The Journal of the
American Chemical Society
with which has been incorporated
The American Chemical Journal
(Founded by Ira Remsen)

VOL. 46 JANUARY, 1924 No. 1

[Contribution from the Department of Chemical Engineering, Massachusetts Institute of Technology]

# RELATION BETWEEN VAPOR PRESSURE AND VAPOR COMPOSITION IN BINARY MIXTURES OF VOLATILE LIQUIDS

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Received April 5, 1923

The following is a method of computation, the purpose of which is, first, to make possible the checking of experimental determinations of vapor composition of binary mixtures against those of vapor pressure and second, to provide a means of computation of the vapor composition of such mixtures from vapor-pressure determinations alone, thereby simplifying the laboratory manipulation necessary in securing the data for distillation calculations.

The Duhem-Margules equation gives a necessary thermodynamic relation between the partial pressures of the components in a binary mixture of volatile liquids at constant temperature in terms of the composition of the liquid mixture. It is usually written as

$$\frac{\mathrm{d}\,ln\,p_1}{\mathrm{d}\,ln\,p_2} = -\frac{1-x}{x} = \frac{\mathrm{d}\,ln\,x}{\mathrm{d}\,ln\,(1-x)} \tag{1}$$

We prefer to express the equation in terms of the vapor composition, $y$, and the total pressure of the mixture, $P$, because both of these quantities are susceptible of direct measurement and both of them are employed directly in the solution of problems in distillation, as is not the case with the partial pressures. Since $p_1 = yP$ and $p_2 = (1-y)P$, the equation becomes

$$\frac{y-x}{y\,(1-y)} = \frac{\mathrm{d}\,ln\,P}{\mathrm{d}y} \tag{2}$$

It is obvious that the integration of this equation, containing as it does three variables, is impossible without further information or assumption as to the relation between them.[1] If, however, one could integrate, one would have an equation with which to compute vapor composition, $y$, from direct measurement of vapor pressure, $P$, at various values of liquid composition, $x$. This would give a ready means of checking the accuracy of measurements of vapor composition or of computing them where direct measurements had not been made. Since the measurement of vapor composition involves a complicated technique difficult to master whereas the determination of vapor pressure is much easier experimentally, the integration would simplify the securing of data in those cases where the highest precision is not essential, as for example in the design of industrial equipment for the separation of liquid mixtures by distillation.

Inspection of the equation in the second form given shows that if $x$ can be expressed as a function of $y$ the equation may be integrated. Over small ranges of variation in $x$ the $y-x$ curve is sufficiently flat so that assumption of a linear relationship between $y$ and $x$ within this narrow range will not introduce serious error in the difference between $y$ and $x$. If, therefore, one assumes $x = a + by$ and substitutes, one obtains upon integration between the limits $(x_1, y_1, P_1)$ and $(x_2, y_2, P_2)$

$$(1 - a - b) \log \frac{1 - y_1}{1 - y_2} - a \log \frac{y_2}{y_1} = \log P_2 - \log P_1 \tag{3}$$

$$\text{where } b = \frac{x_2 - x_1}{y_2 - y_1} \text{ and } a = x_1 - \frac{x_2 - x_1}{y_2 - y_1} y_1$$

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[1] Margules [(a) *Sitzb. Akad. Wiss. Wien,* [2A] **104,** 1243 (1895)] assumed that the integral could be expressed as Raoult's law with a correction term in the form of an exponential series in $x$ and $1-x$, determining certain relations between the coefficients of the series by the assumption of Raoult's law at each end of the diagram. Zawidzki [(b) *Z. physik. Chem*, **35,** 164 (1900)] used this expression as an interpolation formula by discarding all terms beyond the second in each series, that is, by assuming them rapidly converging. Margules pointed out that the coefficients of this simplified form can be determined from the initial slopes of the total-pressure curve at each end of the diagram. Evaluation of constants from these slopes alone is obviously inaccurate. Zawidzki reports partial pressures of various mixtures thus computed but points out that the equation is not general. The methods here presented do not assume Raoult's law in any range. The first procedure determines the constants by directly measured values of total pressures and although the second is based upon initial slope, the constants are determined to correspond quantitatively to the chosen experimental point on the total-pressure curve. In consequence, inaccuracy in determination of the initial slope has little influence on the computed result. Rosanoff [(c) THIS JOURNAL, **36,** 1993 (1914)] has proposed a method of solution of the same problem based upon the empirical relationship that $dP/dx$ is linear in $\log p_1(1-x)/p_2x$, that is, when the second term is plotted against the first, a straight line is obtained. That this relation is not general is shown by the accompanying plot, the data for which were taken from Zawidski [(d) p. 129]. Zawidzki's total pressures were plotted against $x$ on a large scale and the slopes read off carefully. The other data were taken directly from his table. While there may be some error in determining the slopes, there can be no question that the relation between $dP/dx$ and the log term is not linear. One would therefore hesitate to trust Rosanoff's method owing to the fact that at least in specific cases his basic assumption fails to hold.

Given a known point $x_1$, at which the pressure is $P_1$ and the vapor composition $y_1$, one can by the use of this equation calculate by trial and error the vapor composition $y_2$ at the second point $x_2$ at which the vapor pressure is known to be $P_2$. Because of the assumption upon which it is based, the equation must not be used over too wide limits. We find it normally allowable to use it over a concentration range of 10%, except in the neighborhood of the pure component.

Whenever one is dealing with a mixture of maximum or minimum boiling point, the vapor composition of the constant-boiling mixture is known since it must be identical with that of the liquid. Therefore, in such a case one can start from the constant-boiling mixture as a fixed point and by the use of this equation compute the vapor composition of liquids not too far removed from the constant-boiling mixture. Operating from a second point thus determined as a base, one can compute a third, and so on. In all cases one can start at the two ends of the diagram corresponding to the pure components. It is recommended that computations be carried out from both ends and from any constant-boiling mixture so as to overlap, in order to increase the dependability of the results.

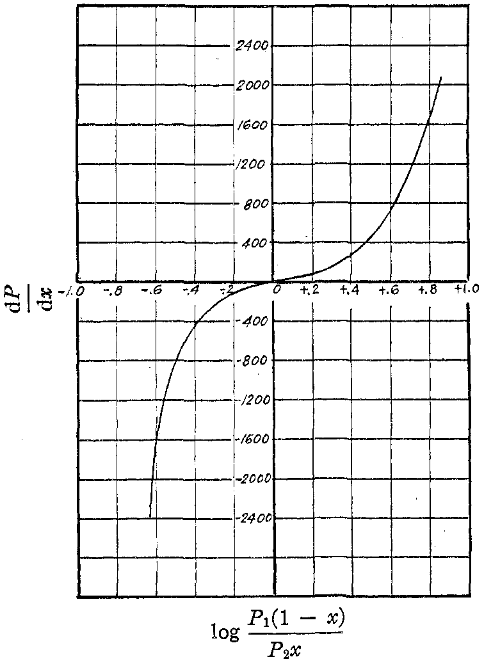
Especially in the neighborhood of the origin the curvature of the $y-x$ curve is likely to be great and where the experimental determinations do not extend quite close to the origin the linear relationship assumed above may not be sufficiently dependable. In such cases it is recommended that one assume the relation between $y$ and $x$ to be represented by a rectangular hyperbola of the form $y = ax/(b + x)$. Assuming this expression for $y$, the slope of the curve obtained by plotting log $P$ versus $x$, that is, $d\,lnP/dx$ at the origin is $(a-b)/b$. Calling this initial slope $s_0$, $a = (s_0 + 1)b$. Substituting and integrating one obtains,

$$\log \frac{b+x}{b} + \left(\frac{b\,s_0 - 1}{1 - b\,(s_0+1)}\right) \log \frac{b + x - bx(s_0+1)}{b} = \log P_1 - \log P_0 \qquad (4)$$

If, for a given value of $x$ not too far removed from the origin (preferably less than 20%) at which $P$ is known, the values for $x$ and $P$ be substituted in this equation, it can be solved for its only unknown, $b$, by trial and error; $s_0$ can be obtained graphically by plotting $ln\ P$ against $x$. While accuracy is of course desirable, moderate error in estimating $s_0$ does not seriously affect the dependability of the equation, since in any case the final equation represents an average relationship between the variables between the origin and the point computed corresponding quantitatively to the Duhem-Margules relationship. Once $b$ has been determined in this way, $a$ can be computed from the relation between $b$ and $s_0$ and $y$ from the original hyperbola assumed. A better method of obtaining $s_0$ is to assume the form of the relation between log $P$ and $x$ such as $\log P/P_0 = cx/(d + x)$. From the experimental average as to the total pressure for two representative points at the start of the curve one can algebraically evaluate $x$ and $d$, and by differentiating obtain $s_0$. We recommend this procedure, but it is also advisable actually to plot the logarithm of the pressure ratio to make sure that the general form of the function in the neighborhood of the origin agrees with the assumed relationship.

Whenever starting from either end of the diagram $x$ and $y$ should represent the mole fraction of the *other* component of the mixture.

This method of computation assumes a simplified relationship between $y$ and $x$ over a narrow range but provides that on the average over this range the relation between $y$, $x$ and $P$ corresponds quantitatively to the Duhem-Margules equation.



Plot for carbon disulfide and acetone.

$\frac{dP}{dx}$ as ordinates

*vs*

$\log \frac{P_1(1-x)}{P_2x}$ as abscissas

The method has been tested by applying it to data carefully chosen for dependability. Four cases are presented: one normal, one having a vapor-pressure minimum and two having a maximum. The first three columns in each of the tables give the experimental figures as taken from the sources cited. The remaining columns are the result of computation. In all cases each successive point tabulated was computed by a single step, that is, the relationship assumed, whether linear or hyperbolic, was held constant over the whole intervening range.

It will be noted that in only one case is the deviation between the observed and computed value of $y$ as great as 2%.

The computation of the $x/y$ relationship depends upon experimentally determined pressure difference. Where the total-pressure curve is flat these pressure differences must be determined with precision, and small errors in the pressure will completely vitiate results. On the other hand, if the curve is always computed by starting at both ends and working in opposite directions, error of this sort will immediately be made manifest by failure of the results to check satisfactorily in the middle range. It is believed that when such checks are obtained danger of serious error is removed.[2]

In using this method of computation it must be kept in mind that the integration is an approximate one and that the assumptions made in each case must be justifiable. One should therefore observe the following general rules.

1. Inspection of vapor-composition diagrams which include constant boiling mixtures shows that the $y-x$ curves are flat in the neighborhood of these mixtures. Hence, in any given case it is allowable to start from the constant-boiling mixture and work in both directions by the first method.

2. Similar study will show that the curvature of the $y-x$ curves is usually great whenever the more volatile component of the mixture is present in small amount. It must be kept in mind that this applies to both ends of the diagram in all cases of mixtures showing a minimum boiling point. Therefore, in such cases, when working from one end of the diagram toward the middle the first step should be made by the second method, that is, by assuming a hyperbolic relationship.

TABLE I

METHYL ALCOHOL AND WATER

Data from M. Wrewsky.[3] $t = 59.44°$.
$y-x$ relationship assumed hyperbolic for first point, linear for next; calculation started from the water end ($x = 0$); $x$ and $y$ are mole fractions of alcohol.

| $x$ | $P$ | $y$ (obs.) | $s_0$ | $b$ | $y$ (calc.) |
|---|---|---|---|---|---|
| 0 | 145.4 | ... | ... | ... | ... |
| 0.222 | 317 | 0.663 | 7.520 | 0.118 | 0.656 |
| .332 | 368.7 | .738 | ... | ... | .733 |
| $y-x$ relationship assumed linear; calculation started from the alcohol end ($x = 1$). | | | | | |
| 0.332 | 368.7 | 0.738 | ... | ... | 0.731 |
| .471 | 420.4 | .798 | ... | ... | .798 |
| .555 | 450.6 | .829 | ... | ... | .833 |
| .692 | 497.2 | .884 | ... | ... | .884 |
| .785 | 530.4 | .917 | ... | ... | .918 |
| .859 | 557.0 | .946 | ... | ... | .946 |
| 1.000 | 609.3 | 1.000 | ... | ... | ... |

3. Normal mixtures, those not showing a maximum or minimum in the vapor-pressure curve, are usually flat where the less volatile component is present in small amount, so that in such cases one can work from this end of the diagram by the first method. Under these conditions the equation becomes

$$(b-1)\, ln\,(1-y) = ln\,\frac{P}{P_0}, \text{ since } a = 0 \text{ and } x = by \qquad (5)$$

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[2] Difficulty of this sort is encountered in calculating the data of Wrewsky (see below) for the alcohol-water isotherm of 74.8° in the range from 65 to 80 moles per cent. alcohol. On the other hand, the whole discrepancy disappears upon assuming an error of about 2 mm. in his experimentally determined value for the pressure in this range.

[3] Wrewsky, *Z. physik. Chem.*, **81**, 1 (1912).

4. The computed values of $y$ should always be plotted against $x$ and the resulting diagram inspected to make sure that the assumptions made in each range are valid over that range and furthermore that points computed by working up the curve check those working down.

5. It is advantageous to determine the total-pressure curve with especial care in the neighborhood of the pure components and wherever unduly flat, and also to measure accurately the composition of the constant-boiling mixture if such exists.

The method looks tedious, but once its technique is mastered computations can be made quickly, especially since the unknown vapor composition can be closely estimated. Ten or twelve points on a complete curve can usually be computed in a few hours.

### TABLE II

### ETHYL ALCOHOL AND WATER

Data from M. Wrewsky.[3] $t$ = 54.81°.
$x-y$ relationship assumed hyperbolic; calculation started from water end ($x$ = 0); $x$ and $y$ are mole fractions of alcohol.

| $x$ | $P$ | $y$(obs.) | $s_0$ | $b$ | $y$ (calc.) |
|---|---|---|---|---|---|
| 0 | 116.6 | ... | .. | ... | ... |
| 0.167 | 220.7 | 0.545 | 11.8 | 0.055 | 0.529 |

$x-y$ relationship assumed linear, calculation started from C. B. M.[a] ($x$ = 0.915.)

| $x$ | $P$ | $y$(obs.) | $s_0$ | $b$ | $y$ (calc.) |
|---|---|---|---|---|---|
| 0.167 | 220.7 | 0.545 | .. | ... | 0.522 |
| .267 | 237.3 | .589 | .. | ... | .576 |
| .370 | 247.5 | .615 | .. | ... | .613 |
| .479 | 256.6 | .655 | .. | ... | .653 |
| .617 | 265.7 | .720 | .. | ... | .709 |
| .777 | 273.2 | ... | .. | ... | .800 |
| .915 | 275.9 | .915 | .. | ... | ... |
| 1.000 | 275.2 | ... | .. | ... | ... |

[a] Constant-boiling mixture.

### TABLE III

### CARBON DISULFIDE AND ACETONE

Data from J. v. Zawidzki.[1d] $t$ = 35.17°.
$x-y$ relationship assumed hyperbolic for first point, linear thereafter; calculation started from acetone end ($x$ = 0); $x$ and $y$ are mole fractions of carbon disulfide.

| $x$ | $P$ | $y$ (obs.) | $s_0$ | $b$ | $y$ (calc.) |
|---|---|---|---|---|---|
| 0 | 343.8 | ... | ... | ... | ... |
| 0.0711 | 451.8 | 0.272 | 5.200 | 0.135 | 0.287 |
| .186 | 553.8 | .467 | ... | ... | .477 |
| .276 | 598.5 | .540 | ... | ... | .546 |
| .350 | 622.2 | .576 | ... | ... | .584 |
| .406 | 634.1 | .599 | ... | ... | .605 |
| .493 | 646.0 | .624 | ... | ... | .631 |

$x-y$ relationship assumed linear; calculation started from C. B. M. ($x$ = 0.667.)

| $x$ | $P$ | $y$ (obs.) | $s_0$ | $b$ | $y$ (calc.) |
|---|---|---|---|---|---|
| 0.493 | 646.0 | 0.624 | ... | ... | 0.616 |
| .573 | 652.5 | .644 | ... | ... | .641 |
| .667 | 655.0 | .667 | ... | ... | ... |
| .828 | 645.1 | .721 | ... | ... | .731 |

$x-y$ relationship assumed hyperbolic for first point, linear thereafter; calculation started from the carbon disulfide end ($x$ = 1).

| | | | | | |
|---|---|---|---|---|---|
| 0.828 | 645.1 | 0.721 | ... | ... | 0.712 |
| .919[a] | 614.1 | .799 | 5.550 | .054 | .788[b] |
| 1.000 | 512.3 | ... | ... | ... | ... |

[a] $x' = 0.081 = 1 - x$.

[b] $y'$ calc. $= 0.212 = 1 - y$.

### TABLE IV

### CHLOROFORM AND ACETONE

Data from J. v. Zawidzki.[1d] $t$ = 35.17°.

$x-y$ relationship assumed linear; calculations started from C. B. M. ($x$ = 0.625); $x$ and $y$ are mole fractions of chloroform.

| $x$ | $P$ | $y$ (obs.) | $S_0$ | $b$ | $y$ (calc.) |
|---|---|---|---|---|---|
| 0 | 344.4 | 0 | ... | ... | ... |
| 0.1 | 323.3 | 0.050 | ... | ... | 0.048 |
| .2 | 303.5 | .115 | ... | ... | .108 |
| .3 | 283.8 | .201 | ... | ... | .194 |
| .4 | 267.3 | .312 | ... | ... | .298 |
| .5 | 254.0 | .445 | ... | ... | .437 |
| .625 | 248.0 | .625 | ... | ... | ... |
| .750 | 255.6 | .800 | ... | ... | .812 |
| .850 | 269.0 | .900 | ... | ... | .910 |
| .950 | 284.5 | .971 | ... | ... | .976 |
| 1.000 | 293.1 | 1.000 | ... | ... | ... |

$x-y$ relationship assumed hyperbolic; calculations started from acetone end ($x$ = 0).

| | | | | | |
|---|---|---|---|---|---|
| 0.1 | 323.3 | 0.050 | −0.626 | −0.280 | 0.058 |

$x-y$ relationship assumed hyperbolic; calculations started from chloroform end ($x$ = 1).

| | | | | | |
|---|---|---|---|---|---|
| 0.95[a] | 284.5 | 0.971 | −0.583 | −1.750 | 0.978[b] |

[a] $x'$ = 0.05.

[b] $y'$ calc. = 0.022.

## Summary

A stepwise approximate integration is presented for the Duhem-Margules equation, which makes possible the calculation of the vapor-liquid composition curve from the isothermal total-pressure curve alone.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 432]

# THE VELOCITY OF THE HYDROGEN ELECTRODE REACTION ON PLATINUM CATALYSTS

BY LOUIS P. HAMMETT

RECEIVED AUGUST 18, 1923

The reversible reaction $H_2 \rightleftarrows 2H + 2e$ may be considered a step in many if not all reactions in which hydrogen is produced or in which it reacts. Conditions affecting the velocity of the electrochemical reaction should therefore be of fundamental importance in the study of the numerous chemical reactions of which it forms a part. In particular the close parallelism between the catalysis of the electrode reaction and the catalysis