalt and Sulfur in Iron Separations

BY E. T. PINKNEY, R. DICK AND R. S. YOUNG

Introduction.—It has long been observed by analytical chemists that cobalt is very tenaciously held in a ferric hydroxide precipitate formed by adding ammonia to a solution containing iron and cobalt. The difficulty of separating cobalt from iron with ammonia has been recognized by the use of the zinc oxide or ether separations in cobalt analyses for many years, and latterly by the employment of a phosphate to remove iron. Iron may of course also be separated from cobalt by the aid of cupferron or by pyridine.[1,2] Iron and cobalt may be removed in a sulfur determination by electrolysis with a mercury cathode.

In the metallurgical industries, iron is sometimes removed with ammonia prior to the precipitation of barium sulfate in a sulfur determination. It was noticed in this laboratory, working with samples of cobalt and iron sulfates, that one or two precipitations with ammonia gave complete recovery of sulfur, whereas cobalt was still heavily entrained in the ferric hydroxide precipitate. An investigation of the entrainment of cobalt and sulfur in iron separations appeared desirable.

Experimental Procedure and Results

A standard solution was made up from B.D.H. AnalaR cobalt sulfate and Merck analyzed ferric sulfate to contain approximately the quantities commonly found in many local metallurgical samples. The values were checked by careful analyses and found to represent the following in grams per liter: Co 3.92, S 5.72, and Fe 3.88.

In the first experiments 25-ml. aliquots, representing 0.0980 g. Co, 0.1430 g. S, and 0.0970 g. Fe, were treated in the standard manner for the separation of iron using trisodium phosphate, ammonium hydroxide and ammonium chloride, and zinc oxide, respectively. One precipitation only was made, the sample was filtered immediately after boiling, and the quantity of hot wash water was kept constant throughout. Cobalt and sulfur were determined on different aliquots in each case after separation of the iron. The results shown in Table I are typical of those obtained.

TABLE I

RETENTION OF COBALT AND SULFUR IN IRON PRECIPITATES

	% Recovery in first filtrate			
	First series		Second series	
Precipitant for iron	Co	S	Co	S
Na_3PO_4	99.6	99.8	99.5	99.3
NH_4OH and NH_4Cl	73.7	99.6	67.2	99.4
	87.0	99.3		
NH_4OH and $(NH_4)_2CO_3$	..	..	53.9	98.9
ZnO	98.3	95.8	95.8	95.0

In the second series cobalt and sulfur were

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(1) Spacu, *Compt. rend.*, **200**, 1595 (1935).

(2) Lingane and Kerlinger, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 77 (1941).