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The Applicability of the Ramsay–Young and Dührung Rules, and an Accurate Method for Calculating Θ, the Characteristic Temperature of a Compound. An Investigation Using the Best Modern Data

BY R. R. DREISBACH

The Ramsay–Young rule is proved to be accurate for polar, non-polar, and associated compounds when the Θ value of the theoretical Antoine equation is used instead of the value 273.2. Dühring's rule is only accurate for chemically related compounds; for these compounds the error apparently is less than 0.1°, whereas, for compounds which are chemically unrelated, the error apparently will vary from about 0.6–1.0°. An accurate method for computing Θ for nineteen Cox Chart families is developed.

Ramsay and Young[1] developed an empirical equation for relating the boiling points of two substances at the same pressures. This equation is

$$\frac{T_A}{T_B} - \frac{T_{A'}}{T_{B'}} = K(T_A - T_{A'}) \qquad (1)$$

where T_A, T_B are the absolute boiling points of two compounds at the same pressure, $T_{A'}$, $T_{B'}$ are the boiling points at a second pressure and K is a constant.

This equation has also been developed from the Antoine equation in the form (see ref. (2) for derivation)

$$\log P = A - B/T \qquad (2)$$

Gutmann and Simmons[3] developed the Antoine equation from the theoretical van der Waals and Debye equations and presented it in the form

$$\log P = A - \frac{B}{(T - 3\Theta/8)} \qquad (3)$$

The Cox Chart is based on the Antoine equation in the form

$$\log P = A - \frac{B}{(t + C)} \qquad (4)$$

where

P = pressure in mm.
t = temperature, °C.
T = temperature, °K.
A,B,C = constants
Θ = characteristic temperature for each compound C in equation (4) is equal to $273.2 - 3\Theta/8$.

The Antoine equation in the form of eq. (3) has now a theoretical basis. Even if the derivation of the Antoine equation is questionable, it is the best equation yet devised for expressing the relationship between the temperature and pressure. Rossini[4] states that the most generally used equation appears to be the Antoine equation, and that it is the only temperature–vapor pressure equation that can be extrapolated great distances beyond the range of experimental observation without too large uncertainties.

It is well known that when the log of the vapor pressure is plotted against $1/T$, the line is slightly curved. Equation (3) explains that the line can only be straight when $C = 273.2$. It also explains why equation (1) can only be expected to be accurate when C, or $3\Theta/8$, is the same for the two compounds compared.

Dühring's[5] rule can be expressed as

$$(t_a - t_{a'})/(t_b - t_{b'}) = \text{constant} \qquad (5)$$

Ramsay and Young found K in equation (1) to be small when the compounds were related chemically, and they stated that K could be eliminated to give

$$T_A/T_B = T_{A'}/T_{B'} \qquad (6)$$

Equations (1) and (2) do not apply accurately to any compound unless Θ is 0 or unless Θ is the same for the two compounds in equation (1).

When C ($273.2–3\Theta/8$) is determined for two compounds, equation (1) becomes

$$\frac{t_a + C_a}{t_b + C_b} - \frac{t_{a'} + C_a}{t_{b'} + C_b} = K(t_a - t_{a'}) \qquad (7)$$

where $(t_a + C_a) = T_A$, etc. of equation (1).

When accurately determined vapor pressures are available so that Θ can be determined, equations (3), (5) and (7) are accurate for all compounds, polar, non-polar and associated.

American Petroleum Institute (A.P.I.) Research Project 44[6] proved the applicability of equations (3) or (4) for saturated aliphatic and cyclic hydrocarbons and for the unsaturated aliphatic hydrocarbons.

The vapor pressure–temperature data of Dreisbach and Shrader[7] on fifteen Cox Chart families together with the A.P.I. data permit the evaluation of equation (5) as well as an extension of equation (3) or (4) to fifteen other Cox Chart families.

Apparently the reason for assuming that the above equations did not hold for associated compounds was the lack of accurate vapor pressure–temperature data. From the data of Dreisbach and Shrader the following C values (equation 4) are obtained.

Compound	C value	Compound	C value
Ethyl alcohol	222.65	*n*-Butyl alcohol	196.3
t-Butyl alcohol	218.9	*n*-Octyl alcohol	131.6
Acetic acid	200	α-Methyl-α-ketobutanol	142
Propionic acid	190		
Chloroacetic acid	180		

From the values it can be readily seen why equation (1) will not hold when 273.2 is used for all the compounds.

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[1] W. Ramsay and S. Young, *Phil. mag.*, **20**, 515 (1885).

[2] S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 2nd ed., 1946, p. 455.

[3] F. Gutmann and L. M. Simmons, Jr., *Chem. Phys.*, **18**, 696 (1950).

[4] R. D. Rossini, "Chemical Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 435.

[5] R. Dühring, "Neu Grundgesetze zur rationelle Physick und Chemie," Leipzig, 1878.

[6] American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

[7] Dreisbach and Shrader, THIS JOURNAL, **41**, 2879 (1949).

It has been stated a number of times in the literature that for compounds boiling below 150° the C value should be around 230 to 254. If those values should be used in the Antoine equation for alcohols it can also be seen why the Antoine equation, equations[2,4] would not be accurate.

The accuracy which may be expected by the use of equations (5) and (7) can be obtained by the use of the A.P.I.[4] data. The data on *n*-propylbenzene and toluene are

	Boiling points at			
	760 mm.	500 mm.	10 mm.	C value
n-Propylbenzene	159.218	143.552	43.44	207.171
Toluene	110.625	96.520	6.37	219.377

When the boiling points at the first two pressures and the C value are substituted in equation (7) the K value is found to be 0.00000115. When this K value and the boiling points of *n*-propylbenzene at 760 mm. and 10 mm. and the boiling point of toluene at 760 mm. are substituted in equation (7), the boiling point of toluene at 10 mm. comes out to be 6.372°. This compares to the determined value of 6.37°.

If equation (5) is used by substituting the known values above, the boiling point of toluene at 10 mm. is 6.385. Thus it is seen that for chemically related compounds equation (5) is excellent. The fact that K is so small indicates that equation (5) would be very accurate.

By the use of the data for *n*-propylbenzene above and the smoothed values for chlorobenzene determined by Dreisbach and Shrader,[7] equations (5) and (7) can be evaluated for unrelated compounds.

	Boiling points at		
	760 mm.	500 mm.	10 mm.
n-Propylbenzene	159.218	143.552	43.44
	131.70	116.80	22.49

	A	B	C
n-Propylbenzene	6.95175	1491.548	207.171
Chlorobenzene	6.83327	1338.7	207.0

Proceeding as in the case of toluene and using equation (7), K is found to be 0.000089174. Using this value of K and the other known values in equation (7) and the boiling point of chlorobenzene at 10 mm. is 22.48°. This is in excellent agreement with the determined value of 22.49°.

If equation (5) is used the constant is 1.05141 and the boiling point (using equation (5)) is calculated to be 21.58°. Thus it is seen that equation (7) is much better than equation (5). This is especially true at low pressures.

In the Dreisbach–Shrader[7] paper the boiling point at 760 mm. is the least accurate value, since values were determined at say 745 mm. and 785 mm. and these then plotted on the Cox Chart and the 760 mm. values read. This method is inaccurate. Hence in the determination of the C value the temperatures read at the three values below 760; *i.e.*, 507.5 mm., 315.52 mm. and 123.76 mm., were used. C was calculated by Thomson's[8] method. In order to obtain a good value of C these values must be very accurate.

A.P.I.[4] has shown the very exact relationship that can be obtained by the use of the Antoine equation, equation (4), when the value of C (or $T - 3\theta/8$) is known. Thomson[8] developed a simple method for calculating C. When the boiling points corresponding to three pressures are accurately known, namely

$$\left(\frac{y_3 - y_2}{y_2 - y_1}\right) \times \left(\frac{t_2 - t_1}{t_3 - t_2}\right) = 1 - \frac{t_3 - t_1}{t_3 + C} \qquad (8)$$

where $y_3, y_2, y_1 = \log P_3, \log P_2, \log P_1$.

In his paper Thomson[8] says it would be very desirable if a general correlation of the value of C with some common physical property of the compound could be obtained. As he was unable to find such a correlation, he set up empirical equations based on the number of carbon atoms, and on the value of C as a linear function of the boiling point. These were supposed to predict C to within 20°. However, if his third rule

$$C = 240 - 0.19t_B \qquad (9)$$

should be applied to octyl alcohol the result would be

$$C = 240 - 0.19(195.23) = 203.0 \qquad (10)$$

When this is compared to the value obtained from experimental data, namely, 131.6, it is obviously very much in error.

When Gutmann and Simmons'[3] paper was published this offered a new angle of approach. In addition the paper of Dreisbach and Shrader[7] gave accurate data on fifteen Cox Chart families not before available. When the C values for all the compounds listed in reference[7] were calculated, it was found that θ was a function of the absolute boiling point. The compounds seemed to fall into two classes, one of which the relation of θ/T_B was a constant for the Cox Chart family, and the other in which θ/T_B was a linear function of the normal boiling point. The families in which this ratio was a constant were those which did not have too wide a boiling range between the lower and higher members. In the case where the ratio was a linear function of the boiling point, there was considerable range in boiling point between lower and upper members of the family. The first table below lists the Cox Chart families in which this ratio was constant, together with these constants. The second table lists the Cox Chart families in which the ratio θ/T_B is a linear function of the normal boiling point (°C.) and the a and b parameters of the formula $\theta/T_B = a + bt_B$. The values of C as obtained in the two methods given above generally vary less than one, and in only rare instances as much as four from the C value calculated from determined values.

AVERAGE VALUES OF θ/T_B FOR EIGHT COX CHART FAMILIES

Family	θ/T_B
Benzene hydrocarbons (satd.)	0.3773
Benzene hydrocarbons (unsatd.)	.4307
Halobenzenes	.4334
Nitrobenzenes	.4335
Cyclohexanes	.3777
Phenyl ethyl alcohol	.6480
Aliphatic ethers	.4767
Aliphatic aromatic ethers (hydrocarbons)	.4627
Aliphatic aromatic ethers (chloro)	.4781

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(8) G. W. Thomson, *Chem. Revs.*, **48**, 13, 17 (1946).

THE PARAMETERS a AND b FOR THE FORMULA $\Theta/T_B = a + bt_B$ FOR TEN COX CHART FAMILIES

Family	a	b
Phenols	0.03733	0.00296
Anilines	−.1447	.00309
Aliphatic–aromatic ketones	.4630	.000432
Aliphatic hydrocarbons (satd.)	.3262	.000795
Aliphatic hydrocarbons (unsatd.)	.3437	.000736
Aliphatic ketones	.3180	.000144
Aliphatic esters	.3547	.000936
Aliphatic acids[a]	.0943	.000281
Aliphatic alcohols	.1164	−.00353
Cyclopentanes	.3100	.0000700

[a] Not including formic acid.

The Ramsay–Young rule (equation (7)) was used in the estimation of the accuracy of the determined data in reference.[7]

Conclusions.—The Ramsay–Young rule is shown to be as accurate as the data used, and can be used for chemically unrelated compounds as well as for chemically related compounds. Dühring's rule is excellent for chemically related compounds, but for chemically unrelated compounds the error varies from 0.6–1.0°. The Θ value of the theoretical Antoine equation is shown to be either a constant for Θ/T_B, or a linear function of the normal boiling point for Θ/T_B.

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Observations on the Rare Earths. LX.[1] The Ultraviolet Absorption Spectrum of the Gadolinium Ion in Aqueous Solutions

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The ultraviolet absorption spectrum of the gadolinium ion has been reinvestigated for both aqueous chloride and perchlorate solutions under conditions of high resolution. The spectrum is characterized by eighteen absorption peaks and two definite inflections in the wave length region 2400-3150 Å. The major and most complex absorption bands lie in the range 2720-2765 A., where greater resolution than previously reported has been obtained. Absorption is essentially the same for both chloride and perchlorate solutions. For both, absorptions at 2729, 2741-2 and 2756 Å. are in accord with Beer's law to concentrations above 0.25 M.

Introduction

The gadolinium ion is colorless, but it is characterized by a complex absorption spectrum in the ultraviolet region, presumably because of transitions involving the $4f$ orbitals. The spectra of aqueous chloride solutions were investigated comprehensively by Prandtl and Scheiner,[2] but the photographic technique employed and the method used for expressing the results render the data obtained of little value beyond accurate positioning of the absorption maxima. More recent spectrophotometric investigations, although recording the major absorption bands and characterizing their intensities relative to each other, fail to detect certain of the more minor bands and are not in complete agreement with each other. Thus, although Prandtl and Scheiner[2] recorded wave lengths for ten bands and suggested the existence of two others, Moeller and Brantley[3,4] could find only ten for chloride solutions, and these not all at the same wave lengths given by Prandtl and Scheiner. Stewart,[5] using perchlorate solutions, reported eight bands and gave evidences for a ninth but failed to find certain ones reported by other investigators.

Lack of complete agreement between data obtained by photographic and spectrophotometric techniques is apparently due to difficulties in the resolution of closely spaced absorption bands as imposed by the Beckman instruments used in the latter studies. The major absorption bands of the gadolinium ion all lie in the relatively narrow wave length interval 2720–2765 Å. and are extremely sharp. They are difficult, therefore, to pick up and to reproduce by anything but the most exacting manual adjustment of the measuring instrument. The ±10% deviations from Beer's law noted in the vicinity of 2730 Å. have been ascribed to this difficulty.[4] Inasmuch as the Cary Automatic Recording Quartz Spectrophotometer combines excellent resolution in the ultraviolet region with an enhanced spreading out of the wave length scale through suitable combinations of scanning and chart speeds, a reinvestigation of the gadolinium spectrum with this instrument was deemed advisable. Studies with both chloride and perchlorate solutions have effected resolutions beyond those previously reported and have shown adherences of the data to Beer's relation providing the wave lengths employed are accurately fixed.

Experimental

Materials Used.—Atomic weight gadolinium oxide (Inventory No. GD-5)[6] was converted to chloride and perchlorate by treatment with the appropriate acid and evaporation to remove excess acid. Acid-free solutions were standardized by the usual oxalate precipitation procedure and diluted to 0.5 M. Further dilutions were made as necessary.

Absorption Spectra Measurements.—All measurements were made with the Cary Spectrophotometer. The instrument was adjusted to zero optical density with blank cells containing distilled water, and these settings were used: scanning gear, small (1.0 Å. per sec.), "Lo" position; chart drive gear, 80 driving and 40 driven (4 in. per min.);

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(1) For the preceding communication in this series, see T. Moeller and D. E. Jackson, *Anal. Chem.*, **22**, 1393 (1950).

(2) W. Prandtl and K. Scheiner, *Z. anorg. allgem. Chem.*, **220**, 112 (1934).

(3) T. Moeller and J. C. Brantley, Technical Report, Office of Naval Research Contract N6ori-71, T. O. VII, University of Illinois, September 1, 1949.

(4) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

(5) D. C. Stewart, United States Atomic Energy Commission Declassified Document 2389, September 22, 1948.

(6) C. W. Naeser and B. S. Hopkins, THIS JOURNAL, **57**, 2183 (1935).