TABLE VII.

		x.	Log *x*.
1 cc.-atms.	= *x* joules	0.10133	9.005737
1 cc.-atms.	= *x* cals.	0.02423	8.384353
1 cal. (15°)	= *x* joules	4.182	0.621384
Absolute zero	= — *x*° C.	273.09	2.436306
Molal gas volume (0° C., 1 atms.)	= *x* cc.	22412	4.350481
R′	= *x* cals. per degree	1.9885	0.298528
R	= *x* joules per degree	8.3160	0.919912
R″	= *x* cc.-atms. per degree	82.07	1.914175
F	= *x* coulombs per equiv.	96494	4.984500
F’	= *x* cals. per volt-equiv.	23074	4.363116
ln ( )	= *x* log ( )	2.3026	0.362216
R’ ln ( )	= *x* log ( )	4.5787	0.660744
(R/**F**) ln ( )	= *x* log ( )	0.00019844	6.297626
25° C.	= *x*° A	298.1	2.474362
ln 298.1	= *x*	5.6974	0.755679
298.1 ln ( )	= *x* log ( )	686.40	2.836578
298.1 R′ ln ( )	= *x* log ( )	1364.9	3.135106
298.1 ln 298.1	= *x*	1698.4	3.230041
298.1 (R/**F**) ln ( )	= *x* log ( )	0.05915	8.771988

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

A METHOD OF FINDING THE PARTIAL FROM THE TOTAL VAPOR PRESSURES OF BINARY MIXTURES, AND A THEORY OF FRACTIONAL DISTILLATION.

BY M. A. ROSANOFF, C. W. BACON AND JOHN F. W. SCHULZE.[1]

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Section 1. A Relationship between the Total and Partial Pressures of Binary Mixtures.

A simple method of measuring the partial vapor pressures of liquid mixtures was described in another joint communication from these laboratories.[2] The method depends upon the analysis of a series of consecutive distillates from a given mixture, and presents no manipulative difficulties. The fractions are "analyzed" by determining their refractive indices[3] or, in the case of ternary mixtures, by determining the index of refraction and one other physical property, such as the density or the boiling temperature.[4] There are important cases, however, where mixtures cannot be so simply analyzed with any degree of accuracy, and consequently the experimental determination of the partial pressures would be unreliable.

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[1] A brief preliminary account of the contents of this paper was published in the *J. Frank. Inst.*, December, 1911.

[2] Rosanoff, Bacon and White, THIS JOURNAL, **36**, 1803 (1914).

[3] v. Zawidzki, *Z. physik. Chem.*, **35**, 138 (1900); Rosanoff and Easley, THIS JOURNAL, **31**, 968 (1909).

[4] Schulze, *Ibid.*, **36**, 498 (1914).

That partial pressures can be *calculated* from the total pressures (which are always readily determinable) has been pointed out by Margules.[1] But Margules's method, which depends on the graphic measurement of the slope of the total pressure curve at its two ends, is liable to yield inaccurate results. At best, it permits of finding only two constants for the calculation of partial pressures, and this is often insufficient.[2] For these reasons, and also with a view to the development of a mathematical theory of fractional distillation, it seemed desirable to formulate a general relationship, even if only empirical, between the total and partial vapor pressures.

Such a relationship is suggested by Konowalow's semi-quantitative principles relating to the shape of the total pressure curve.[3] These principles indicate that the greater the slope of the total pressure curve, the greater is the difference in composition between the liquid and its vapor. When the total pressure curve passes through a maximum or a minimum, its slope is zero, and the composition of vapor and liquid is identical. Calling x the molar fraction of one of the components in the liquid, π the total pressure, and p_1 and p_2 the partial pressures, we thus have: when $d\pi/dx = 0$, $(p_1/p_2)/[x/(1-x)] = 1$. This theorem suggested formulating the slope of the total pressure curve as *a logarithmic function of the relative composition of vapor and liquid.*

If, now, in a given case—for instance, in one of the cases discussed below—a set of values of $d\pi/dx$ *are plotted against the corresponding values of* $\log[p_1(1-x)/p_2x]$, *the result is found to be a straight line passing through the origin of the coördinates, which indicates that the simplest possible relationship exists between the two quantities: viz., proportionality.* This apparently general law is expressed by the equation:

$$d\pi/dx = (1/k)\log[p_1(1-x)/p_2x]$$

The constant $1/k$ is evaluated by the following considerations: If the equation just given is applicable generally, it must hold true also in those cases in which the total and partial pressure curves are straight lines. In such cases $d\pi/dx = P_1 - P_2$ (the difference of the vapor pressures of the isolated components), and $[p_1(1-x)]/p_2x = P_1/P_2$. We should, therefore, have:

$$d\pi/dx = P_1 - P_2 = (1/k)\log[p_1(1-x)/p_2x] = (1/k)\log(P_1/P_2)$$

whence,

$$(1/k) = (P_1 - P_2)/(\log P_1 - \log P_2)$$

In general, then, we obtain:

$$d\pi/dx = [(P_1 - P_2)/(\log P_1 - \log P_2)]\log[p_1(1-x)/p_2x] \qquad \text{(A)}$$

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[1] Margules, *Sitzb. Kais. Akad. Wiss. Wien.*, [2] 104, 1243 (1895).

[2] See Rosanoff and Easley, *loc. cit.*, p. 957.

[3] Konowalow, *Wied. Ann.*, 14, 34, 219 (1881).

The complete correspondence between Equation A and the qualitative theorems of Konowalow imparts to the equation something of a theoretical character. Also, (A) is at least not in conflict with the thermodynamic equation of Duhem and Margules. But its chief recommendation is that it faithfully reproduces the experimental results in all known types of cases. Tables I, II, and III show how closely it has permitted of calculating the vapor compositions from the total pressures, in three cases experimentally studied by v. Zawidzki.[1] Table IV relates to a case in which it has rendered valuable practical service, as explained further on.

In the tables below the composition of the liquids is expressed, not in molar fractions, but in molar *per cents.;* further, the partial pressures, which are directly dependent upon the composition of the vapor, are replaced by the corresponding molar per cents. in the vapor.

Case 1. Carbon Tetrachloride and Benzene.—The isothermal total pressure curve for 49.99°, on the basis of Zawidzki's measurements, is well represented by the following equation, obtained by us with the aid of the method of least squares:

$$\pi = 268.075 + 80.853x - 43.826x^2 + 16.531x^3 - 13.695x^4$$

According to this equation,[2] a mixture containing 91.65 molar per cent. of carbon tetrachloride has a vapor pressure of 308.43 mm., which is a maximum, the vapor pressure of pure carbon tetrachloride being 308.0. Further, according to the equation:

$$\frac{\log_{10} P_1 - \log_{10} P_2}{P_1 - P_2} = 0.0015103,$$

and therefore, by Equation A:

$$\log_{10}[p_1(1 - x)/p_2x] = 0.122115 - 0.132383x + 0.0749000x^2 - 0.082734x^3$$

The following table compares the results yielded by these equations with those found by Zawidzki experimentally. The second and third columns give the observed and the calculated total pressures; the fourth and fifth columns compare the experimental and the calculated molar percentages

TABLE I.—CARBON TETRACHLORIDE—BENZENE.

Molar % CCl_4 in liquid.	π obs. mm.	π calc.	Molar % CCl_4 in vapor.	
			Obs.	Calc.
5.07	271.8	272.1	6.81	6.54
11.70	277.6	277.0	14.59	14.51
17.58	281.5	281.0	21.21	21.21
25.15	285.4	285.8	29.05	29.36
29.47	288.3	288.4	33.65	33.81
39.53	294.5	293.9	43.70	43.79
55.87	301.0	301.1	58.61	59.08
67.55	305.2	304.9	69.40	69.83
76.52	306.8	307.0	77.74	77.66

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[1] v. Zawidzki, *loc. cit.*

[2] See also Young, "Fractional Distillation" (London, 1903), p. 65.

of carbon tetrachloride in the vapor. The differences between experiment and our calculations are insignificant.

Case 2. Ethyl Iodide and Ethyl Acetate.—The isothermal total pressure curve (49.99°) is represented by the equation:

$$\pi = 280.325 + 250.403x - 285.085x^2 + 210.995x^3 - 103.147x^4$$

Accordingly, the curve passes through a maximum when the molar per cent. of ethyl iodide in the liquid is 76.49. Further,

$$\frac{P_1 - P_2}{\log_{10} P_1 - \log_{10} P_2} = 726.456,$$

and hence, by Equation A:

$$\log_{10}[p_1(1 - x)/p_2x] = 0.344691 - 0.784865x + 0.871333x^2 - 0.567946x^3$$

TABLE II.—ETHYL IODIDE—ETHYL ACETATE.

Molar % C_2H_5I in liquid.	π obs.	π calc.	Molar % C_2H_5I in vapor. Obs.	Molar % C_2H_5I in vapor. Calc.
5.90	294.3	294.1	9.8	11.1
11.48	304.7	305.3	17.7	19.3
13.76	308.7	309.9	20.9	20.1
19.46	319.5	319.7	27.9	28.6
22.88	325.2	324.9	31.7	32.2
30.57	335.4	335.4	39.0	39.4
37.45	343.4	343.2	45.3	45.4
45.88	350.7	351.0	52.2	52.4
54.86	357.4	357.4	59.7	59.5
63.40	361.7	361.6	66.1	66.1
73.88	363.5	364.1	74.0	74.4
82.53	363.5	363.6	81.5	81.5
90.98	360.7	360.4	89.3	89.4

Case 3. Chloroform and Acetone.—The isothermal total pressure curve (35.17°) is represented by the equation:

$$\pi = 343.719 - 146.168x - 418.752x^2 + 895.099x^3 - 380.240x^4$$

Therefore,

$$\frac{P_1 - P_2}{\log_{10} P_1 - \log_{10} P_2} = 732.3,$$

and, according to Equation A:

$$\log_{10}[p_1(1 - x)/p_2x] = -0.199592 - 1.14361x + 3.66677x^2 - 2.07687x^3$$

In the case of chloroform and acetone there can be little doubt as to complex molecules being formed to a greater or less extent. Therefore, the agreement between the calculated and the experimental molar per cents., while not as close as in the preceding cases, may still be considered very satisfactory.

Case 4. Benzene and Toluene.—In this case the refractive indices of the two pure substances are not sufficiently different to permit of determining the composition of a given mixture refractometrically with any degree of precision. Therefore, at least when the available amount of substance is small, experiment can only yield rough results. A need having arisen here (in connection with a study of isopiestic fractional distillation) to obtain accurate knowledge of the vapors given off by benzene-toluene mixtures, we felt that the mathematical method described above would lead to decidedly better results than any experimental method. The vapor compositions thus found corresponded to liquid mixtures kept at one and the same temperature. From these, however, we had no trouble in calculating also the composition of vapors given off by mixtures boiling isopiestically. We reproduce these calculations both as an illustration of the procedure involved, and because of the intrinsic value of the results.

TABLE III.—CHLOROFORM—ACETONE.

Molar % $CHCl_3$ in liquid.	π obs.	π calc.	Molar % $CHCl_3$ in vapor. Obs.	Molar % $CHCl_3$ in vapor. Calc.
0	344.5	343.7		
6.03	332.1	333.6	2.8	3.4
12.03	320.1	321.6	6.2	6.6
12.32	319.7	320.9	6.4	6.8
18.18	308.0	308.3	10.3	10.1
29.10	285.7	285.1	19.4	18.0
40.50	266.9	265.1	31.8	30.1
50.83	252.9	253.4	45.6	44.7
58.12	248.4	249.7	56.3	56.2
66.35	249.2	250.2	68.3	68.8
79.97	261.9	261.3	85.7	85.5
80.47	262.6	261.9	85.4	86.0
91.79	279.5	279.0	95.0	95.0
100	293.1	293.7		

Thiophene-free benzene and pure toluene were further purified by washing with water, drying with calcium chloride, and fractionating. The utilized fraction of either substance distilled over within 0.1°. A set of ten different mixtures was then accurately made up by weighing, and the total vapor pressures of these, as well as of the two pure substances, all at 79.70°, were determined with the aid of an Oddo ebullioscope connected by *wide tubing* with an empty tank and a baromanometer.[1] The measurements, which are recorded in the second column of Table IV, are almost perfectly reproduced by the following equation:

$$\pi = 288.438 + 466.519x - 56.464x^2 + 100.281x^3 - 49.971x^4$$

where x is the molar fraction of benzene in the liquid. The values of π given by this equation are reproduced in the third column of the table. This equation also gives:

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[1] See Rosanoff and Dunphy, THIS JOURNAL, 36, 1416 (1914).

$$\frac{\log_{10} P_1 - \log_{10} P_2}{P_1 - P_2} = 0.000900,$$

and consequently, according to our Equation A:

$$\log_{10}[p_1(1-x)/p_2x] = 0.4198671 - 0.101635x + 0.270759x^2 - 0.179896x^3$$

The values of p_1 (partial pressure of benzene in the vapor) calculated from this last equation were converted into molar per cents. and are recorded as such in the fourth column of Table IV.

TABLE IV.—BENZENE—TOLUENE (ISOTHERMAL).

Molar % of C_6H_6 in liquid.	π obs.	π calc.	Molar % of C_6H_6 in vapor.
100	748.7	748.8	100
95.65	729.0	728.9	98.27
91.89	711.4	711.6	96.72
82.43	668.0	667.7	92.49
73.27	624.9	625.0	87.82
63.44	579.2	579.2	81.97
54.51	537.5	537.8	75.74
43.52	487.0	487.2	66.56
33.83	443.1	443.0	56.76
22.71	392.8	392.5	42.95
11.61	341.5	342.0	25.30
0	288.5	288.4	0

With a view to the needs of our distillation study, we next proceeded to calculate the composition of the vapors as given off by the liquid mixtures boiling under *constant pressure*. But first the boiling temperatures themselves were determined, under a pressure of 750 ± 1 mm. Only in the case of the two isolated components the atmospheric pressure was higher, but not sufficiently so to affect the final results. These boiling temperatures are shown in the second column of Table V.

To find the vapor compositions at these temperatures, we made use of a principle introduced in an earlier communication.[1] In general, namely, the composition of vapors from binary mixtures may be accurately represented by an expression of the following form:

$$\ln\frac{p_1(1-x)}{p_2x} = \ln\frac{P_1}{P_2} + \alpha_2[(1-x) - {}^1/_2] + \frac{\alpha_3}{2}[(1-x)^2 - {}^1/_3] + \frac{\alpha_4}{3}[(1-x)^3 - {}^1/_4]$$

As shown in the communication referred to, the coefficients α_2, α_3, and α_4 are, in all cases in which the heat of dilution is moderate, practically independent of the temperature, so that changes of temperature influence the vapor composition only by affecting the value of P_1/P_2. If, therefore, from an expression found for some given temperature we should subtract the logarithm of P_1/P_2 corresponding to that temperature, and to the

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[1] Rosanoff and Easley, THIS JOURNAL, 31, 957 (1909).

remainder add an expression representing the logarithm of P_1/P_2 as a function of the temperature, we should obtain a more general expression, from which the vapor composition could be calculated for any temperature or temperatures within the given range.

In the case of benzene and toluene the heat of dilution is very small, and therefore the principle just stated may, within the temperature range involved, be applied without hesitation. On the basis of both Regnault's[1] and Young's[2] measurements of the vapor pressures of benzene, and of Kahlbaum's[3] measurements of the vapor pressures of toluene, we find:

$$P_2/P_1 = 0.2641 + 0.001506t$$

where t is the centigrade temperature, the formula applying between 80° and 110°. For the temperature of our isothermal measurements, *viz.*, 79.70°, and using common logarithms, $\log_{10}(P_2/P_1) = 0.4155238$. Subtracting this from 0.4198671, the constant term of our isothermal equation, and further, introducing, with the appropriate sign, the common logarithm of P_2/P_1 as a function of the temperature, we finally obtain:

$$\log_{10}[p_1(1 - x)/p_2x] = 0.0043433 - 0.101635x + 0.270759x^2 - 0.179896x^3 - \log_{10}(0.2641 + 0.001506t)$$

The composition of the vapors from the mixtures indicated by the first column of Table V, at the temperatures given in the second column, were calculated by this final equation, and are recorded in the third column.

TABLE V.—BENZENE—TOLUENE (ISOPIESTIC).

Molar % of C_6H_6 in liquid.	Boiling point under 750 mm.	Molar % of C_6H_6 in the vapor.	Weight per cent. of benzene	
			in the liquid	in the vapor.
0	109.59°		0	0
10	104.85	20.8	8.6	18.1
20	101.00	37.2	17.5	33.4
30	97.55	50.7	26.7	46.5
40	94.60	61.9	36.1	57.9
50	91.85	71.3	45.9	67.7
60	89.30	79.1	56.0	76.2
70	86.85	85.7	66.4	83.5
80	84.55	91.2	77.2	89.7
90	82.25	95.9	88.4	95.1
95	81.00	98.0	94.2	97.7
100	79.70		100	100

In spite of the circuitous calculation, we believe these results to be quite exact. For convenience of reference, we add a fourth and fifth columns, expressing the same results in terms of per cents. by weight.

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[1] Regnault, *Mem. de l'Acad.*, 26, 339 (1862).

[2] Young, *J. Chem. Soc.*, 55, 486 (1889).

[3] Kahlbaum, *Z. physik. Chem.*, 26, 603 (1898).

Section 2. A Theory of Fractional Distillation without Reflux Condensation.

In principle, two different ways must be distinguished in which fractional distillation may be carried on: the vapor may either be allowed to escape from the still without any reflux condensation at all, or else it may be partially recondensed on its way, the condensate returning to the boiling liquid in the still. In all practical work, whether on a laboratory or an industrial scale, partial reflux condensation is employed invariably, because it greatly increases the efficiency of the process by increasing the difference between the composition of the vapor and that of the boiling liquid. A rational process of this type will shortly be described in a special series of publications. In this present communication we will consider only distillation involving no reflux condensation—a process, to be sure, of academic rather than of practical interest, but nevertheless worthy of consideration.

Since the appearance of Konowalow's classic paper[1] on the total vapor pressures of mixtures, it has been clearly understood that in all cases, except where the vapor pressure of the given mixture is a maximum or a minimum, distillation divides a mixture into fractions of unequal volatility, the residue being less volatile than the distillate and even less volatile than the original mixture. In other words, during a distillation at constant temperature the total pressure of the liquid in the still must continually diminish; during a distillation under constant pressure, the temperature of the boiling mixture must continually rise. But these Konowalow principles, being purely qualitative, do not constitute a theory of distillation in the truer sense of the term. A true theory of distillation should furnish a general answer to questions like the following: given a mixture of a certain specified composition, what proportion by weight of the total must be distilled off in order that the composition may change from what it was originally to some new specified value?

An attempt to solve this problem was made some twenty years ago by Barrell, Thomas, and Young.[2] The assumption underlying their solution is that throughout the distillation the ratio of the weights of the components in the vapor is proportional to the ratio of the weights in the liquid. Denoting by ξ and η the weights in the liquid, and by $d\xi$ and $d\eta$ the weights in the vapor, the assumption is expressed by the equation:

$$d\xi/d\eta = c.\xi/\eta$$

or

$$d\ln\xi/d\ln\eta = c,$$

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[1] Konowalow, *Wied. Ann.*, 14, 34, 219 (1881).

[2] Barrell, Thomas and Young, *Phil. Mag.*, [5] 37, 8 (1894); Young, "Fractional Distillation" (London, 1903), p. 93; Nernst, *Theoretische Chemie* (Ed. 7, Stuttgart, 1913) p. 109.

c being a constant. This assumption had some years previously been proposed by F. D. Brown.[1] But, as Young himself has pointed out in his monograph on fractional distillation, Brown's assumption cannot possibly be true as a general rule, and leads to absurdities in those cases in which the total pressure curve passes through a maximum or a minimum. It must, however, be added that Brown's formula does hold good for the isothermal distillation of mixtures whose partial and total vapor pressure curves are perfect straight lines; only such cases are rare.

Another theory of distillation was proposed in 1902 by Lord Rayleigh.[2] Let the weight of a given liquid mixture be denoted by w, and the weight of the first component in it by y. Then y/w is the fraction of the total weight constituted by the first component. If this fraction is denoted by ξ, we have: $y/w = \xi$, or

$$y = w\xi$$

Let, at the same time, the entire weight of the vapor be dw, and the weight of the first component in the vapor dy. Then the fraction by weight of the first component in the vapor is dy/dw. In any given case the fraction of the first component in the vapor will be some function of the fraction in the liquid:

$$\frac{dy}{dw} = f(\xi),$$

or since $y = w\xi$

$$\frac{d(w\xi)}{dw} = f(\xi),$$

whence, if w_0 and ξ_0 denote the initial values of w and ξ,

$$\ln\frac{w}{w_0} = \int_{\xi_0}^{\xi}\frac{d\xi}{f(\xi) - \xi}$$

To turn this mode of formulation into a theory, it is necessary to make some assumption regarding the nature of the function $f(\xi)$. Lord Rayleigh assumes that *in very dilute solutions, i. e.*, in mixtures containing very little of what we call the first component, the fraction of that component in the vapor is simply proportional to its fraction in the liquid: $dy/dw = f(\xi) = \kappa\xi$; whence, by integration,

$$\xi/\xi_0 = (w/w_0)^{\kappa - 1},$$

the constant κ to be found empirically.

Lord Rayleigh's theory is thus confined to very dilute mixtures only and leaves room for a more general theory, based on some reliable assumption regarding the relation between the composition of the vapor and of the liquid for all possible concentrations. Such a relationship, even if only

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[1] Brown, *Trans. Chem. Soc.*, **39**, 317 (1881).

[2] Lord Rayleigh, *Phil. Mag.*, [5] **4**, 527 (1902); see also Plücker, *Pogg. Ann.*, **92**, 198 (1854).

semi-theoretical in character, is furnished by Equation A developed in the preceding section; and as that equation appears to hold true in all types of cases, a mathematical theory of distillation based upon it must likewise be generally applicable.

As in connection with the Brown formula above, we will again denote by ξ and η the absolute weights of the components in the liquid, and by $d\xi$ and $d\eta$ their absolute weights in the vapor. Let, further, p_1 and p_2 represent the partial pressures of the components, and let x represent the molar fraction of the first component in the liquid. Then p_1/p_2, the ratio of the partial pressures, equals the ratio of the molar fractions in the vapor, these molar fractions being based, of course, on the actual molecular weights of the two vapors. But, as pointed out in a previous communication,[1] if the purely thermodynamic equation of Duhem and Margules is not to be contradicted, the molar fractions x and $1 - x$ in the liquid must be based on the same molecular weights as the molar fractions in the vapor. It may, therefore, be stated with certainty, that the quotient of the ratios of the *molar fractions* in vapor and liquid is equal to the quotient of the ratios of the weights, as expressed by the equation:

$$\frac{p_1(1-x)}{p_2 x} = \frac{\eta d\xi}{\xi d\eta},$$

or

$$\frac{d \ln \xi}{d \ln \eta} = \frac{p_1(1-x)}{p_2 x}$$

Now, our Equation A teaches that

$$\log \frac{p_1(1-x)}{p_2 x} = k\frac{d\pi}{dx},$$

or

$$\frac{p_1(1-x)}{p_2 x} = e^{kd\pi/dx},$$

e denoting, as usual, the base of natural logarithms. We therefore have:

$$\frac{d \ln \xi}{d \ln \eta} = e^{kd\pi/dx} \qquad \text{(B)}$$

and all conclusions regarding the course of a fractional distillation based on this formula will be as reliable as Equation A itself.

Calling M_1 and M_2 the molecular weights of the two components, we have:

$$\frac{x}{1-x} = \frac{\xi/M_1}{\eta/M_2},$$

whence

$$d \ln(\xi/\eta) = dx/x(1-x)$$

and

$$d \ln\eta = d \ln\xi - dx/x(1-x)$$

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[1] Rosanoff, THIS JOURNAL, 36, 1410 (1914).

Then, by simple transformation, from (B):

$$d \ln \xi = \frac{e^{kd\pi/dx}}{(e^{kd\pi/dx} - 1)(1 - x)x} dx$$

Denoting by ξ_0 and x_0 the initial weight and the initial molar fraction of the first component in the liquid, we get

$$\ln \frac{\xi}{\xi_0} = \int_{x_0}^{x} \frac{e^{kd\pi/dx}}{(e^{kd\pi/dx} - 1)(1 - x)x} . dx \ldots\ldots\ldots\ldots (C)$$

For the second component we obtain analogously:

$$\ln \frac{\eta}{\eta_0} = \int_{x_0}^{x} \frac{dx}{(e^{kd\pi/dx} - 1)(1 - x)x} \ldots\ldots\ldots\ldots (D)$$

Needless to say, the integrations may be readily carried out by one of the ordinary approximation methods. Also, only one of these integrations must be carried out, as the quantities ξ and η are connected by the equation:

$$\eta = \frac{1 - x}{x} \cdot \frac{M_2}{M_1} \cdot \xi$$

It will be noted that Equations C and D express the relation between the changes of weight and composition accompanying isothermal fractional distillation, in terms of $d\pi/dx$, the slope of the total pressure curve. They may thus be regarded as an attempt at a quantitative formulation of the Konowalow theory of distillation.

In the rare cases in which the total and partial pressure curves are straight lines, our theory becomes essentially identical with the Brown-Young theory of distillation. Since $d\pi/dx$ is then constant ($= P_1 - P_2$), our Equation B turns into the Brown formula:

$$\frac{d \ln \xi}{d \ln \eta} = \frac{P_1}{P_2} = \text{constant},$$

and the integrals in (C) and (D) assume the values:

$$\frac{\xi}{\xi_0} = \left[\frac{x(1 - x_0)}{x_0(1 - x)}\right]^{P_1/(P_1 - P_2)}$$

and

$$\frac{\eta}{\eta_0} = \left[\frac{x(1 - x_0)}{x_0(1 - x)}\right]^{P_2/(P_1 - P_2)}$$

It is easy to read into these last equations that if the total pressure line were parallel to the x axis, so that $P_1 = P_2$, then no matter what weight were distilled off from the original mixture, the composition would remain unaltered: $x/(1 - x) = x_0/(1 - x_0)$, as must of course be the case.

The theory, in the form of Equations C and D, has been tested out here by direct experiment. It would, however, be superfluous to publish the results, seeing that the theory is based on no other principles than those involved in Equation A, and that the validity of the latter is, sufficiently indicated by the cases discussed in the preceding section.

In conclusion, we will mention that the above is one of a series of studies (mostly experimental) that have been made possible by a grant from the Rumford Fund of the American Academy of Arts and Sciences. It is a pleasure to again express our thanks to the Rumford Committee for their generous interest in this work.

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PASSIVITY OF METALS.

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Introduction.

In a previous paper by one of us,[1] the term passivity was defined as properly applying to an element when it "shows abnormal electrochemical relations, and a chemical inactivity not corresponding to its ordinary behavior and not in accord with its position in the electromotive series of the elements." These characteristics are exhibited by a number of elements under a variety of circumstances and to varying degrees, but the passivity of iron has been most carefully studied and the present paper is limited to a study of one phase of its behavior. Iron becomes passive when immersed in certain electrolytes, which are always oxygen compounds. It also becomes passive under certain conditions when used as an anode. In this case also, the electrolyte is almost always an oxygen compound in solution in water. The most apparent evidences of transition from the active to passive condition of iron, as an anode, are: the metal no longer dissolves, its surface brightens, oxygen is evolved from its surface and, coincident with these changes, an ammeter, in series in the circuit, shows a sudden drop in the current. Considerable work has been done in this laboratory on this behavior and the conclusion reached,[2] that the following factors influence the establishment of the passive state in iron used as an anode: (*a*) the character and condition of the metal; (*b*) the electrolyte employed; (*c*) the temperature; (*d*) the curent *density;* (*e*) the duration of passage of the current; and (*f*) the character of movement of the electrolyte.

In the hope that the above variables represented a complete catalogue, it was thought that light could be thrown upon the subject by a study of the behavior of an anode when *two of the factors were allowed to vary mutually while all others were held constant.* Below, is given, briefly, the experi-

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[1] THIS JOURNAL, 30, 1718 (1908).

[2] *Ibid.*, 35, 759 (1913).