

Correlation of Latent Heats of Vaporization

JOSEPH J. MARTIN and JOHN B. EDWARDS

The University of Michigan, Ann Arbor, Michigan

Generalized equations for vapor pressure and PVT behavior are used to develop a functional relationship between latent heat of vaporization and reduced temperature and pressure. This function leads to a graphical correlation which utilizes the slope M of the vapor-pressure curve at the critical point. The correlation gives the latent heat of vaporization at any temperature in the two-phase region for any substance for which the critical point and one vapor-pressure point are known. The correlation is particularly useful for prediction of latent heat of vaporization near the critical point by the use of information far removed from the critical. Included in the study are polar, nonpolar, organic, inorganic, and metallic substances. General predictions of latent heat as a function of temperature are within a few percent wherever comparisons can be made with experimental data.

The prediction of latent heats of vaporization has been the objective of many investigations. Sherwood and Reid (1) and Fishtine (2, 3) present excellent summaries of previous work in this area. Only three correlations most closely related to the method developed in this paper will be mentioned. Meissner (4) presented a graphical representation of $\Delta H_v/T_c$ as a function of the reduced temperature and pressure. Watson (5) developed an exponential

expression to predict the latent heat of vaporization of any temperature if the latent heat at one temperature and the critical temperature of the substance are known. Su (6) proposed a correlation for latent heat of vaporization based on a reference state. He suggested the use of a generalized vapor-pressure plot of $\log P_R$ vs. $1/T_R$ to give the ratio of the latent heat at any temperature to that at the reference point.

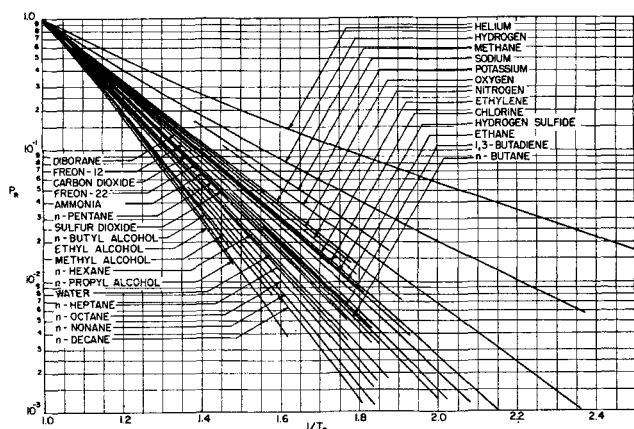


Fig. 1. Reduced vapor pressure curves for thirty compounds.

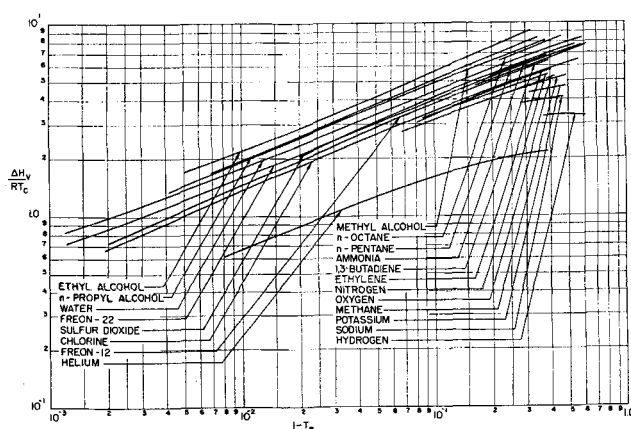


Fig. 3. Reduced latent heat of vaporization curves for twenty compounds.

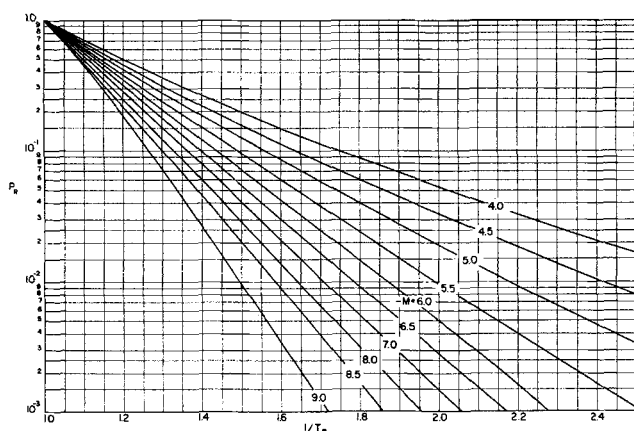


Fig. 2. Smoothed reduced vapor pressure plot.

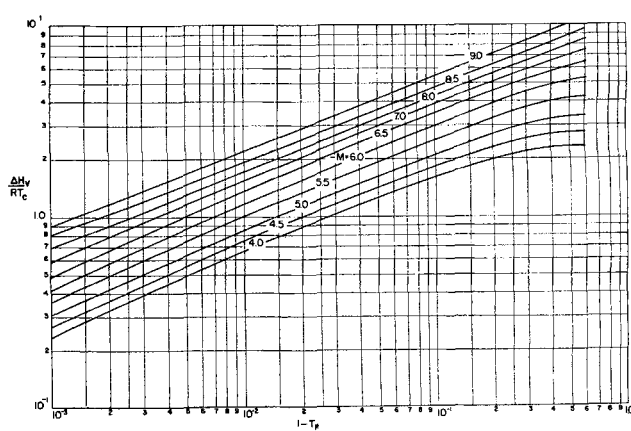


Fig. 4. Smoothed reduced latent heat of vaporization plot.

TABLE 1

Compound	T_c (°R.)	P_c (lb./sq. in. abs.)	$-M$ from data in Figure 1	$-M$ smoothed Figure 2	Range of T_R	Range of P_R	Average % error in $\frac{\Delta H}{RT_c}$ for four points	References
Helium	9.36	33.07	3.95	4.00	0.618 to 0.992	0.1400 to 0.9400	1.24	15, 19
Hydrogen	59.74	190.68	5.00	5.00	0.422 to 0.616	0.0056 to 0.0785	0.61	32
Sodium	4,620	4,410	5.50	5.50	0.532 to 0.722	0.0167 to 0.1665	0.63	23, 24, 27, 14
Potassium	3,555	1,400	5.75	5.80	0.524 to 0.692	0.0107 to 0.1070	0.50	23, 24, 27
Methane	343.89	673	6.00	6.20	0.527 to 0.988	0.0073 to 0.9316	1.16	18
Oxygen	280	730.1	6.35	6.25	0.584 to 0.971	0.0201 to 0.8490	1.15	11
Nitrogen	226.9	490.9	6.45	6.35	0.614 to 0.912	0.0218 to 0.5750	0.45	11
Chlorine	650.8	1,117.9	6.55	6.50	0.439 to 0.998	0.0005 to 0.9900	0.56	17
Ethylene	509.51	741.84	6.60	6.55	0.599 to 0.981	0.0198 to 0.8820	1.65	9
Hydrogen sulfide*			6.60	6.60				26
Ethane*			6.65	6.65				29
Diborane*			6.78	6.75				34, 35
Freon 12	693.29	596.9	6.80	6.90	0.444 to 0.998	0.0002 to 0.9851	1.76	13
Propane	665.82	617.13	6.80	6.80	0.846 to 0.943	0.3142 to 0.6665	0.51	25, 26
1, 3 butadiene	765	626.5	6.95	7.05	0.391 to 0.836	0.00002 to 0.2790	0.50	12
<i>n</i> -butane*			7.12	7.15				29
Freon-22	664.50	721.91	7.15	7.20	0.458 to 0.999	0.0003 to 0.9915	1.09	39
Carbon dioxide*			7.16	7.20				38
Ammonia	729.72	1,637	7.25	7.50	0.548 to 0.794	0.0034 to 0.1750	0.54	10
<i>n</i> -pentane*			7.30	7.55				30, 31
Sulfur dioxide	774.36	1,140	7.45	7.60	0.464 to 0.980	0.0002 to 0.8640	1.14	16
<i>n</i> -hexane*			8.00	8.00				29
Water	1,165.09	3,206.2	8.20	8.10	0.422 to 0.995	0.00002 to 0.9640	0.77	14
<i>n</i> -heptane*			8.30	8.25			0.77	29
<i>n</i> -octane	1,024.2	361.37	8.40	8.35	0.546 to 0.781	0.0016 to 0.1199	0.65	28, 29
<i>n</i> -nonane*			8.50	8.50				26
<i>n</i> -decane*			8.60	8.65				33
<i>n</i> -butanol*			8.75	8.75				36, 37
Methanol	924	1,155	8.80	8.70	0.6061 to 0.996	0.0039 to 0.9732	1.07	21, 40
<i>n</i> -propanol	966.33	736.1	8.83	8.85	0.690 to 0.993	0.0199 to 0.9450	1.24	22, 36, 37
Ethanol	929.25	927.09	9.00	8.90	0.681 to 0.995	0.0158 to 0.9480	1.52	20

* Data for these compounds used to establish Figures 1 and 2 only.

DEVELOPMENT OF CORRELATION

As with practically all previous correlations, this development starts with the Clapeyron (7) equation

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V'' - V')} \quad (1)$$

The P-V-T behavior of the vapor and the liquid may be described by

$$PV'' = Z''RT \quad (2)$$

and

$$PV' = Z'RT \quad (3)$$

Combining Equations (1), (2), and (3) and utilizing reduced properties one gets a well-known relation:

$$\frac{\Delta H_v}{RT_c} = - (Z'' - Z') \frac{d \ln P_R}{d(1/T_R)} \quad (4)$$

An earlier paper (8) demonstrated that a plot of $\log P_R$ vs. $1/T_R$ for many compounds gives a family of curves, each distinguished by its slope at the critical point. This slope is designated by M which is defined as

$$M = - \left(\frac{dP_R}{dT_R} \right)_{T_R = 1, P_R = 1} = \left(\frac{d \log P_R}{d(1/T_R)} \right)_{T_R = 1, P_R = 1} \quad (5)$$

Figure 1 is such a reduced vapor-pressure plot for thirty-one substances tabulated in Table 1. This plot indicates that in general none of the curves cross. Figure 2 is a smoothed plot at specific values of M , obtained by cross plotting the data of Figure 1. Column 2 of Table 1 is the M value for each substance on Figure 1 obtained from the slope of its curve at the critical, while column 3 gives the value of M obtained from the smoothed data of Figure 2.

The earlier study (8) showed that M is not only the slope of the vapor-pressure curve at the critical but is also the slope of the critical volume line, meaning that the PVT behavior is determined by this slope and the critical compressibility factor. Since the right-hand side of Equation (4) involves P_R , T_R , and the PVT behavior (that is the compressibility factor), which in turn depends upon Z_c and M , a functional relation may be written as

$$\frac{\Delta H_v}{RT_c} = \phi(T_R, P_R, Z_c, M) \quad (6)$$

Now Z_c increases fairly regularly with a decrease in M , and M also determines P_R as a function of T_R on Figure 2. Therefore, Equation (6) may be simplified to

$$\frac{\Delta H_v}{RT_c} = \phi(T_R, M) \quad (7)$$

A plot of this function which gives nearly linear curves and good precision near the critical is that of $\log(\Delta H_v/RT_c)$ vs. $\log(1 - T_R)$ with M as a parameter. This has been done for twenty substances in Figure 3, where each curve has a unique position depending on M . The data of Figure 3 were cross plotted to give Figure 4, which is the working plot. Figures 2 and 4 provide a simple way to determine quickly the latent heat of vaporization at any temperature from a knowledge of the critical point and a vapor-pressure point that establishes M .

DISCUSSION

The accuracy of the correlation has been tested for a total of twenty substances at four points for each substance. The results are presented in Table 1. The average error is 0.94%. By comparison with other correlations, Fishtine (2) found average errors for the Klein, Giacomone, and Riedel correlations of 1.29, 1.70, and 1.52%, respectively, when tested for a wide variety of substances. The correlation presented here is especially good for the region near the critical point.

An interesting comparison can be made between the curves in Figures 3 and 4 and the relation suggested earlier by Watson (5):

$$\frac{\Delta H_{v_1}}{\Delta H_{v_2}} = \left(\frac{1 - T_{R_1}}{1 - T_{R_2}} \right)^{0.38}$$

This relation that a straight line of slope 0.38 should result if $\log(\Delta H_v/RT_c)$ is plotted vs. $(1 - T_R)$. The curves in Figures 3 and 4 are nearly straight over wide ranges of T_R , and their slopes are approximately 0.38. Deviations occur in the extreme right- and left-hand regions where pronounced curvature is observed.

The reduced vapor pressure curves of Figure 1 are of further interest because previous studies (8, 29) showed that the curves are concave downward at lower pressures and concave upward near the critical with an inflection in the region $0.8 < T_R < 0.85$. The new plots show that methane is almost straight, while the substances above it, of smaller M value, have only upward curvature. Also the highest M -value compounds such as the alcohols exhibit little upward curvature but considerable downward curvature. Thus, one cannot say that all vapor-pressure curves have an S shape (8, 29); their shape depends in a regular manner on the region in which they lie, hence on their value of M .

LITERATURE CITED

1. Sherwood, T. K., and R. C. Reid, "Properties of Liquids and Gases," Chap. 3, McGraw-Hill, New York (1958).
2. Fishtine, S. H., *Ind. Eng. Chem.*, **55**, No. 4, 20 (1963).
3. *Ibid.*, No. 6, 47 (1963).
4. Meissner, H. P., *Ind. Eng. Chem.*, **33**, 1440 (1941).
5. Watson, K. M., *ibid.*, **35**, 398 (1943).
6. Su, C. J., *ibid.*, **38**, 923 (1946).
7. Clapeyron, B. P. E., *J. Ecole Polytech.*, **14**, 143 (1834).
8. Martin, J. J., and Y. C. Hou, *A.I.Ch.E. Journal*, **1**, 142 (1955).
9. York, R., and E. E. White, *Trans. Am. Inst. Chem. Engrs.*, **40**, 227 (1944).
10. U.S. Bureau of Standards Circular 123.
11. Miller, R. W., and J. D. Sullivan, U.S. Bureau of Mines Tech. Paper No. 424 (1928).
12. Meyers, C. H., C. S. Cragg, and E. F. Mueller, *J. Res. Natl. Bureau Standards*, **39**, 507 (1947).
13. E. I. du Pont de Nemours and Co. publication.
14. Keenan, J. H., and F. G. Keyes, "Thermodynamic Properties of Steam," Wiley, New York (1936).
15. Scott, R. B., "Cryogenic Engineering," Van Nostrand, New Jersey (1959).
16. Rynning, D. F., and C. O. Hurd, *Trans. Am. Inst. Chem. Engrs.*, **41**, 265 (1945).
17. Kapoor, R. M., and J. J. Martin, *Univ. of Mich. Res. Inst. Pub.*, **19**.
18. Mathews, C. S., and C. O. Hurd, *Trans. Am. Inst. Chem. Engrs.*, **42**, 55 (1946).
19. Vance, R. W., and W. M. Duke, "Applied Cryogenic Engineering," Wiley, New York (1962).
20. "International Critical Tables," Vol. 5, p. 138, McGraw-Hill, New York (1927).
21. Kay, W. B., and W. E. Donham, *Chem. Eng. Sci.*, **4**, No. 1, 1 (1955).
22. Martin, J. J., J. A. Campbell, and E. M. Seidel, *J. Chem. Eng. Data*, **8**, 4 (1963).
23. Makansi, M., Ph.D. dissertation, Columbia University, New York (1957); University Microfilms, Ann Arbor, Michigan.
24. ———, W. A. Selke, and C. F. Bonilla, *J. Chem. Eng. Data*, **5**, 441 (1960).
25. Sage, B. H., H. D. Evans, and W. N. Lacy, *Ind. Eng. Chem.*, **31**, 763 (1939).
26. Stull, D. R., *ibid.*, **39**, 517 (1947).
27. Weatherford, W. D., J. C. Tyler, and P. M. Ku, WADD Tech. Report 61-96 (1961).
28. McKay, R. A., and B. H. Sage, *J. Chem. Eng. Data*, **5**, 21 (1960).
29. Thodos, George, *Ind. Eng. Chem.*, **42**, 1514 (1950).
30. Kozicki, W., and B. H. Sage, *J. Chem. Eng. Data*, **5**, 331 (1960).
31. Maxwell, J. B., "Data Book on Hydrocarbons," 5 printing, Van Nostrand, New Jersey (1958).
32. Woolley, H. W., H. B. Scott, and F. G. Brickwedde, *J. Res. Natl. Bureau Standards*, **41**, 379 (1948).
33. Jordan, T. E., "Vapor Pressure of Organic Compounds," Interscience, New York (1954).
34. Wurth, H. E., and E. D. Palmer, *J. Phys. Chem.*, **60**, 911 (1956).
35. Paridon, L. J., and G. R. MacWood, *The Ohio State University Research Foundation Report 116-F-S* (1956).
36. Ambrose, D., and R. Townsend, *J. Chem. Soc.*, 3614 (1963).
37. Biddiscombe, D. P., R. R. Collerson, R. Handley, E. F. G. Herington, J. F. Martin, and C. H. S. Sprabe, *ibid.*, 1954 (1963).
38. Perry, J. H., "Handbook for Chemical Engineering," 4 ed., McGraw-Hill, New York (1962).
39. Martin, J. J., Unpublished research sponsored at Univ. of Mich. by E. I. du Pont de Nemours and Co.
40. Smith, J. M., *Ind. Eng. Chem.*, **44**, 521 (1948).
41. Sowa, E. S., *Nucleonics*, **21**, 76 (1963).

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