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Exactly Integrated Clapeyron Equation. Its Use To Calculate Quantities of Phase Change and To Design Vapor Pressure–Temperature Relations

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The vaporization enthalpies ΔH of water, methanol, ethanol, and benzene are calculated, from p,T data and auxiliary data, with the differential Clapeyron equation and with an equation derived from the exactly integrated Clapeyron equation, and the methods are compared as regards the sensitivity of ΔH to deviations in the p,T data. The integral method is found to be 1–2 orders less sensitive. It is demonstrated how the Clapeyron equation, hitherto believed to be unsolvable without preliminary substitution of simple expressions for ΔH and ΔV, can be transformed to an "exact differential equation" by multiplying by an integrating factor, and the rigorous and general integration is performed. The advantage of the integral method with respect to the "third-law method" in detecting deviating data points is discussed. From the integrated Clapeyron equation, several equations are derived and their possible use as pressure–temperature relations is discussed. It is shown how empirical equations like that of Cragoe and Frost/Kalkwarf can be derived from a thermodynamically based equation, and how new equations can be designed which are focused on special properties such as association.

Introduction

The present study is a corollary of the question of how to extrapolate enthalpies of vaporization, ΔH, as accurately as possible from accurate vapor pressure data. Our interest arises from our studies in combustion calorimetry of the condensed normal primary alkanols (*1–3*) and from the finding of Sunner, Wulff, and co-workers (*4–6*) that this group of compounds is interesting in a formulation for the CH_2 increment in the enthalpy of formation of α-substituted n-alkanes.

Usually, the Clapeyron equation is used with a differentiated empirical pressure–temperature relation (EPTR) like that of Rankine, Cragoe, Cox, etc. The subject of EPTRs received and receives much attention. Partington (*7*) listed over 50 EPTRs in 1951 (for reviews, see ref *7–11*). Because EPTRs are not thermodynamically founded, they may give physically unrealistic extrapolations without this being recognized (*8*, *11*, *12*).

A basically identical approach is integration of the Clapeyron equation after making assumptions about ΔH and ΔV that make the integration possible (see, e.g., ref *11*, *13*, and *14*). Subsequently, the integrated equation is empirically modified by many-term expressions on the basis only of vapor pressure data. As a consequence, extrapolation outside this region can again be risky.

Therefore, we have investigated whether there would be an advantage in the use of the exactly integrated Clapeyron equation.

Exact Integration

It has been suggested that the Clapeyron equation can only give approximate integral solutions (*15*), and Lewis and Randall (*9*) stated that integration would be cumbersome and only possible after writing out ΔH and ΔV as functions of pressure p and temperature T. However, Martynov (*16*) proved the integrability of the Clapeyron equation even for different pressures on the phases. Unfortunately, Martynov was only interested in the latter aspect, and, in order to carry out the integration, he made several approximations, including the traditional restriction to ideal vapors and the constancy of ΔC_p at coexistence. This makes his solution unsuitable for our purpose. In addition, his final equation (11) for the vapor–liquid equilibrium does not follow in the way that he states.

The Clapeyron equation in its traditional form $dp = (\Delta H/T\Delta V)\,dT$ is not an "exact differential equation" (for the terminology, see, e.g., ref *17*). When it is multiplied by the integrating factor $T^{-1}\Delta V$ (T, T^{-1}, ΔV, $T\Delta V$, and ΔH^{-1} are not integrating factors)

$$T^{-1}\Delta V(p,T)\,dp + \Delta H(p,T)\,dT^{-1} = 0 \qquad (1)$$

it is an exact differential equation because

$$[\partial\Delta H(p,T)/\partial p]_T = [\partial T^{-1}\Delta V(p,T)/\partial T^{-1}]_p$$

Bearing in mind that p and T are independent in $\Delta V(p,T)$ (analogously in $\Delta H(p,T)$), a fact that is implicitly used, e.g., always when one inserts an equation of state (p and T independent) for ΔV in the Clapeyron equation, we can state that these partial derivatives exist. This is both a physical and a mathematical requirement.

The solution of eq 1 is (*17*)

$$T^{-1}\int_{p_0}^{p}\Delta V(p,T)\,dp + \int_{T_0^{-1}}^{T^{-1}}\Delta H(p_0,T)\,dT^{-1} = 0 \qquad (2a)$$

$$T_0^{-1}\int_{p_0}^{p}\Delta V(p,T_0)\,dp + \int_{T_0^{-1}}^{T^{-1}}\Delta H(p,T)\,dT^{-1} = 0 \qquad (2b)$$

The right-hand side of eq 2a,b, that is, the integration constant, has been set equal to zero, since we want p and T to be able to assume the values p_0 and T_0 simultaneously.

To our knowledge, the integrated form of the Clapeyron equation has not been given before.

To obtain an expression with $\Delta H(p_0,T_0)$, we make the necessary substitution in the second integrand of eq 2a, which gives

$$T^{-1}\int_{p_0}^{p}\Delta V(p,T)\,dp + \int_{T_0^{-1}}^{T^{-1}} dT^{-1}\int_{T_0}^{T}\Delta C_p(p_0,T)\,dT = \Delta H(p_0,T_0)(T_0^{-1} - T^{-1}) \qquad (3)$$

An equation with a comparable objective has been given earlier (*15*), but it is wrong, since it has a form for ΔC_p which would, in our notation, be $\Delta C_p(p_0,T_0)$ instead of $\Delta C_p(p_0,T)$.

Equation 3 permits the calculation of ΔH at any coexistence situation (p_0,T_0) from the p,T data if the equations of state and ΔC_p at one pressure (not necessarily p_0 since conversion is possible by means of the equations of state) are known (see Applications).

An expression for $\Delta V(p_0,T_0)$ analogous to eq 3 is yielded by eq 2b. The analogue here of the heat capacity term in eq 3

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is an isothermal compressibility term.

One will be interested often in $\Delta H(T_0)$ at some pressure other than the coexistence pressure, e.g., at a chosen standard pressure p_1. From eq 3 is derived (derivation in Appendix I)

$$T^{-1}\int_{p_1}^{p}\Delta V(p,T)\,\mathrm{d}p - T_0^{-1}\int_{p_1}^{p_0}\Delta V(p,T_0)\,\mathrm{d}p + \int_{T_0^{-1}}^{T^{-1}}\mathrm{d}T^{-1}\int_{T_0}^{T}\Delta C_p(p_1,T)\,\mathrm{d}T = \Delta H(p_1,T_0)(T_0^{-1} - T^{-1}) \quad (4)$$

Also, this relation is the starting point for designing pressure–temperature relations (see Designing p,T Relations).

Applications

To show how eq 3 and 4 can be used in practice, let one of the phases be a gas and let the equations of state be

$$V(\mathrm{g},p,T) = RT/p + c_0(\mathrm{g},T) + c_1(\mathrm{g},T)p + \ldots + c_n(\mathrm{g},T)p^n \quad (5)$$

and an analogous expression, but without the term RT/p, for the volume of the condensed phase, $V(\mathrm{co},p,T)$. The difference in molar volumes is then

$$\Delta V(p,T) = RT/p + \sum_{l\geq 0} c_l(T)p^l \qquad (\textstyle\sum \text{ short for } \sum\Delta) \quad (6)$$

When eq 6 is substituted into eq 3, one obtains

$$R\ln p + \int_{T_0^{-1}}^{T^{-1}}\mathrm{d}T^{-1}\int_{T_0}^{T}\Delta C_p(p_0,T)\,\mathrm{d}T + T^{-1}\sum_{l\geq 0}(l+1)^{-1}c_l(T)(p^{l+1} - p_0^{\,l+1}) = \Delta H(p_0,T_0)(T_0^{-1} - T^{-1}) + R\ln p_0 \quad (7)$$

Condensed systems are described by eq 7 when the ln terms are dropped.

When the values of the left side of eq 7 are plotted against $T_0^{-1} - T^{-1}$, $\Delta H(p_0,T_0)$ is obtained as the slope. Iteration for p_0 is required. For ΔH at a chosen p_0, instead of T_0, the procedure should be comparable.

When ΔC_p and c_l are known in the region to be extrapolated into, eq 7 cannot give physically unrealistic results. The quality of the extrapolation is merely governed by the accuracy of the measurements (in contrast to EPTRs). As an illustration of an application of eq 7, the p,T data for ethanol of Drücker (*18*) will be examined. These data are the only well-documented low-temperature p,T data for ethanol in existence. An extrapolation of a Cragoe fit on the p,T data of Ambrose and Sprake (*19*) suggests that Drücker's pressure values are up to 1 order too high. This is merely a suggestion, not a proof, since there is no reason that a long extrapolation of an EPTR should yield a correct value. However, application of eq 7 to the p,T data of Ambrose and Sprake (*19*) shows unequivocally that Drücker's values are far off in the low-temperature part (Table I). In the third column of pressures, the experimental values of Klumb and Lückert (*20*) are given. Although these are of low accuracy, they confirm the picture.

The following auxiliary data were used. The virial coefficients and the heat capacity of the vapor were taken from the work of Counsell et al. (*21*) (the denominators in the coefficients *a* and *c* should be RT^2 instead of RT (*22*)). The degree of saturation in the C_p measurements did not exceed two-thirds and was in general less than that. We have assumed that the pertinent C_p,p,T relation (*21*) could be extrapolated to saturation, because the values for C_p at 80% saturation at 101.325 kPa (*23*) and at 90% saturation at 99.992 kPa (*24*) agree well with the value calculated from the C_p,p,T relation. This relation shows good agreement with the values about 280 K (*25*, *26*) and even with that at 200 K (*25*); we have therefore found it justified to make our calculations down to 200 K. The 1975 p,T data of Ambrose (*27*) could not be used, since heat capacity data at high degrees of saturation are lacking at high temperatures. The liquid volume as a linear function of temperature (taken as independent of pressure for the range of interest) was calculated from data in Timmerman's book (*18*). Fiock's equation for the relation between the temperature and the heat capacity of the liquid at saturation pressure (*28*) was used in the form given by Green (*29*) in his eq 2. The liquid heat capacity was considered to be independent of pressure, in accordance with the linear temperature dependence of the volume. All temperatures were recalculated to IPTS-68. The gas constant R was taken as 8.31441 J K^{-1} mol^{-1}, except where it was necessary to use a value appropriate to a calculation in the literature.

Table I. Comparison of Observed and Calculated Vapor Pressures of Ethanol and Enthalpies of Vaporization at Saturation[a]

T	P(obsd)[b]	P(calcd)[c]	P(obsd)[d]	ΔH[c]
173.85	0.168	(0.015)	(0.020)	(47.964)
177.45	0.232	(0.029)	(0.037)	(47.791)
181.35	0.319	(0.057)	(0.070)	(47.603)
188.45	0.584	(0.188)	(0.21)	(47.269)
191.65	0.795	(0.311)	0.34	(47.121)
202.25	2.320	1.452	1.4	46.651
211.95	5.866	5.138	4.7	46.234
220.55	13.719	14.244	13	45.872
232.15	39.463	49.413	(42)	45.392
233.85	51.729	58.626	(49)	45.321

[a] Temperatures are given in Kelvin, pressures in pascals, and enthalpies of vaporization in kJ mol^{-1}. [b] Reference *18*. [c] Calculated from eq 7 with auxiliary data in text; values in parentheses are based on extrapolated auxiliary values. [d] Reference *20*; values in parentheses are extrapolated.

The Cragoe fit on the p,T data of ref *19* follows the calculated vapor pressure of Table I very well (<5%) in this case.

Equation 7 can also be used to detect "sour" p,T data points. In other studies, the so-called "third-law method", advocated by Lewis and Randall (*9*), is used (see, e.g., ref *12* for an application). Unfortunately, that method can be applied only if the difference in $G°$ between the phases is known down to 0 K. In practice, this will generally mean that ΔC_p and c_l must be known down to 0 K. Contrarily, the use of eq 7 requires knowledge of ΔC_p and c_l merely down to the lowest temperature of the vapor pressure measurements.

When the 25 vapor pressures measured by Ambrose and Sprake (*19*) are calculated with eq 7, i.e., the results of the iteration, the series of residuals turns out to be nonrandom (Table II). The highest pressure value appears to be particularly high (by about 0.1 kPa). When this measurement is left out, the remaining 24 residuals are found to constitute a random set, and the standard deviation of the series is reduced by a factor 2.

An analysis of p,T data is much less likely to be successful when an EPTR is used. This is so because, in general, the type and number of terms are chosen to obtain the best fit with the data points. When the Cragoe equation is applied in the case mentioned above, the set of 25 residuals is random (*19*) and the sour point is not detected. Omission of this point leaves the standard deviation unchanged.

Our main point of interest is the accuracy in the p,T data, required to obtain a preset accuracy in ΔH. As will be shown below, the accuracy in the p,T data must be 1 order or more better in the differential method than in the integral method using eq *7*. A simple test was made by calculating the deviation in ΔH of water, methanol, ethanol, and benzene resulting from an intentional error in T. The procedure is described here in detail for ethanol. (For the other three compounds, the procedure and the criteria, as has been described, for accepting the data were comparable.)

First, all $\Delta H(p_0,T_0)$'s pertaining to the list of the 25 p,T data (*19*) were calculated with eq 7, as described under it, and then

Table II. Comparison of Observed and Calculated Vapor Pressures of Ethanol and Enthalpies of Vaporization at Saturation[a]

T	p(obsd)[b]	p(calcd)[c]	p(obsd) − p(calcd)	ΔH[c]
292.766	5.726	5.726	−0.000	42.683
296.776	7.269	7.268	0.001	42.470
298.864	8.205	8.205	0.000	42.356
301.299	9.430	9.428	0.002	42.221
306.475	12.566	12.564	0.002	41.926
309.747	14.981	14.979	0.002	41.732
312.377	17.200	17.200	0.001	41.573
316.368	21.109	21.108	0.001	41.325
320.489	25.914	25.917	−0.003	41.059
324.221	31.047	31.049	−0.002	40.810
327.804	36.760	36.765	−0.005	40.563
332.013	44.584	44.595	−0.011	40.264
336.006	53.267	53.279	−0.012	39.969
339.719	62.572	62.589	−0.017	39.686
343.701	74.032	74.050	−0.018	39.372
348.122	88.763	88.773	−0.010	39.011
350.548	97.821	97.834	−0.013	38.808
351.132	100.121	100.127	−0.006	38.758
351.483	101.518	101.525	−0.007	38.728
351.640	102.151	102.156	−0.005	38.714
352.331	104.983	104.972	0.011	38.655
355.506	118.719	118.742	−0.023	38.378
358.981	135.519	135.487	0.032	38.067
362.752	155.824	155.793	0.031	37.720
366.629	179.321	179.196	0.125	37.351

[a] Temperatures are given in Kelvin, pressures in kilopascals, and enthalpies of vaporization in kJ mol^{-1}. [b] Reference *19*. [c] Calculated from eq 7 with auxiliary data given in text.

by means of the differential method with the calculated Cragoe and Frost/Kalkwarf coefficients and with Chebyshev polynomials of the orders 3, 4, and 5 (*8*). Subsequently, the figure for the lowest temperature in the list, 292.766 K, was changed by −0.05 K, and all calculations were repeated. Next, the same was done for a +0.05 K change in the highest temperature, 366.629 K. Giving this example does not imply that deviations of this magnitude were plausible in the accurate work of Ambrose and Sprake, but such deviations can easily occur in work of lower accuracy. Besides, it is merely to illustrate what is meant.

The following literature data were used for water, methanol, and benzene: water, C_p(l) (*32*), C_p(g) (ref *33* and Appendix III), c_l(g) (*34*), V(l) (*33*), p,T (*12*); methanol, C_p(l) (*28*, *35*), C_p(g) (*36*), c_l(g) (*36*), V(l), (*18*), p,T (*19*); benzene, C_p(l) (*18*), C_p(g) (*37*), c_l(g) (*37*), V(l) (*18*), p,T (*12*). The virial coefficient B_v in ref *37* was accounted for by writing $V(g) = RTp^{-1} + B_v - B_v^2R^{-1}T^{-1}p$.

Some of our results for the four compounds are given in Table III. Only ΔH at the lowest and highest temperatures are given. In the middle of the interval, all effects are smaller. A slight correction in ΔH (a few joules at the most) is incorporated into the calculated values, to obtain the ΔH value pertaining to the original, measured temperatures where these have been changed by 0.05 K. The change of ΔH with temperature, ±50–100 J K^{-1}, apparent from the literature data, was used as a basis for this correction.

The five EPTRs are strikingly more strongly affected by the change of one temperature value than the integral equation. The effect is most pronounced with the fifth-order Chebyshev polynomial.

Unexpected is the magnitude of the change in ΔH at the high-temperature end when the intentional change of 0.05 K is made at the low-temperature side and vice versa. This effect is only present in EPTRs, and is again most pronounced with the fifth-order Chebyshev polynomial (see, e.g., methanol and ethanol, lowest T − 0.05 K, high T end). This suggests consequences for the application of EPTRs in general. A set of vapor pressure measurements often includes measurements at medium pressures (accurate) together with measurements at either high or low pressures (less accurate). The accuracy of calculated enthalpies of vaporization at the medium-pressure end is thus, unexpectedly, impaired by the less accurate measurements at the other end.

The vaporization enthalpies as calculated here from p,T data, whether by means of the differential or integral method, agree well with the calorimetric values. This is to be expected, since only data of high quality were used (it was not necessary to use all pertaining high-quality data in the literature to make our point in Table III). The discrepancy for water at 400 K may be due to the long extrapolation of the virial coefficients. The "integral value" agrees with the calorimetric value.

The insensitivity of ΔH calculated by the integral method to deviations in the p,T data makes the method suitable where the differential method would fail, i.e., when only few p,T data (minimum: 2) of low accuracy are available. On the other hand, ΔH calculated by the integral method is subject to deviations in ΔC_p (see Table III). The choice to use either the differential or integral method must depend on availability and quality of the data, either measured, calculated, or estimated.

We emphasize that the fact that eq 7 has been derived as exactly as possible does not restrict its use to those cases where ΔC_p and c_l are exactly known. Equation 7 can also be useful when, e.g., only estimates are available.

Calculation of ΔH in Arbitrary States

ΔH in arbitrary states is obtained by substitution of eq 6 into eq 4

$$R \ln p + \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} \Delta C_p(p_1,T)\,\mathrm{d}T + T^{-1} \sum_{l\geq 0} (l+1)^{-1} c_l(T)(p^{l+1} - p_1^{l+1}) = \Delta H(p_1,T_0)(T_0^{-1} - T^{-1}) + R \ln p_0 + T_0^{-1} \sum_{l\geq 0} (l+1)^{-1} c_l(T_0)(p_0^{l+1} - p_1^{l+1}) \quad (8)$$

The quantities $c_l(T)$ and $c_l(T_0)$ are the values of c_l at T and T_0. Equation 8 is used as a linear relation, as is eq 7.

The importance of eq 8 lies in the possibility to calculate ΔH directly in arbitrary states without an intervening calculation at coexistence via eq 7.

$\Delta H(p_1=0,T_0)$ by eq 8 differs slightly from $\Delta H°$ for the phases in their standard states, since the standard-state pressure for a condensed phase is 1 atm by convention. Numerically, the difference is negligible. Therefore, $\Delta H(p_1=0,T_0)$ can often be taken to represent $\Delta H°(T_0)$. If necessary, the difference can be calculated from the equation of state of the condensed phase. When the conversion to 1 atm for a condensed phase is actually applied to eq 8, the result produces the special case (*9*) where the ΔH looked for is $\Delta H°(\mathrm{g}^{\mathrm{id}}, p(\mathrm{co}) = 1\,\mathrm{atm})$.

Designing p,T Relations

When ΔC_p and c_l are known, eq 7–9 are complete vapor pressure equations once the two parameters ΔH at chosen T_0 (or p_0) and p_0 (or T_0) have been adjusted to the p,T data. However, the required values for ΔC_p and c_l will often not be available. This does not mean that an EPTR is then the only way out. Estimates can be made of ΔC_p or c_l and used with eq 7–9. These equations have the forceful advantage that they show exactly how these quantities must be inserted, whereas an arbitrary EPTR has no clear relationship between its terms and their coefficients on the one side and ΔC_p and c_l on the other side. The latter fact also makes it impossible to translate

Table III. Consequences for $\Delta H(p_0,T_0)$ of Intentional Changes[a] in Measured Temperatures (without Changing the Corresponding Pressures) and Heat Capacities $\Delta C_p(p_0,T)$ and Comparison of the Consequences for the Integral and Differential Methods[b]

	$\Delta H(p_0,T_0)$/(J mol^{-1}) for correct T values	change in $\Delta H(p_0,T_0)$/(J mol^{-1}) upon changing lowest T by −0.05 K	change in $\Delta H(p_0,T_0)$/(J mol^{-1}) upon changing highest T by +0.05 K	change in $\Delta H(p_0,T_0)$/(J mol^{-1}) upon changing $\Delta C_p(p_0,T)$ by +1 J K^{-1} mol^{-1}		$\Delta H(p_0,T_0)$/(J mol^{-1}) for correct T values	change in $\Delta H(p_0,T_0)$/(J mol^{-1}) upon changing lowest T by −0.05 K	change in $\Delta H(p_0,T_0)$/(J mol^{-1}) upon changing highest T by +0.05 K	change in $\Delta H(p_0,T_0)$/(J mol^{-1}) upon changing $\Delta C_p(p_0,T)$ by +1 J K^{-1} mol^{-1}
		Water, T_0 = 300.000 K					Ethanol, T_0 = 292.766 K		
Integ	43 886	−13	−5	−47	Integ	42 683	−9	−4	−35
Crag	43 900	−160	−20		Crag	42 695	−181	−26	
Fr/K	43 893	−149	−16		Fr/K	42 697	−170	−24	
Cheb 3	43 956	−177	−40		Cheb 3	42 703	−189	−43	
Cheb 4	43 903	−241	+43		Cheb 4	42 715	−298	+53	
Cheb 5	43 901	−338	−39		Cheb 5	42 728	−458	−69	
Cal	43 915[c]				Cal	42 558[f]			
		Water, T_0 = 400.000 K					Ethanol, T_0 = 366.629 K		
Integ	39 424	−15	−6	+54	Integ	37 351	−8	−4	+38
Crag	39 171	−79	−83		Crag	37 444	−73	−59	
Fr/K	39 182	−84	−96		Fr/K	37 431	−72	−68	
Cheb 3	39 134	−50	−83		Cheb 3	37 439	−50	−58	
Cheb 4	39 166	+58	−176		Cheb 4	37 422	+78	−158	
Cheb 5	39 164	−56	−270		Cheb 5	37 438	−116	−295	
Cal	39 402[d]				Cal	37 397[f]			
		Methanol, T_0 = 288.044 K					Benzene, T_0 = 308.322 K		
Integ	37 880	−11	−5	−31	Integ	33 285	−10	−5	−37
Crag	37 948	−177	−25		Crag	33 251	−132	−21	
Fr/K	37 943	−168	−22		Fr/K	33 248	−131	−20	
Cheb 3	37 962	−186	−40		Cheb 3	33 285	−145	−33	
Cheb 4	37 973	−183	+57		Cheb 4	33 262	−218	+42	
Cheb 5	37 988	−418	−71		Cheb 5	33 263	−321	−43	
Cal	37 795[e]				Cal	33 269[g]			
		Methanol, T_0 = 356.822 K					Benzene, T_0 = 388.847 K		
Integ	33 927	−9	−4	+35	Integ	28 601	−10	−3	+43
Crag	33 934	−73	−60		Crag	28 593	−60	−63	
Fr/K	33 934	−76	−69		Fr/K	28 584	−62	−64	
Cheb 3	33 923	−53	−60		Cheb 3	28 571	−45	−64	
Cheb 4	33 901	+77	−151		Cheb 4	28 580	+60	−150	
Cheb 5	33 920	−91	−321		Cheb 5	28 581	−66	−246	
Cal	33 959[e]				Cal	28 534[g]			

[a] A correction of a few joules is incorporated in the second and third columns because of this change; see text. [b] Abbreviations for the equations: Integ, integral equation 7; Crag, Cragoe; Fr/K, Frost/Kalkwarf; Cheb 3, 4, 5, Chebyshev polynomials of order three, four, and five, respectively. Cal means calorimetrically determined value. [c] From ref *32* by quadratic interpolation. [d] From ref *32* by quadratic extrapolation. [e] From ref *22, 28, 30, 31,* and *36* by quadratic fitting; the value at 288.044 K is extrapolated. [f] From ref *21, 28, 30,* and *31* by quadratic fitting; the value at 292.766 K is extrapolated. [g] From ref *37*.

data or estimates into constraints for the coefficients of the EPTR.

The starting point for designing a p,T relation is eq 8 with $p_1 = 0$:

$$R \ln p + \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} \Delta C_p(p_1{=}0,T)\,\mathrm{d}T + T^{-1} \sum_{l\geq 0} (l+1)^{-1} c_l(T) p^{l+1} = \Delta H(p_1{=}0,T_0)(T_0^{-1} - T^{-1}) + R \ln p_0 + T_0^{-1} \sum_{l\geq 0)} (l+1)^{-1} c_l(T_0) p_0^{\,l+1} \quad (9)$$

Putting $p_1 = 0$ not only simplifies eq 8 but also shows a ΔC_p independent of pressure. Leaving the heat capacity of the liquid out of consideration for the moment, the heat capacity of the gas is now clearly separated from the terms c_l(g). The terms accounting for the intermolecular interaction in the vapor are now not distributed among ΔC_p and c_l (and ΔH) but are concentrated in c_l only, thus making a simple formulation adequate to describe C_p(g) as a function of temperature.

The reader will be able to verify the following example. If we put, for instance, $\Delta C_p(p_1{=}0,T) = \Delta a + \Delta bT + \Delta cT^2$, $V(\mathrm{g},p,T) = RTp^{-1} + B_p$, where B_p is a virial coefficient of the type developed by Hirschfelder, McClure, and Weeks (*38*) for dimerization or a square-well potential energy function $B_p = b_p + KT \exp(JT^{-1})$, and if V(co) is taken in this example as equal to b_p, substitution in eq 9 with the aid of eq 5 and 6 gives a tailored vapor pressure equation of the form

$$\ln p = A + BT^{-1} + C \ln T + DT + ET^2 + Fp \exp(JT^{-1}) \quad (10)$$

The meaning of the coefficients is given in Appendix II. Equation 10 bears a close resemblance to eq 15 of Scott and Osborn (*12*), which they derived ingeniously in a semiempirical way. They demonstrated that their equation accurately reproduced the measured vapor pressures for normal and abnormal fluids (water) alike.

The clarity of the physical significance of the terms, and their coefficients, of the equations derived from eq 9 enables one to effectively impose constraints. Without constraints, if need be estimates, equations like eq 10 will not give necessarily good results in extrapolations. This is because the fitting is then entirely directed to the quality of the fit in the interval of the measured p,T data (useful for interpolation), but the last terms in eq 10 and analogous relations then can acquire unrealistically large values, whereas they were merely meant as corrections. Ambrose (*8*) gives an example of a Cragoe equation (eq 10 with terms 3 and 6 left out) with four terms of comparable magnitude. This situation has given rise to some popularity of Chebyshev polynomials, a mathematical device which can give large deviations in derived quantities, as we have shown.

Table IV. Approximations in ΔC_p, Virial Coefficients, and Condensed Volume Implied[a] in Some Frequently Used Vapor Pressure Relations

	equation[e] $\ln p = A + BT^{-1} +$	ΔC_p- $(p_1 = 0)$	type nonideality of gas	V(co)[f]
Clapeyron/ Clausius[c]	$+ 0$	0	none	0
Rankine/ Kirchhoff[c]	$+ C \ln T$	Δa	none	0
van Laar[c,d]	$+ C \ln T + DT$	$\Delta a + \Delta bT$	none	0
Cragoe[c]	$+ CT + DT^2$	$\Delta bT + \Delta cT^2$	none	0
Frost/Kalkwarf	$+ C \ln T + DPT^{-2}$	Δa	$c_0 = -a'R^{-1}T^{-1} + b'$[b]	b'[b]

[a] Approximations found, in this study, to be actually implied in the equations. These are not always the approximations meant, by the designers of the equations, to be implied. See text. [b] a' and b' are the van der Waals constants. According to Partington (7), using a second virial coefficient of this form is approximately equivalent to using the van der Waals equation. [c] Vapor pressure relations in which the c_i terms are neglected can be produced as well from eq 7 and 8 as from eq 9. However, in cases where the c_i terms are not neglected, eq 7 and 8 would yield vapor pressure relations with mixed additional terms, in T and p_0 and in T and p_1, respectively, which eq 9 does not. For homogeneity of formulation, we have derived all five relations from eq 9. [d] The Nernst equation has the same form, but its coefficient C has a fixed value. The van Laar equation should yield better extrapolations than the Cragoe equation, since its assumption about ΔC_p as a function of T is more realistic. [e] Coefficients in Appendix II. [f] Condensed volume.

Finally, we show in Table IV how eq 9 yields some well-known vapor pressure relations. We emphasize that the approximations in Table IV are those to which a particular equation is actually found to correspond in the present study. These are not always the same as those which some authors had in mind. For instance, van Laar (*39*) used the van der Waals equation, but, presumably through some cancellation, his resulting equation does not account for nonideality of the gas. Some of the assumptions made by Frost and Kalkwarf (*40*) together merely amount to the effect of taking $\Delta C_p(p_1{=}0)$ as a constant.

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Appendix I

Equation 4 is developed from eq 3 as follows.

$$\Delta H(p_0,T_0) = \Delta H(p_1,T_0) + \int_{p_1}^{p_0} \left(\frac{\partial T^{-1}\Delta V(p,T)}{\partial T^{-1}}\right)_p\Bigg|_{T=T_0} \mathrm{d}p \tag{11}$$

Analogously, we have for ΔC_p

$$\int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} \Delta C_p(p_0,T)\, \mathrm{d}T = \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} \Delta C_p(p_1,T)\, \mathrm{d}T + A \tag{12}$$

where

$$A = \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} \mathrm{d}T \int_{p_1}^{p_0} \left[\frac{\partial}{\partial T}\left(\frac{\partial T^{-1}\Delta V(p,T)}{\partial T^{-1}}\right)_p\right]_p \mathrm{d}p \tag{13}$$

The form of the last integral has been obtained by using the equality

$$[\partial(\partial \Delta H/\partial T)_p/\partial p]_T = [\partial(\partial \Delta H/\partial p)_T/\partial T]_p$$

and then substituting $(\partial T^{-1}\Delta V/\partial T^{-1})_p$ for $(\partial\, \Delta H/\partial p)_T$. The term A is worked out as follows. The integrations are interchanged

$$A = \int_{p_1}^{p_0} \mathrm{d}p \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} \left[\frac{\partial}{\partial T}\left(\frac{\partial T^{-1}\Delta V(p,T)}{\partial T^{-1}}\right)_p\right]_p \mathrm{d}T$$

so

$$A = \int_{p}^{p_0} \mathrm{dp} \int_{T^{-1}}^{T^{-1}} \left[\left(\frac{\partial T^{-1}\, \Delta V(p,T)}{\partial T^{-1}}\right)_p - \left(\frac{\partial T^{-1}\, \Delta\Delta(p,T)}{\partial T^{-1}}\right)_p\Bigg|_{T=T_0}\right] \mathrm{d}T^{-1}$$

$$A = \int_{p_1}^{p_0} \left\{T^{-1}\Delta V(p,T) - T_0^{-1}\Delta V(p,T_0) - \left[\left(\frac{\partial T^{-1}\Delta V(p,T)}{\partial T^{-1}}\right)_p\Bigg|_{T=T_0}(T^{-1} - T_0^{-1})\right]\right\} \mathrm{d}p \tag{14}$$

Upon substitution of eq 11, 12, and 14 into eq 3, we obtain eq 4.

Appendix II

The coefficients of the equation

$$\ln p = A + BT^{-1} + C \ln T + DT + ET^2 + Fp \exp(JT^{-1})$$

are

$$A \equiv R^{-1}\{-\Delta a - \Delta a \ln T_0 - \Delta bT_0 - \tfrac{1}{2}\Delta cT_0^2 + \Delta H(p_1{=}0,T_0)T_0^{-1} + R \ln p_0 + Kp_0 \exp(JT_0^{-1})\}$$

$$B \equiv R^{-1}\{\Delta aT_0 + \tfrac{1}{2}\Delta bT_0^2 + \tfrac{1}{3}\Delta cT_0^3 - \Delta H(p_1{=}0,T_0)\}$$

$$C \equiv R^{-1}\Delta a$$

$$D \equiv \tfrac{1}{2}R^{-1}\Delta b$$

$$E \equiv \tfrac{1}{6}R^{-1}\Delta c$$

$$F \equiv -R^{-1}K$$

The coefficients of the vapor pressure relations in Table IV are as follows (see also footnote c of Table IV):

van Laar

$$A \equiv R^{-1}\{-\Delta a - \Delta a \ln T_0 - \Delta bT_0 + \Delta H(p_1{=}0,T_0)T_0^{-1} + R \ln p_0\}$$

$$B \equiv R^{-1}\{\Delta aT_0 + \tfrac{1}{2}\Delta bT_0^2 - \Delta H(p_1{=}0,T_0)\}$$

$$C \equiv R^{-1}\Delta a$$

$$D \equiv \tfrac{1}{2}R^{-1}\Delta b$$

Rankine: see van Laar, with $\Delta b = 0$; in the Clapeyron–Clausius equation, $\Delta a = \Delta b = 0$.

Cragoe

$$A \equiv R^{-1}\{-\Delta bT_0 - \tfrac{1}{2}\Delta cT_0^2 + \Delta H(p_1{=}0,T_0)T_0^{-1} + R \ln p_0\}$$

$$B \equiv R^{-1}\{\tfrac{1}{2}\Delta bT_0^2 + \tfrac{1}{3}\Delta cT_0^3 - \Delta H(p_1{=}0,T_0)\}$$

$$C \equiv \tfrac{1}{2}R^{-1}\Delta b$$

$$D \equiv \tfrac{1}{6}R^{-1}\Delta c$$

Frost/Kalkwarf

$$A \equiv R^{-1}\{-\Delta a - \Delta a \ln T_0 + \Delta H(p_1{=}0,T_0)T_0^{-1} + R \ln p_0 - R^{-1}a'p_0T_0^{-2}\}$$

$$B \equiv R^{-1}\{\Delta a T_0 - \Delta H(p_1{=}0,T_0)\}$$

$$C \equiv R^{-1}\Delta a$$

$$D \equiv R^{-2}a'$$

Appendix III

Apparently, $C_p(\mathrm{g},p,T)$ for water has not been measured. However, the virial coefficients and the ideal heat capacity $C_p(\mathrm{g},p_1{=}0,T)$ are known. To account for $C_p(\mathrm{g},p_0,T)$ in eq 7 without double differentiation followed by double integration of the very complex virial coefficients, we retained the ideal gas part in the double integral and shifted the rest to the $c_i(\mathrm{g})$ terms (in the following, we omit g for gas).

$$\int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} C_p(p_0,T)\,\mathrm{d}T = \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} C_p(p_1{=}0,T)\,\mathrm{d}T - \sum_{i\geqslant 0} (i+1)^{-1}p_0^{i+1} \int_{T_0^{-1}}^{T^{-1}} \mathrm{d}T^{-1} \int_{T_0}^{T} T[\mathrm{d}^2c_i(T)/\mathrm{d}T^2]\,\mathrm{d}T \qquad (15)$$

Applying partial integration with T as the primitive and $\mathrm{d}^2c_i(T)/\mathrm{d}T^2$ as the derivative in the last integrand and adding the result of the integration of the last term of eq 15 to the gas part of the $\sum c_i$ term in eq 7 yields the combined term

$$+T^{-1} \sum_{i\geq 0} (i+1)^{-1}\{c_i(T)p^{i+1} - c_i(T_0)p_0^{i+1} + (T_0 - T) \times [\mathrm{d}c_i(T)/\mathrm{d}T]_{T_0}p_0^{i+1}\}$$

At the same time, this yields yet another type of vapor pressure equation.

Into this term, a substitution is made to account for the fact that Wexler's virial coefficients are $c_i(T)R^{-1}T^{-1}$. (There is a printing error in Wexler's expression for C'. It should read log $(-C')$ instead of $-\log C'$.)

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Aqueous Dissociation of Phenylpropiolic Acid

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The acid dissociation constant of aqueous phenylpropiolic acid (3-phenyl-2-propynoic acid) has been determined between 15 and 45 °C by pH potentiometry. The standard enthalpy and entropy of dissociation are calculated from the temperature variation of the dissociation constant. The ^{13}C NMR resonance displacement of the carboxylate carbon upon acid dissociation was measured, and its correlation with the standard entropy of dissociation implies that the molecular form of aqueous phenylpropiolic acid exists partly as an ion pair in equilibrium with the covalently bonded structure.

The literature seems not to contain reliable values of acid dissociation parameters for aqueous phenylpropiolic acid (3-phenyl-2-propynoic acid). The "Handbook of Biochemistry and Molecular Biology" lists two entries, a value of $\mathrm{p}K_a = 2.269$ at 16.8 °C together with $\Delta H° = -0.792$ kcal mol^{-1} and $\Delta S° = -13$ cal mol^{-1} K^{-1} (*1*) and a value of $\mathrm{p}K_a = 2.23$ at 25 °C (*2*). The entry at 16.8 °C makes reference to a paper by Walde (*3*), but this paper makes further reference to a paper by Harned and Sutherland (*4*) as the primary source. Harned and Sutherland, however, do not mention phenylpropiolic acid so that details of the 16.8 °C experiment are unknown. The 25 °C entry in the handbook is attributed to Mansfield and Whiting (*5*), who, indeed, report a pH potentiometric measurement of $\mathrm{p}K_a$

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