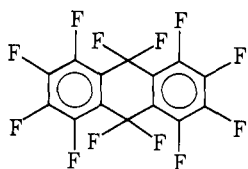
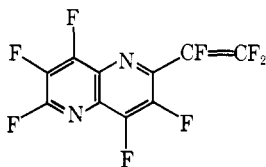
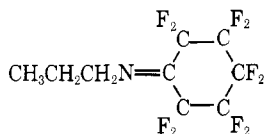
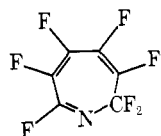


Examples:

*F*-9,10-Dihydroanthracene2-(*F*-Vinyl)-*F*-1,5-diazanaphthalene*N*-(*F*-Cyclohexylidene)-propylamine

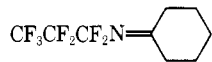
4.4 Similarly, the symbol “*H*”, representing “indicated” hydrogen, is an integral part of the name of the parent compound or radical.

Examples:

*F*-2*H*-Azepine

4.5 On the other hand, substitutive prefixes (chloro, hydryl, amino, nitro, etc.) are separable and are placed *before* the symbol “*F*” (see also Rules 4.1 and 4.2).

Examples:

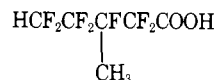
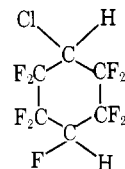
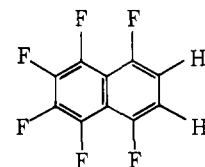
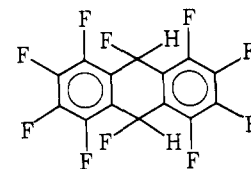
Nitro-*F*-benzene*N*-Cyclohexylidene-*F*-propylamine

5. Naming Hydrogen Attached to Carbon

When the symbol “*F*” is used, any hydrogen atoms attached to carbon atoms in the parent compound or radi-

cal are regarded as substitutive and must be specifically designated. Designation is accomplished by use of the substitutive prefix “hydryl.”

Examples:

1,1,5-Trihydryl-*F*-1-pentanol5-Hydryl-3-methyl-*F*-pentanoic acid1-Chloro-1,4-dihydryl-*F*-cyclohexane2,3-Dihydryl-*F*-naphthalene9,10-Dihydryl-*F*-9,10-dihydroanthracene

ACKNOWLEDGMENT

The author is indebted to the following members of the nomenclature committee of the Division of Fluorine Chemistry for their cooperation and contributions: Dr. Henry C. Brown, Dr. Alan F. Clifford, Dr. George H. Crawford, Dr. Murray Hauptschein, Dr. Douglas A. Rausch, and Dr. F. W. Swamer. The nomenclature committee of the American Chemical Society, under the chairmanship of Dr. Kurt L. Loening, has been most helpful in critically reviewing all the successive versions in the evolution of these revisions.

LITERATURE CITED

- (1) *Chem. Eng. News*, **30**, 4514 (1952).

Vapor Pressure Data in Recent Handbook Unreliable

DANIEL R. STULL

Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

Received February 25, 1974

The Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (1)$$

treats the general case of the thermodynamically reversible transformation of matter from one phase to another at an equilibrium pressure, *P*, and an absolute temperature *T*. ΔH is the net enthalpy change, and ΔV is the net volume change associated with the transformation. By adopting

three assumptions—(i) that the volume of the condensed phase may be neglected in comparison with that of the vapor, (ii) that the vapor phase behaves like a perfect gas, and (iii) that the enthalpy change is constant for the range of temperature under consideration—eq 1 can be converted to the form

$$\log P = \frac{-\Delta H}{2.303RT} + B = \frac{-0.2185\Delta H}{T} + B \quad (2)$$

Table I. Vapor Pressure, Sublimation and Vaporization Enthalpy, and Net Volume Changes for Ice and Water

(1) ^a Vapor pressure, Torr	(2) ^a Tabulated temp, °C	(3) ^b Calculated temp, °C	(4) Col 3 less col 2, °C	(5) ^c Net vol change, l./g mol	(6) ^d Net enthalpy change, kcal/(g mol)
165,467	374.0	333.0	-41.0	0.00081406	0.261
124,002	350.0	314.4	-35.6	0.0070581	3.855
64,432.8	300.0	276.2	-23.8	0.020245	6.051
29,817.8	250.0	237.2	-12.8	0.048786	7.379
11,659.2	200.0	196.5	-3.5	0.12600	8.342
3,570.5	150.0	153.6	+3.6	0.39135	9.094
760.0	100.0	108.1	+8.1	1.67195	9.713
92.51	50.0	59.8	+9.8	12.04485	10.255
4.579	0.0	8.8	+8.8	206.306	10.767
0.02955	-50.0	-48.8	+1.2	37,850.0	12.203
0.000015	-98.0	-101.6	-3.6	96,680,000.0	12.190
					12.248

^a Data listed in ref 1a-c. ^b Calculated from eq 3. ^c From ASME Steam Tables as listed in ref 1e. Ice data from ref 2a. ^d From ASME Steam Tables as listed in ref 1e. Ice data calculated from vapor heat capacity data (ref 3), ice heat capacity data (ref 4), and enthalpy of fusion of ice (ref 2b).

where R is the universal gas constant, and B is another constant.

This note compares the vapor pressure data for ice and water tabulated in a recent handbook¹ with vapor pressure values calculated from a mathematical expression like eq 2 listed in the same handbook. In it we read that the vapor pressure for water is given by "the following equation:

$$\log P = (-0.2185A/K) + B \quad (3)$$

where P is expressed in Torr, K is the temperature in degrees Kelvin, and A is the molar heat of vaporization in calories per gram mole. The temperature range over which this equation is applicable is also listed. The critical temperatures are given in degrees Celsius and critical pressures in atmospheres."^{1d} The data listed for water are: $A = 10,999.4$ calories per gram mole, the molar heat of vaporization. $B = 9.183837$. The range of applicability is given as -98.0 to 374.0°C . Critical temperature = 374.2°C . Critical pressure = 218.3 atmospheres.

Vapor pressures and temperatures read from the tabulations (ref 1a-c) are listed in columns 1 and 2 of Table I, while the temperatures calculated from eq 3 over its claimed range of validity appear in column 3 for the same pressures. The differences between the calculated and tabulated temperatures are listed in column 4 and are plotted in Figure 1. Column 5 lists the difference in volume between the vapor and condensed phases, and Figure 2 is a plot of these data. Column 6 and Figure 3 present the enthalpy of sublimation or vaporization over the temperature range claimed for eq 3.

Figure 1 shows that near the critical temperature the calculated value is more than 40° lower than the tabulated (measured) value that is taken as authentic. Between 0 and 100°C the calculated values are more than 8°C higher than the tabulated values. At -98°C the calculated value is more than 3°C lower than the tabulated value. These severe discrepancies result because the assumptions made in the derivation of eq 2 are not valid over the extended temperature range claimed for eq 3.

Figure 2 is a plot of the difference between the vapor volume and the volume of the condensed phase over the temperature range claimed for eq 3. From -100° to about 40°C , neglect of the condensed volume causes a discrepancy that does not exceed 0.1% . As the temperature progresses above 40°C , the discrepancy becomes progressively greater until at 100°C it becomes 1.1% . As the temperature progresses above 100°C , assumption i becomes increasingly less valid.

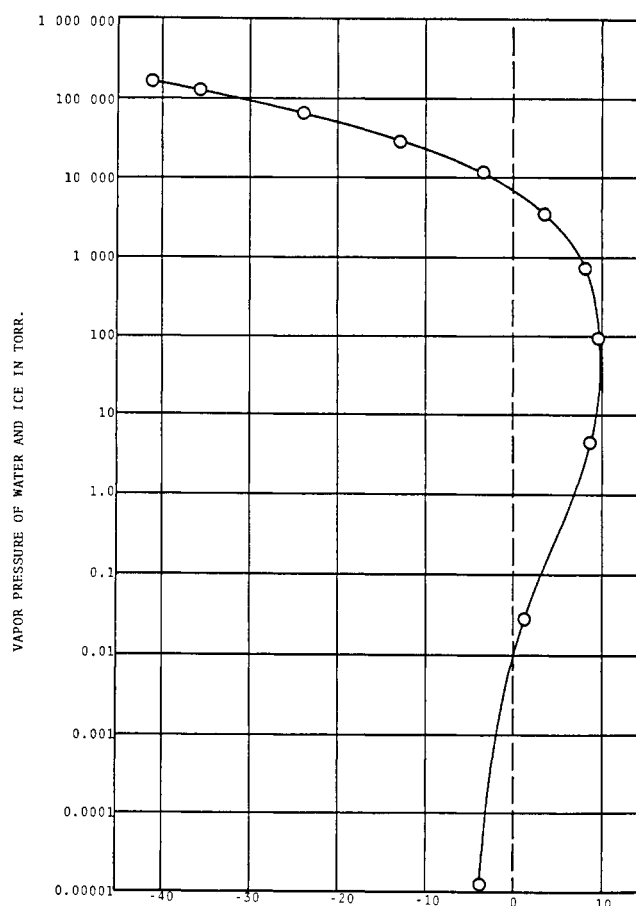


Figure 1. Celsius temperature difference (calculated from eq 3 less tabulated value from "International Critical Tables.")

At pressures of one or two thousand Torr, assumption ii is quite valid, but it becomes more and more invalid as the pressures begin to increase above these levels.

Figure 3 is a plot of the enthalpy of sublimation and vaporization over the temperature range claimed for eq 3 and is certainly not constant. Thus, assumption iii is invalid over the temperature range claimed.

The tabulated values represented by the open circles in Figure 1 reproduce the measured values as faithfully as possible within the reliability of the published values. The dotted line in Figure 1 represents the linear approximation of the data by eq 3 and clearly shows how poorly such a lin-

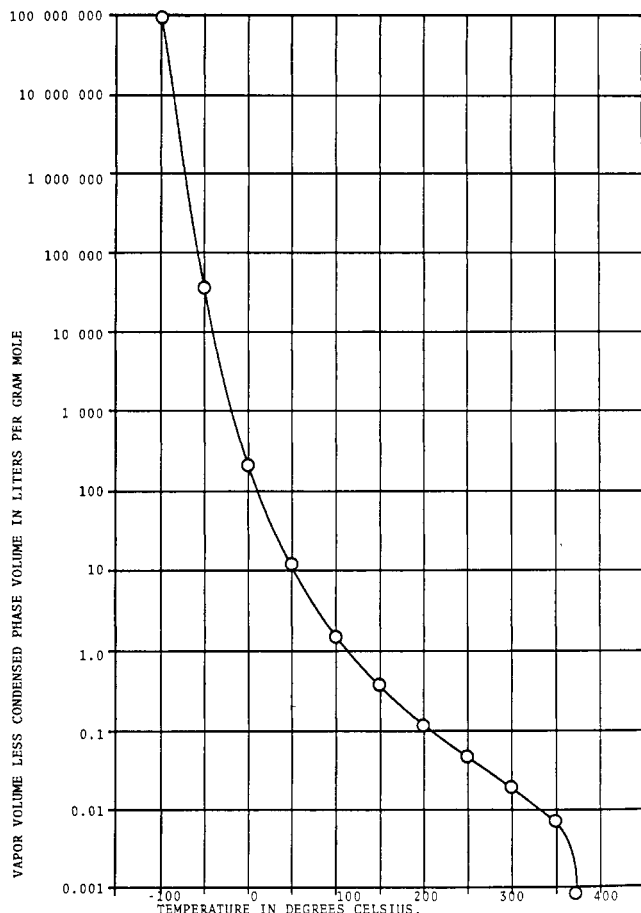


Figure 2.

ear approximation represents the vapor pressure data for water. The tabulated data are far more accurate and useful than the values calculated from the mathematical linear approximation. For decades prior to 1970, earlier editions of this handbook presented all of the vapor pressure data in reliable tabular form and fully referenced the sources of the data. It is most unfortunate that the recently published handbook¹ replaced reliable vapor pressure data that were tabulated many years ago with grossly unreliable equations.^{1d} Such substitution takes unfair advantage of an unsuspecting scientific public.

Handbook publishers are duty bound to supply the most accurate data available; to take the utmost care to ensure

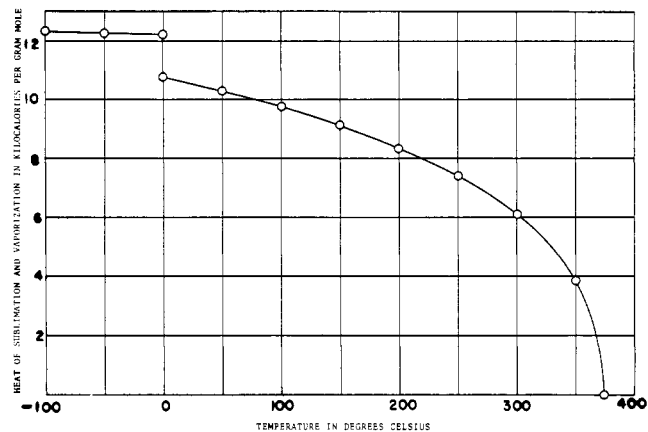


Figure 3.

the reliability of what they print; and to give the basic sources of the data they present.

LITERATURE CITED

- (1) "Handbook of Chemistry and Physics," 54th ed, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1973-1974: (a) Vapor Pressure of Ice, p D-158 [unreferenced, but prepared by E. W. Washburn; "International Critical Tables," Vol. III, Mc-Graw Hill, New York, N. Y., 1928, pp 210-212]; (b) Vapor Pressure of Water below 100°C, p D-159 [unreferenced, but prepared by E. W. Washburn, *ibid.*, from the Physikalisch-Technische Reichsanstalt "Wärmepressuren," by Holborn, Scheel and Henning, Vieweg und Sohn, Braunschweig, 1909, by permission]; (c) Vapor Pressure of Water above 100°C, p D-160 [referenced to F. G. Keyes, "International Critical Tables," Vol. III, 1928, pp 233-234]; (d) Vapor Pressures, Critical Temperatures and Critical Pressures of Organic Compounds, pp D-162 through D-181, and Inorganic Compounds, pp D-182 through D-188 [unreferenced, prepared by G. G. Schlessinger]; (e) Steam Tables, Properties of Saturated Steam and Saturated Water, pp E-18 through E-23 [referenced to the 1967 American Society of Mechanical Engineers Steam Tables, United Engineering Center, 345 East 47th Street, New York, N.Y. 10017].
- (2) Dorsey, N. E., "Properties of Ordinary Water-Substance," Reinhold Publishing Corp., New York, N. Y., 1940: (a) p 601; (b) p 562.
- (3) "JANAF Thermochemical Tables," Vol 37, 2nd ed, D. R. Stull and H. Prophet, Project Directors, National Standard Reference Data Series, U. S. National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1971.
- (4) Giaque, W. R., and Stout, J. W., *J. Amer. Chem. Soc.*, **58**, 1144-1150 (1936).