Thermodynamics

of the

Liquid State

GENERALIZED PREDICTION OF PROPERTIES

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On the basis of a modified application of the theorem of corresponding states, new methods are presented for the general prediction of the following thermodynamic properties of liquids: thermal expansion and compressibility, pressure correction to enthalpy, pressure correction to entropy, pressure correction to heat capacity at constant pressure, heat of vaporization, difference between heat capacity of a saturated liquid and its ideal gas, and difference between heat capacity of saturated liquid and heat capacity at constant pressure.

The only data required are the boiling point, the critical temperature, critical pressure, and the liquid density at some one temperature.

Like all applications of the theorem of corresponding states, these relations are not rigorously correct. However, deviations from the available experimental data on a variety of compounds, both polar and nonpolar, are sufficiently small to warrant their use for many process problems where reliable data are not available, and for rationalizing fragmentary experimental data.

DURING the past ten years much attention has been directed (*2, 4, 7, 8, 10, 23–26*) toward the development of generalized relations which permit prediction of the thermodynamic properties of the gaseous state, even at extreme conditions of temperature and pressure, with accuracy sufficient for general engineering purposes. The similar properties of the liquid state have received little attention because of their lesser importance and because of the failure of the theorem of corresponding states to directly correlate liquid properties with accuracy. However, by a modified application of this theorem it is possible to correlate liquid properties with a degree of accuracy similar to the correlations of the gas phase.

THERMAL EXPANSION AND COMPRESSIBILITY

The equation of state for the gaseous phase is ordinarily written,

$$pv = zRT \qquad (1)$$

where z, the compressibility factor, is a function of reduced temperature and pressure, approximately the same for all substances. If this relation were applied to the liquid state, an expression for liquid density might be written,

$$\rho = \frac{pM}{zRT} = \left(\frac{p_r}{zRT_r}\right)\frac{P_cM}{T_c} = \omega \frac{P_cM}{T_c} \qquad (2)$$

where ω, which might be termed the "expansion" factor, would be a function only of reduced temperature and pressure.

Unfortunately it is found that factor ω of Equation 2 is not a generalized function of reduced conditions. Values of ω at the same reduced conditions may vary by more than 20 per cent for different compounds. Accordingly, Equation 2 is a rough approximation useful only where no direct liquid density data of any type are available.

Since at least one value of liquid density is available for almost any compound, a more useful relation results by applying Equation 2 to obtain an expression for the ratio of the density at any given condition to that at some reference state designated by subscript 1:

$$\frac{\rho}{\rho_1} = \frac{\omega}{\omega_1}$$

$$\text{or } \rho = \frac{\rho_1}{\omega_1}\,\omega \qquad (3)$$

It has been found that if ω is evaluated as a function of reduced temperature and reduced pressure for one compound on which complete data are available, Equation 3 may be used with satisfactory accuracy for predicting the densities of any other compound for which one liquid density value is available to establish ρ_1/ω_1.

Table I. Values of Expansion Factor ω

T_r	$P_r = 0$	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.0$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.5	(0.1328)	....	....	0.1332	....	0.1338	....	0.1350
0.6	0.1242	....	....	0.1250	....	0.1258	....	0.1275
0.7	0.1144	0.1150	....	0.1158	....	0.1170	0.1182	0.1202
0.8	0.1028	0.1042	0.1050	0.1056	0.1070	0.1077	0.1098	0.1125
0.9	....	0.0900	0.0915	0.0926	0.0949	0.0968	0.1002	0.1043
0.95	....	....	0.0810	0.0831	0.0872	0.0902	0.0943	0.1000
1.0	....	....	....	0.0440	0.0764	0.0818	0.0875	0.0954

Figure 1 and Table I give values of ω for isopentane, calculated from the measurements of Young (11) and extended to higher pressures by the data of Sage and Lacey (16, 18) on propane and n-pentane and Equation 3. Tables II and III compare liquid densities calculated from these curves and Equation 3 with experimental data from the indicated sources for compressed and saturated liquids of various polar and nonpolar types. The agreement is reasonably good with deviations, in general, less than 5 per cent, even for the case of water at 100° C. and above. The anomalous density changes of water at low temperature are not in agreement with the correlation, and selection of 4° C. as the reference conditions instead of 100° C. would increase the maximum deviations in the high-temperature range to approximately 10 per cent. In general, it is desirable to use the highest temperature at which data are available as the reference state, particularly when the high-temperature behavior of polar substances such as water are being calculated.

PRESSURE CORRECTION TO ENTHALPY

The effect of pressure on the enthalpy of any substance is expressed by the rigorous thermodynamic equation:

$$J\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{4}$$

Rearranging in terms of reduced conditions,

$$\frac{J}{P_c}\left(\frac{\partial H}{\partial p_r}\right)_T = V - T_r\left(\frac{\partial V}{\partial T_r}\right)_p \tag{5}$$

Combining Equations 3 and 5,

$$\frac{J\rho_1}{P_c\omega_1}\left(\frac{\partial H}{\partial p_r}\right)_T = \frac{1}{\omega} - T_r\left(\frac{\partial \frac{1}{\omega}}{\partial T_r}\right)_p \tag{6}$$

Through Equation 6 the group

$$\frac{J\rho_1}{P_c\omega_1}\left(\frac{\partial H}{\partial p_r}\right)_T$$

may be expressed as a general function of reduced temperature and pressure by the graphical differentiation of Figure 1, remembering that $\partial(1/\omega) = -(\partial\omega/\omega^2)$. The results of this operation are summarized in Figure 2 and Table IV for the range of conditions not close to the critical point.

The effect of pressure on enthalpy may be expressed in a more useful form by graphically integrating Equation 6 to obtain the differences between the enthalpy of a liquid under
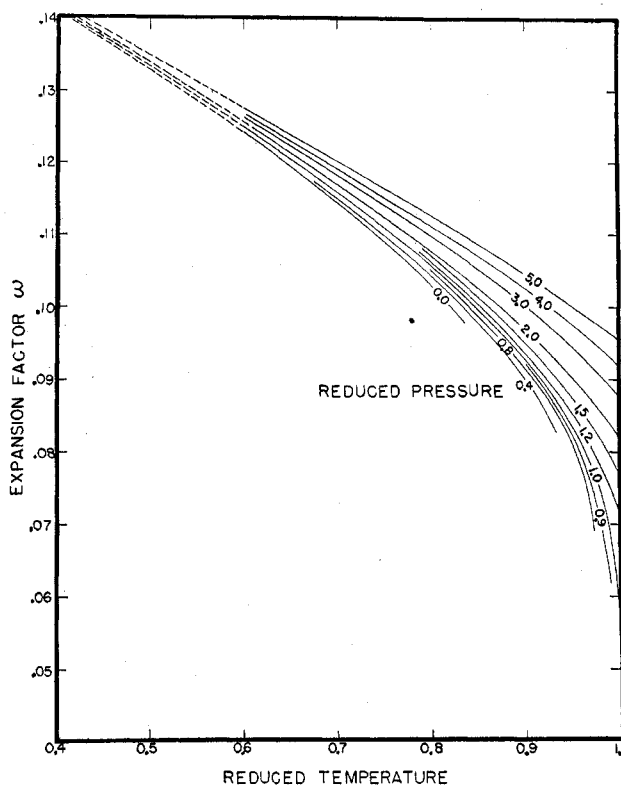

Figure 1. Thermal Expansion and Compressibility of Liquids

Table II. Densities of Compressed Liquids

Pressure, Lb./Sq. In.	Reduced Pressure	Density, Gram/Cc.					

WATER (12): $\rho_1/\omega_1 = 7.586$ AT 100° C., 1 ATM.

Pressure, Lb./Sq. In.	Reduced Pressure	204.4° C., $T_r = 0.738$		348.9° C., $T_r = 0.961$		374.3° C., $T_r = 1.0$	
		Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
1000	0.312	0.842	0.864	....	....	....	....
3206	1.0	0.851	0.874	0.611	0.616	0.326	0.318
4000	1.248	0.854	0.878	0.633	0.639	0.551	0.543
5500	1.715	0.858	0.885	0.658	0.660	0.603	0.603

PROPANE (17): $\rho_1/\omega_1 = 4.807$ AT 21.0° C., 200 LB./SQ. IN.

Pressure, Lb./Sq. In.	Reduced Pressure	54.5° C., $T_r = 0.878$		71.1° C., $T_r = 0.921$		87.9° C., $T_r = 0.966$	
		Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
300	0.466	0.453	0.447	....	....	....	....
600	0.934	0.460	0.458	0.416	0.422	0.374	0.368
1500	2.35	0.485	0.482	0.460	0.458	0.431	0.430
3000	4.66	0.508	0.506	0.489	0.489	0.469	0.470

BUTANE (19): $\rho_1/\omega_1 = 5.037$ AT 21.1° C., 250 LB./SQ. IN.

Pressure, Lb./Sq. In.	Reduced Pressure	71.1° C., $T_r = 0.809$		104.4° C., $T_r = 0.887$		121.1° C., $T_r = 0.926$	
		Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
250	0.462	0.521	0.522	0.467	0.461	0.427	0.411
500	0.945	0.526	0.527	0.475	0.472	0.438	0.434
1500	2.84	0.546	0.545	0.508	0.501	0.487	0.475
3000	5.67	0.567	0.564	0.536	0.528	0.521	0.507

Table III. Densities of Saturated Liquids

Temperature, ° C.	Density, G./Cc.		Temperature, ° C.	Density, G./Cc.	
	Calcd.	Exptl.		Calcd.	Exptl.

AMMONIA (21): $\rho_1/\omega_1 = 5.463$ AT −33.3° C., SATD. PRESSURE

Temperature, ° C.	Calcd.	Exptl.	Temperature, ° C.	Calcd.	Exptl.
−73.3	0.729	0.730	37.8	0.586	0.584
−45.6	0.698	0.699	93.3	0.488	0.475
−17.8	0.664	0.664	121	0.388	0.380
+10	0.626	0.625	133 (T_c)	0.240	0.234

ETHYL ALCOHOL (11): $\rho_1/\omega_1 = 6.210$ AT 20° C., SATD. PRESSURE

Temperature, ° C.	Calcd.	Exptl.	Temperature, ° C.	Calcd.	Exptl.
0	0.809	0.806	60	0.746	0.755
40	0.768	0.772	80	0.721	0.735
			243.1 (T_c)	0.273	0.275
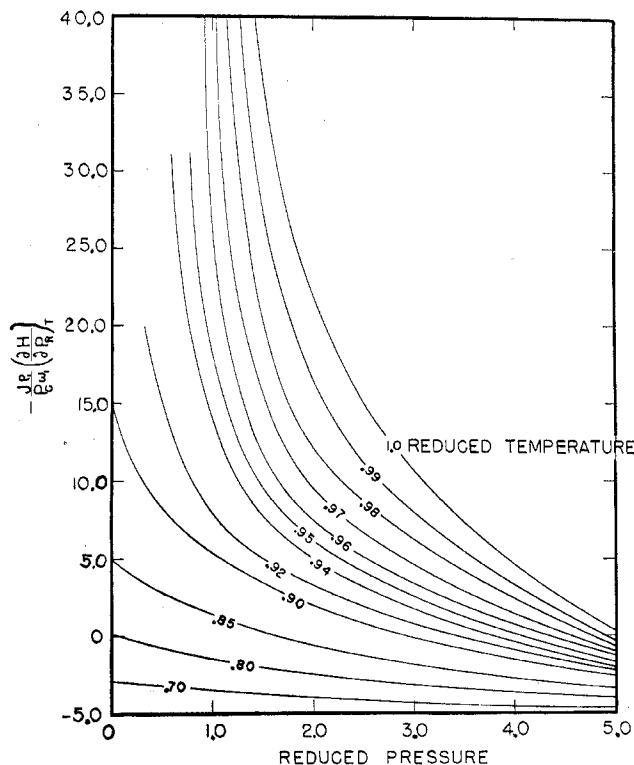
Figure 2. Differential Effect of Pressure on Enthalpy of Liquids

Expressing in terms of reduced conditions and combining with Equation 3,

$$\frac{J\rho_1 T_c}{\omega_1 P_c}\left(\frac{\partial S}{\partial p_r}\right)_T = -\left(\frac{\partial \frac{1}{\omega}}{\partial T_r}\right)_p \qquad (9)$$

Equation 9 may be integrated to obtain a useful correction chart relating the difference between entropy under the critical pressure and entropy at any other pressure under the same temperature:

$$\frac{J\rho_1 T_c}{\omega_1 P_c}(S_{cp} - S)_T = \int_{p_r}^{1.0} -\left(\frac{\partial \frac{1}{\omega}}{\partial T_r}\right)_p dp_r \qquad (10)$$
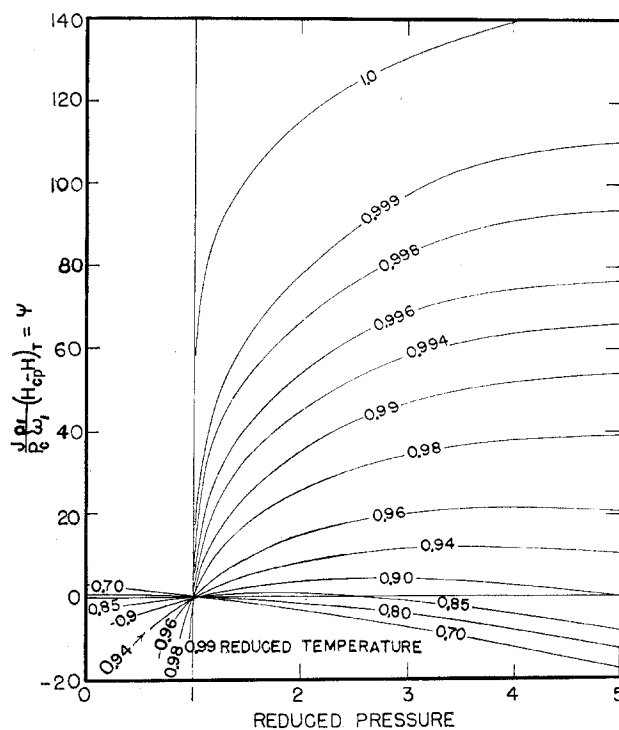

Figure 3. Pressure Correction to Enthalpy of Liquids

its critical pressure and the enthalpy at the same temperature and other pressures:

$$\frac{J\rho_1}{P_c\omega_1}(H_{cp} - H)_T = \int_{p_r}^{1.0} \frac{J\rho_1}{P_c\omega_1}\left(\frac{\partial H}{\partial p_r}\right)_T dp_r \qquad (7)$$

The results of this integration are summarized in Figure 3 and Table V.

Unfortunately few data are available with which to compare the enthalpy corrections calculated from Figure 3. Table VI compares the calculated values and those experimentally evaluated for water and propane. The agreement is reasonably good for both compounds. In view of the fact that the pressure correction is relatively small as compared to the enthalpy changes ordinarily encountered in industrial operations, it is believed that Figure 3 may be safely used for many engineering applications. The fact that a relation based on data for pentane is in even fair agreement with such dissimilar materials as water and propane is reassuring as to its generality.

PRESSURE CORRECTION TO ENTROPY

The effect of pressure on the entropy of any substance is expressed by the rigorous thermodynamic equation:

$$J\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad (8)$$

Table IV. Values of $-\dfrac{J\rho_1}{P_c\omega_1}\left(\dfrac{\partial H}{\partial p_r}\right)_T$

T_r	$P_r = 0$	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.0$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.7	− 3.0	−3.2	− 3.4	− 3.5	− 3.8	− 4.0	− 4.4	−4.7
0.8	+ 0.1	−0.6	− 1.3	− 1.6	− 2.2	− 2.6	− 3.3	−4.1
0.85	+ 5.0	+3.1	+ 1.8	+ 1.3	+ 0.2	− 0.7	− 1.9	−3.4
0.90	+15.0	+9.1	+ 6.3	+ 5.3	+ 3.4	+ 1.9	− 0.2	−2.7
0.94	....	...	+19.0	+14.0	+ 7.7	+ 4.9	+ 1.7	−2.0
0.98	....	...	....	....	+20.3	+12.1	+ 6.2	−0.7
1.0	....	...	....	....	+36.0	+21.8	+10.7	+0.4

Table V. Values of $\dfrac{J\rho_1}{P_c\omega_1}(H_{cp} - H)_T = \psi$

T_r	$P_r = 0$	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.2$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.7	+3.1	+2	+0.8	− 0.7	− 1.8	− 3.4	− 7.3	− 17.2
0.8	+0.8	+0.5	+0.1	− 0.2	− 0.7	− 1.4	− 4.0	− 12.3
0.85	−3.2	−1.8	−0.5	+ 0.4	+ 0.9	+ 1.0	− 0.9	− 8.0
0.9	...	−5.0	−1.7	+ 1.0	+ 2.2	+ 3.7	+ 4.4	+ 0.2
0.94	...	...	−3.5	+ 2.1	+ 5.2	+ 8.2	+ 11.8	+ 10.8
0.98	...	...	...	+10.0	+ 18	+ 25.8	+ 20.2	+ 39.3
0.99	...	...	...	+15.0	+ 24.9	+ 35.0	+ 47	+ 54.1
0.999	...	...	...	+46.5	+ 62.5	+ 77.8	+ 97.6	+110.3
1.0	...	...	...	+87.0	+101.5	+115.2	+130.5	.....

Values $[\partial(1/\omega)/\partial T_r]_p$ were obtained from Figure 1 in deriving Figure 2. The resulting integrated pressure correction to entropy is plotted against reduced temperature and pressure in Figure 4 and summarized in Table VII. Table VIII compares values calculated from Figure 4 with experimental values for water and propane. The agreement appears to be somewhat better than that of the enthalpy correction, indicating that generalization is sufficiently sound for useful application.

PRESSURE CORRECTION TO HEAT CAPACITY AT CONSTANT PRESSURE

A useful expression for the effect of pressure on heat capacity at constant pressure may be derived by designating the right-hand side of Equation 7 as ψ, a function of reduced temperature and pressure:

$$\frac{J\rho_1}{P_e\omega_1}(H_{cp}-H)_T = \psi \qquad (11)$$

Upon differentiation at constant pressure,

$$\frac{J\rho_1}{P_e\omega_1}\left[\left(\frac{\partial H_{cp}}{\partial T}\right)_p - \left(\frac{\partial H}{\partial T}\right)_p\right]_T = \frac{1}{T_e}\left(\frac{\partial\psi}{\partial T_r}\right)_p$$

or $\quad \dfrac{J\rho_1 T_c}{\omega_1 P_e}(C_{cp}-C_p)_T = \left(\dfrac{\partial\psi}{\partial T_r}\right)_p \qquad (12)$

The results of graphically differentiating Figure 3 in accordance with Equation 12 are summarized in Figure 5 and Table
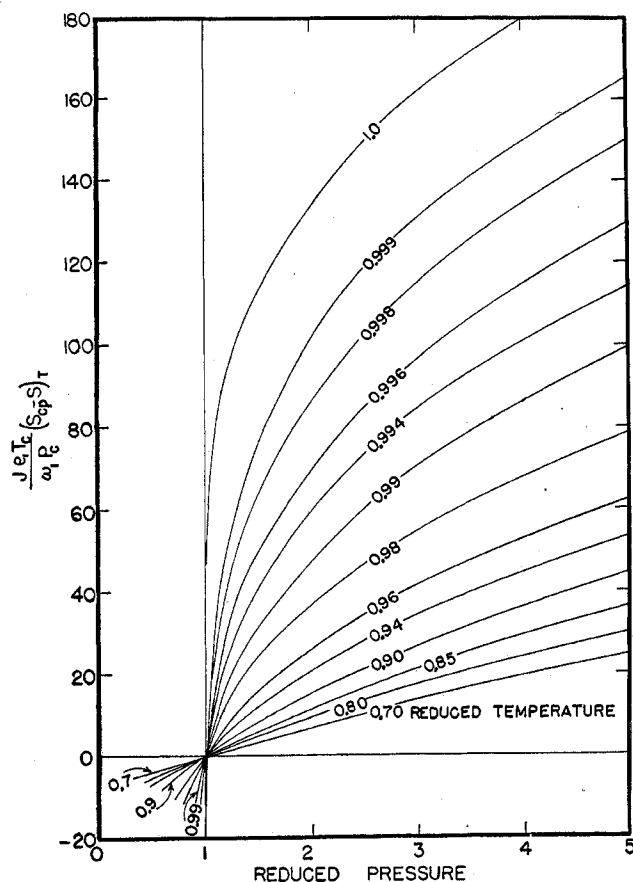
Table VI. Pressure Correction to Enthalpy

Pressure, Lb./Sq. In.	$(H_{cp}-H)_T$, cal./gram mole					
	204.4° C.		348.9° C.		374.3° C.	
	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
	WATER (12)					
1000	23	28.	....	....	....	....
2500	8	10	−107	−115	....	....
4000	− 8	− 9	+ 75	+ 79	+1130	+1266
5500	−26	−32	+164	+172	+1370	1526
	PROPANE (17)					
	54.5° C.		71.1° C.		87.9° C.	
300	−29	−25	...	...	...	...
1500	+18	+12	+68	+63	+205	+200
3000	−28	−21	+58	+45	+260	+256

Table VII. Values of $\dfrac{J\rho_1 T_c}{\omega_1 P_e}(S_{cp}-S)_T$

T_r	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.2$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.7	−4.6	−1.7	+ 1.1	+ 3.2	+ 6.9	+ 13.8	+ 25.0
0.9	...	−3.6	+ 3.8	+ 8.5	+ 15.5	+ 26.9	+ 44.9
0.94	...	−7.1	+ 5.6	+ 12.2	+ 20.8	+ 34.7	+ 53.8
0.98	...	...	+13.2	+ 24.6	+ 37.3	+ 55.1	+ 79.0
0.99	...	...	+18.3	+ 31.9	+ 47.7	+ 71.0	+ 99.9
0.996	...	...	+32.1	+ 50.0	+ 70.2	+ 96.9	+130.0
0.999	...	...	+50.7	+ 76.9	+102.0	+130.9	+165.6
1.0	...	...	+93.2	+113.0	+134.0	+161.5	.....

IX. A comparison of values calculated from Figure 5 with those derived from experimental data for water is shown in Table X. Additional data for testing this relation are scanty, but the agreement with the data on water is sufficiently good to indicate that the generalization did not lose greatly in accuracy through the series of manipulations employed in deriving Figure 5.

HEAT OF VAPORIZATION

An empirical graphical generalization was developed by the author (22) which satisfactorily represents the effect of temperature on the heat of vaporization of a variety of polar and nonpolar compounds. A curve, based on the available data for all materials, was presented from which the heat of vaporization at any reduced temperature can be calculated if one value at a known reduced temperature is available. The Kistiakowsky equation offers a satisfactory method of estimating heats of vaporization at the normal boiling points for nonpolar compounds but does not apply to polar materials.

A satisfactory generalized method for estimating the heat of vaporization of any substance at any temperature was developed by Meissner (14). This method shows good agreement with experimental results, particularly at high temperatures. It becomes somewhat unsound at low reduced temperatures, but even in this range the errors are not ordinarily serious. The method here presented is an alternate to Meiss-

Figure 4. Pressure Correction to Entropy of Liquids

Table VIII. Pressure Correction to Entropy

Pressure, Lb./Sq. In.	$(S_{cp}-S) \times 10^3$ cal./gram mole/° K.					
	204.4° C.		348.9° C.		374.3° C.	
	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
	WATER (12)					
1000	−115	−100	...	...	....	....
2500	− 37	− 32	− 249	−242	....	....
4000	+ 38	+ 33	+ 194	187	1900	2030
5500	+112	+ 96	+ 430	445	2400	2545
	PROPANE (17)					
	54.5° C.		71.1° C.		87.9° C.	
300	−235	−238	...	...	...	...
1500	+470	+442	+ 630	591	+ 915	+ 970
3000	+990	+984	+1215	1200	+1670	+1790
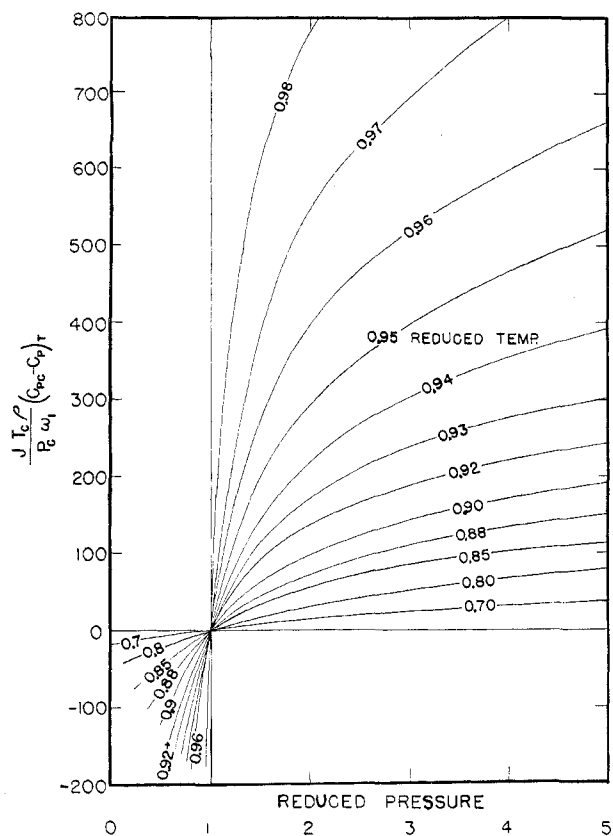
Figure 5. Pressure Correction to Heat Capacity at Constant Pressure of Liquids

Table IX. Values of $\dfrac{JT_c\rho_1}{P_c\omega_1}(C_{cp} - C_p)_T$

Tr	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.2$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.7	− 9	− 3	+ 3	+ 7	+ 14	+ 23	+ 38
0.8	−28	− 9	+ 6	+ 16	+ 30	+ 52	+ 80
0.9	..	− 42	+ 30	+ 62	+ 98	+142	+192
0.94	..	− 75	+ 70	+143	+216	+303	+392
0.96	..	−190	+146	+272	+400	+518	+662
0.97	..	...	+208	+387	+550	+695	...
0.98	..	...	+385	+608	+778	...	...

by Cox (*5*) which permits ready determination of dp_s/dT from the corresponding values for the reference substance. However, this method is rather tedious, and the added labor is frequently not warranted by the improved accuracy obtained.

If the application of Equation 14 is restricted to the normal boiling point, a reasonably good approximation is obtained with the following modified form of the Clausius-Clapeyron equation in which the factor 0.95 represents the average deviation of the vapor from the ideal gas laws at these conditions, together with the effect of the liquid volume:

$$\left(\frac{dp_s}{dT}\right)_B = \frac{p_B\lambda_B}{0.95RT_B^2} \tag{15}$$

A simple relation between temperature and vapor pressure was developed by Calingaert and Davis (*3*) as a result of a study of the Cox method of vapor-pressure plotting:

$$\ln p_s = A - \frac{B}{T - 43} \tag{16}$$

where T is expressed in degrees Kelvin. This equation is not particularly reliable for many materials and is not recommended as a general method of predicting vapor pressures where considerable accuracy is required. However, it can be used satisfactorily for evaluating dp/dT for generalized thermodynamic relations where a high order of accuracy is not required or inherent in the other relations. Thus, differentiating Equation 16,

$$\frac{dp_s}{dT} = \frac{p_sB}{(T - 43)^2} \tag{17}$$

The constant B may be determined from any two vapor pressure values, such as the boiling point and critical point:

$$B = \frac{\ln \dfrac{p_c}{p_B}}{\dfrac{1}{T_B - 43} - \dfrac{1}{T_c - 43}} \tag{18}$$

Combining Equations 12 and 14,

$$\lambda_B = 0.95RB\left(\frac{T_B}{T_B - 43}\right)^2 \tag{19}$$

ner's method, with the advantage of not involving any graphical relations and consequently being adaptable to mathematical manipulation for the derivation of other thermodynamic functions. It is perhaps somewhat more dependable than Meissner's method at low reduced temperatures.

It has been found that the general curve, referred to above (*22*) and expressing the relation between heat of vaporization and reduced temperature, is represented by the following empirical equation:

$$\lambda = \lambda_1\left(\frac{1 - T_r}{1 - T_{r_1}}\right)^{0.38} \tag{13}$$

This equation is more convenient to use than the original curve and gives considerably more reproducible results, particularly at temperatures near the critical. It is in good agreement with the available data with the exception of water at low temperatures, below the normal boiling point. As previously mentioned, water is unusual in many of its characteristics in this region.

Heats of vaporization may be accurately calculated at any temperature from the rigorously correct Clapeyron equation:

$$\frac{dp_s}{dT} = \frac{\lambda}{T(v_g - v_l)} \tag{14}$$

The molal volume of the vapor, v_g, may be calculated from the generalized gas compressibility factors while the volume of the liquid, v_l, is obtained from Equation 3 and Figure 1. Where complete vapor pressure data are not available, excellent approximations can be obtained from only the boiling point and the critical temperature and pressure by use of a reference substance method of plotting such as that introduced

Table X. Pressure Correction to Heat Capacity of Water at Constant Volume (*12*)

Pressure, Lb./Sq. In.	260° C., $T_r = 0.824$ Calcd.	Exptl.	315.6° C., $T_r = 0.910$ Calcd.	Exptl.	337.8° C., $T_r = 0.943$ Calcd.	Exptl.
1000	−0.88	−0.81	....	....	....	....
2000	−0.46	−0.38	−1.98	−1.93	....	....
2500	−0.27	−0.23	−1.15	−0.99	−2.48	−2.61
4000	+0.25	+0.27	+0.87	+0.90	+1.94	+2.02
6000	+0.74	+0.86	+2.18	+2.32	+4.40	+4.41

$(C_{cp} - C_p)_T$ cal./gram mole/° K.

This equation gives results generally not differing from reliable experimental values by so much as 5 per cent when constant B is determined from the critical point and boiling point. Somewhat better results are obtained if B is evaluated from a vapor pressure value less distant from the normal boiling point than the critical temperature, and if the actual compressibility factor of the vapor is used instead of the average value of 0.95.

HEAT CAPACITY DIFFERENCE BETWEEN SATURATED LIQUID AND ITS IDEAL GAS

By combining the equations developed above with the generalized expression for the effect of pressure on the enthalpy of gases, it is possible to derive a generalized thermodynamic method for calculating the difference between the heat capacity of a saturated liquid and the same material as an ideal gas at the same temperature and zero pressure. Such a
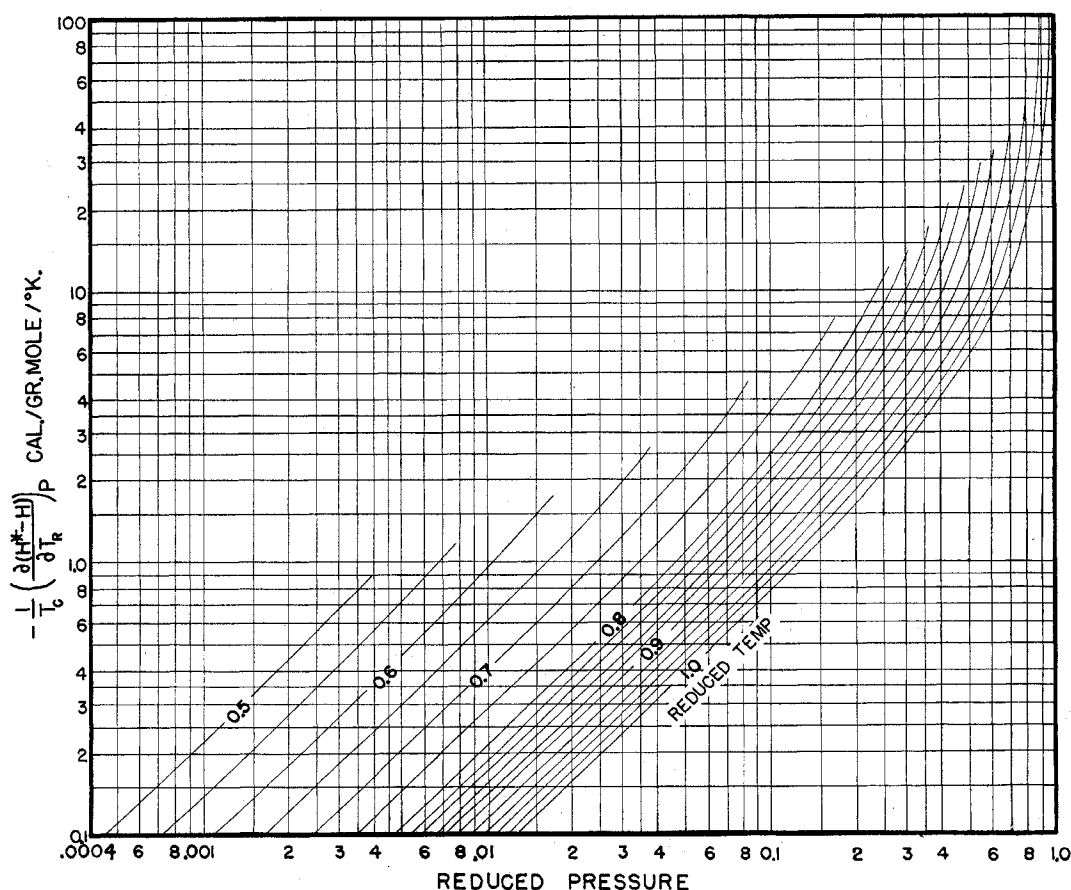

Figure 6. Differential Pressure Correction to Enthalpy of Gases

Combining Equations 13 and 19, an expression is obtained which permits calculation of the heat of vaporization of any substance at all conditions from a knowledge merely of the boiling point and critical temperature and pressure, since B is also found from T_c and P_c:

$$\lambda = 0.95RB \left(\frac{T_B}{T_B - 43}\right)^2 \left(\frac{1 - T_r}{1 - T_{rB}}\right)^{0.38} \tag{20}$$

Table XI compares values calculated from Equation 20 with experimental data for several compounds on which measurements were made at elevated temperatures. The deviations are of the same order as shown by Meissner's method; they are greater in some cases and less in others. Further comparisons indicated that the major source of error is Equation 19 rather than Equation 13, and the over-all accuracy is improved by using the actual compressibility factor at the boiling point instead of the average value of 0.95.

method is of considerable value because of the scarcity and general unreliability of heat capacity data. Recent development of generalized statistical methods (1, 6) derived from spectroscopic observations permits reasonably satisfactory prediction of the heat capacities of the more simple molecules in the ideal gaseous state. These methods, combined with a thermodynamic relation between gaseous and liquid heat capacities and the relations for thermodynamic properties of liquids developed above, will permit complete prediction of heat capacities at all conditions, both liquid and gaseous. Conversely, for complex high-boiling liquids on which liquid heat capacity measurements have been made, such a thermodynamic relation may offer a more reliable method of estimating gaseous heat capacities than the statistical methods. The relation will also be useful in rationalizing experimental observations of gaseous and liquid heat capacities and making them consistent with each other.

There are several methods by which a saturated liquid at temperature T_1 may be converted into a saturated vapor at a

higher temperature T_2. One is to heat the liquid (maintaining saturation) to T_2 and vaporize it. Another is to vaporize the liquid at T_1, isothermally expand the vapor to zero pressure, heat the ideal vapor to T_2, and isothermally compress to saturation conditions. Since the initial and final states are the same in both cases, the enthalpy changes of the two operations must be equal:

$$\lambda_1 + (H_1^* - H_{sg_1}) + C_{pg}^* (T_2 - T_1) - (H_2^* - H_{sg_2}) = \lambda_2 + C_{sl}(T_2 - T_1) \quad (21)$$

Rearranging and applying to an infinitesimal temperature change, dT,

$$(C_{sl} - C_{pg}^*) dT = - d\lambda - d(H^* - H_{sg})$$

$$C_{sl} - C_{pg}^* = - \frac{d\lambda}{dT} - \frac{d(H^* - H_{sg})}{dT} \quad (22)$$

Since the term $d(H^* - H_{sg})$ involves both a temperature and a pressure change, it must be expressed in terms of partial differentials:

$$\frac{d(H^* - H_{sg})}{dT} = \left[\frac{\partial(H^* - H_{sg})}{\partial T}\right]_p +$$
$$\left[\frac{\partial(H^* - H_{sg})}{\partial p}\right]_T \frac{dp_s}{dT} \quad (23)$$

All the terms on the right-hand side of Equation 24 may be obtained from generalizations, presumably applicable to all substances. Thus, differentiating Equation 20,

$$\frac{d\lambda}{dT_r} = \frac{-0.361RB}{(1 - T_{rB})^{0.38}} \left(\frac{T_B}{T_B - 43}\right)^2 \frac{1}{(1 - T_r)^{0.62}} \quad (25)$$

A generalized relation between $(H^* - H_s)$ and reduced temperature and pressure was introduced by Watson and Nelson (23) and improved by several others (8, 10, 24, 26). Graphical differentiation of this relation with respect to reduced temperature at constant pressure permits evaluation of the second term of Equation 24. The first part of the third term similarly may be evaluated by differentiation with respect to reduced pressure at constant temperature. The last part of the third term is evaluated by Equation 17.

For differentiation, a pressure-enthalpy correction chart for the gaseous state was prepared, taking into account the improved data calculated by Edmister (8) and York and Weber (26) and extended to the low reduced temperature range by the Joule-Thomson data on water (11). This chart was graphically differentiated with respect to temperature and pressure, and the data obtained are summarized in Figures 6 and 7 and in Tables XII and XIII. Because of the uncertainty of the basic enthalpy correction chart at conditions in
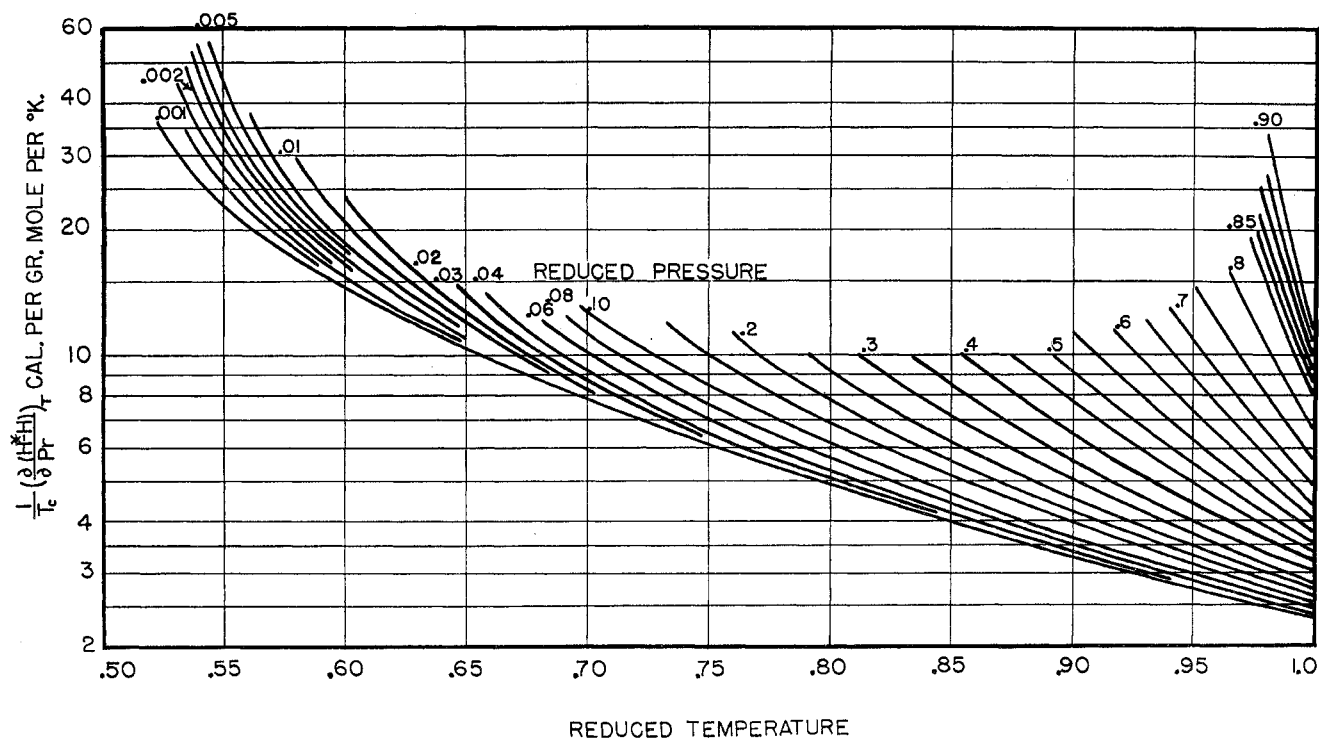

Figure 7. Differential Pressure Correction to Enthalpy of Gases

Substituting Equation 23 in 22 and writing in terms of reduced conditions,

$$C_{sl} - C_{pg}^* = - \left(\frac{d\lambda}{dT_r}\right)\frac{1}{T_c} - \left[\frac{\partial(H^* - H_s)}{\partial T_r}\right]_p \frac{1}{T_c} - \left[\frac{\partial(H^* - H_s)}{\partial p_r}\right]_T \frac{1}{P_c}\frac{dp_s}{dT} \quad (24)$$

the saturated region, particularly at low temperatures, the curves of Figures 6 and 7 were adjusted by cross plotting to obtain consistent relations which, when incorporated in Equation 24, gave the best average agreement with the ex-

Table XI.   Heats of Vaporization

Temperature, ° C.	λ, cal./gram mole Calcd.	λ, cal./gram mole Exptl.	Temperature, ° C.	λ, cal./gram mole Calcd.	λ, cal./gram mole Exptl.
WATER (12)					
83	9,680	9,890	277	6,380	6,720
115	9,250	9,530	307	5,460	5,740
147.5	8,800	9,110	322	5,020	5,240
180.5	8,300	8,660	335	4,500	4,670
210.5	7,740	8,140	348.5	3,850	3,980
245	7,100	7,470	364	2,960	3,040
			373.3	1,020	1,060
AMMONIA (21)					
−49.9	5,870	5,770	91.8	3,310	(3,180)
− 9.5	5,340	5,260	100	3,045	(3,050)
+31.0	4,690	4,640	108.1	2,730	(2,700)
71.6	3,870	(3,780)	116.2	2,340	(2,250)
			124.3	1,800	(1,640)
BENZENE (11)					
0	8,250	8,350	180	5,700	5,790
60	7,680	7,600	220	4,780	4,850
100	7,000	7,060	260	3,420	3,420
140	6,400	6,440	280	2,160	2,140
ETHYL ALCOHOL (11)					
0	10,450	10,110	160	6,950	7,150
40	9,760	9,900	200	5,650	5,280
80	8,970	9,350	220	4,260	3,960
120	8,090	8,350	240	1,990	1,760
BUTANE (19)					
24.9	5,140	5,050	110.9	3,380	3,170
67.9	4,400	4,310			
PROPANE (17)					
20.8	3,680	3,460	88.1	1,785	1,490
54.8	2,960	2,780	98.1	916	610
73.8	2,410	2,210			
SULFUR DIOXIDE (11)					
−10	5,930	6,090	40	5,180	4,950
+20	5,490	5,400	60	4,810	4,500

perimental values of $(C_{sl} - C_p^*)$ for water and ammonia. In all of this work Equations 16 and 18 were used for the calculation of vapor pressures, and it is recommended that this procedure be followed in using Figures 6 and 7.

Figure 7 is not in good agreement with $(\partial H/\partial P)_T$ data calculated by Kennedy, Sage, and Lacey (13) from their Joule-Thomson measurements on n-butane and n-pentane. Edmister (8) pointed out that the data of these investigators did not conform with his generalized relations. Similarly, Watson and Smith (24) found that a generalized plot of Joule-Thomson coefficients showed large differences from the experimental data. These discrepancies indicate that differentiation of the generalized enthalpy-pressure relation tends to magnify its inherent errors. It is probable that the absolute values of the

functions plotted in Figures 6 and 7 may differ from experimental values for some substances by as much as 50 per cent. However, it is hoped that these errors will tend to compensate one another when the two charts are used together in conjunction with Equation 24 and Equations 16 and 18 for calculating pressures.

Heat capacity data in general are so unreliable that it is difficult to find good comparable values on both the liquid and gaseous state with which to test Equation 24. Table XIV compares values calculated from the equation with experimental data for water, ammonia, pentane, butane, and propane. The experimental values for the hydrocarbons were taken from the general correlation of Holcomb and Brown (9) at temperatures below 70° F. These are actually heat capacities at constant pressure, but at reduced temperatures below 0.8 the difference from the heat capacity of the saturated liquid becomes small. At higher temperatures the data of Sage and co-workers from the indicated sources were selected. These investigators made actual measurements of the heat capacities of the saturated liquid.

The agreement in Table XIV is reasonably good except in the case of butane at the higher temperatures. Although these few comparisons do not confirm the reliability of Equation 24, it is encouraging that agreement is obtained on both nonpolar and highly polar compounds of both low and high boiling points. Figures 6 and 7 are not recommended for reduced temperatures above 0.96 or below 0.55. At reduced temperatures below 0.55 the difference between the heat capacity of the liquid and the ideal gas appears to approach independence of temperature, and it is believed that this assumption is preferable to attempting to extend Figure 7.

In the recommended temperature range it seems probable that the calculated heat capacity differences should not be in error by more than 25 per cent. Although much better accuracy is to be desired, such errors are not too serious, particularly when one is working with materials of high molal heat capacities for which the difference in heat capacities is

Table XII.   Values of $-\dfrac{1}{T_c}\left(\dfrac{\partial(H^* - H)}{\partial T_R}\right)_p$ in Small Calories per Gram Mole per ° K.

P_r	$T_r = 0.55$	$T_r = 0.6$	$T_r = 0.7$	$T_r = 0.8$	$T_r = 0.9$	$T_r = 0.95$	$T_r = 1.0$
0.001	0.140	...	...	...	....	....	....
0.002	0.275	0.181	...	...	....	....	....
0.003	0.415	0.270	0.121	...	....	....	....
0.006	0.88	0.55	0.242	0.126	....	....	....
0.01	...	0.95	0.40	0.210	0.128	....	....
0.02	...	...	0.80	0.42	0.254	0.195	0.158
0.03	...	...	1.23	0.63	0.38	0.29	0.186
0.06	...	...	2.82	1.33	0.77	0.59	0.47
0.1	...	...	...	2.46	1.34	1.0	0.79
0.2	...	...	...	7.0	3.12	2.20	1.63
0.4	...	...	...	...	9.5	5.7	4.0
0.5	...	...	...	...	18.5	8.6	5.7
0.7	...	...	...	...	....	27	11.4
0.9	...	...	...	...	....	....	33

Table XIII.   Values of $\dfrac{1}{T_c}\left(\dfrac{\partial(H^* - H)}{\partial P_r}\right)_T$ in Small Calories per Gram Mole per ° K.

P_r	$T_r = 0.55$	$T_r = 0.6$	$T_r = 0.7$	$T_r = 0.8$	$T_r = 0.9$	$T_r = 0.95$	$T_r = 0.98$	$T_r = 1.0$
0.001	25.2	14.6	7.8	4.88	3.29	2.73	2.48	2.32
0.002	32.0	15.8	7.9	4.88	3.29	2.73	2.48	2.32
0.005	46	17.5	8.0	4.88	3.29	2.73	2.48	2.32
0.01	..	20.8	8.1	4.88	3.29	2.73	2.48	2.32
0.02	..	24.0	8.2	4.88	3.29	2.73	2.48	2.32
0.03	..	..	8.5	5.0	3.35	2.73	2.48	2.32
0.06	..	..	10.1	5.25	3.4	2.80	2.50	2.34
0.10	..	..	12.8	6.05	3.65	3.00	2.64	2.44
0.2	..	..	..	7.8	4.20	3.29	2.88	2.63
0.3	..	..	..	11.7	5.0	3.70	3.15	2.84
0.5	..	..	..	...	9.0	5.45	4.15	3.5
0.6	..	..	..	...	..	7.3	5.05	4.0
0.7	..	..	..	...	..	10.9	6.6	4.8
0.8	..	..	..	...	..	...	10.7	6.6
0.85	..	..	..	...	..	...	15.0	8.1
0.90	..	..	..	...	..	...	34.0	11.2

Table XIV. Difference between Heat Capacities of Saturated Liquid and Its Ideal Gas

T_r	$T°$ C.	$(C_{sl} - C^*_{pg})$, cal./ g. mole/° K. Calcd.	Exptl.	T_r	$T°$ C.	$(C_{sl} - C^*_{pg})$, cal./ g. mole/° K. Calcd.	Exptl.
			WATER (12)				
0.55	83	11.0	10.0	0.85	277	14.4	13.6
0.60	115	11.5	10.1	0.90	307	17.0	16.4
0.65	147.5	11.5	10.3	0.92	322.5	18.6	18.0
0.70	180.5	11.8	10.7	0.94	335	20.7	20.7
0.75	210.5	11.9	11.2	0.96	348.5	28.0	25.1
0.80	245	12.3	11.6				
			AMMONIA (21)				
0.55	−49.9	9.8	9.8	0.85	71.6	12.9	12.6
0.60	−29.8	9.9	1.0	0.90	91.8	15.1	14.7
0.65	− 9.5	9.8	10.2	0.92	100.0	17.1	16.2
0.70	+10.7	10.4	10.5	0.94	108.1	16.9	17.8
0.75	31.0	10.7	10.9	0.96	116.2	19.9	20.9
0.80	51.3	11.4	11.5				
			n-PENTANE (9)				
0.55	−14.6	9.9	10.0	0.7	55.9	11.4	11.9
0.6	+ 8.9	10.1	10.4	0.8	103.9	11.6	13.6
			n-BUTANE (9, 15, 20)				
0.55	−39.1	8.7	7.6	0.8	67.9	10.3	14.4
0.6	−17.1	8.8	8.7	0.9	110.9	12.9	17.6
0.7	+24.9	9.4	10.9				
			PROPANE (9, 15, 20)				
0.55	−67.7	5.2	6.1	0.8	25.6	8.2	9.3
0.6	−49.1	5.8	6.4	0.9	63.0	13.5	13.4
0.7	−11.7	6.3	8.2				

small in comparison to the heat capacity of the vapor. At present no better general method for estimating these properties is available.

DIFFERENCE BETWEEN HEAT CAPACITY AT CONSTANT PRESSURE AND HEAT CAPACITY OF SATURATED LIQUID

The heat capacity of a saturated liquid C_{sl} expresses the change in enthalpy accompanying a simultaneous increase in both temperature and pressure:

$$C_{sl} = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial p}\right)_T \frac{dp_s}{dT} \tag{26}$$

In terms of reduced conditions,

$$(C_{pl} - C_{sl})_{TP} = -\left(\frac{\partial H}{\partial p_r}\right)_T \frac{1}{P_c}\left(\frac{dp_s}{dT}\right) \tag{27}$$

Values of $\dfrac{1}{P_c}\left(\dfrac{\partial H}{\partial p_r}\right)$ may be obtained from Figure 2, and dp_s/dT is calculated from Equation 17, permitting complete evaluation of Equation 27.

Table XV. Difference between Heat Capacity at Constant Pressure and Heat Capacity of Saturated Liquid (Water, 12)

$T°$ C.	T_r	$(C_p - C_s)$, cal./g. mole/° K. Calcd.	Exptl.
204.4	0.738	−0.08	−0.09
287.8	0.867	+0.33	+0.54
315.6	0.910	+0.92	+1.11
326.7	0.927	+1.75	+2.16
337.8	0.943	+3.0	+3.64

Table XV compares results calculated from Equation 27 with the accepted values for water. The agreement is not particularly good, but the quantity sought is not large except at conditions near the critical. Furthermore, it is believed that maximum errors are probably encountered when Figure 2 is applied to water because of the unusually low reduced pressures corresponding to a given reduced temperature at

saturation. As a result, saturation values for water fall on the extrapolated portion of Figure 2 at pressures below the range of the hydrocarbon data from which it was derived. Better accuracy should be obtained from Equation 27 when applied to other materials of lower critical pressures.

NOMENCLATURE

A, B = constants in Calingaert-Davis vapor pressure equation
C = heat capacity
C^* = heat capacity of ideal gas
d = liquid density
H = enthalpy
H^* = enthalpy of ideal gas
J = mechanical equivalent of heat
M = molecular weight
p = pressure
P = pressure
R = gas law constant
S = entropy
T = absolute temperature
v = molal volume
V = volume of n moles
z = compressibility factor (gaseous)
λ = molal heat of vaporization
ρ = liquid density, mass per unit volume
$\psi = \dfrac{J\rho_l}{P_c\omega_l}(H_{cp} - H)_T$
ω = liquid expansion factor

Subscripts
B = normal boiling point
c = critical value
cp = critical pressure
g = gaseous state
l = liquid state
r = reduced value
s = saturated liquid or vapor

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