Table I. Polymerization of Vinylidene Fluoride and 1-Chloro-1,2-difluoroethylene

Total Charge, Moles	Mole % CH_2CF_2, Charge/Copolymer	Initiation System	Pressure[a]	Reactor[b]	Time, Hours/° C.	Yield, %	$[n]_{inh}$	Remarks
0.03	50/low	A[c]	100-150	FP	96/60	50	0.09	Rather weak plastic
0.05	50/10	B[d]	100-150	FP	21/60	38	0.21	Leathery plastic
0.25	50/20	B[d]	300-500	M	120/50	56	0.8	Leathery rubber
0.21	83/85	B[d]	300-600	M	12/70	95	0.4	Crystalline plastic
0.004	50/52.5	Co^{60}	200-300	G	98/25	75	...	Hard pellet in bottom of reactor (95% CHFCFCl), film in top (52% CH_2CF_2)
0.03	100	A	100-150	FP	116/60	0	...	
0.03	100	B	100-150	FP	24/60	10	2.06	
0.25	100	B	460	M	36/60	24	...	
0.003	100	Co^{60}	200-300	G	24/25	30	...	

[a] Initial pressure at temperature, estimated. [b] FP. Fischer-Porter aerosol compatibility tube, 75 ml.; M. Monel Hoke cylinder, 90 ml.; G. Glass Carius tube, 3 ml. [c] $K_2S_2O_8$, 0.75 part; K_2HPO_4, 2 parts; Na lauryl sulfate, 3 parts; H_2O, 200 parts; monomers, 100 parts. [d] Same as (b), except NH_4 salt Kel-F Acid 8114 replaced the Na lauryl sulfate.

loss of lateral symmetry in progressing from a polymer chain composed of CF_2 units to one composed of CHF units.

A certain amount of difficulty was encountered before even a reasonably broad spectrum of copolymers could be obtained. Since the polymerization behavior of CH_2CF_2 is little discussed outside the patent literature, it is of interest to discuss briefly the experimental findings which are summarized in Table I. In initial experiments, CH_2CF_2 showed much less tendency than CHFCFCl to enter into the copolymer. This might be due to the difficulty in emulsifying significant amounts of this low-boiling reactant (the critical temperature of which is in the vicinity of room temperature). The higher boiling chloroolefin presented no such difficulty, as it was easily liquified under the conditions used. The use of fluorocarbon soap would be expected to increase the concentration of CH_2CF_2 in the liquid phase, and the proportion found in the resulting copolymer was correspondingly higher. Carrying out the reactions under higher pressure was even more effective. A polymerization initiated by Co^{60} gamma radiation presented an interesting situation. The CHFCFCl-rich liquid phase gave a polymer containing 95% CHFCFCl, and the CH_2CF_2-rich vapor phase gave a copolymer containing 52% CH_2CF_2. A concurrent series of experiments in which the homopolymerization of CH_2CF_2 was studied further illustrated the importance of pressure and an effective emulsifier. Thus CH_2CF_2 did not polymerize using a hydrocarbon emulsifier and a relatively low pressure (100 to 150 p.s.i.). Substitution of a fluorocarbon soap resulted in a low yield of polymer being obtained. Carrying out the reaction in a metal cylinder, where a higher pressure could be tolerated, resulted in a higher yield. Thus Co^{60} was more effective, even in a reaction which took place in the gas phase.

ACKNOWLEDGMENT

This work was supported by the George C. Marshall Space Flight Center, Huntsville, Ala. under Contract NAS **8-5352**, "Development of a Vulcanizable Elastomer Stable in Contact with Liquid Oxygen." John T. Schell acted as Technical Representative. The cooperation of R. J. Hanrahan and R. W. Gould, of the University of Florida, Gainesville, Fla. with the Co^{60} irradiations and the x-ray powder patterns, respectively, is appreciated.

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RECEIVED for review July 23, 1964. Accepted February 17, 1965.

Generalized Correlation for Latent Heat of Vaporization

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To calculate latent heats of vaporization, a simple analytical expression without using acentric factor was developed from the Pitzer tabular correlation. Graphical solutions with a nomogram are presented. Results are compared with the existing methods.

EXTENSIVE tabular values were presented in 1955 by Pitzer and associates *(13)*. Part of these values can be used for calculating quite accurately latent heats of vaporization at any temperature when acentric factor and critical temperature are known. Inasmuch as this method was not expressed in a convenient form and, to some extent, the prediction of the acentric factor by the Edmister method *(3)* is quite time consuming, it has been overlooked by many investigators for almost 10 years. This article extends their work by transforming their tabular correlation into analytical and graphical ones thereby eliminating use of the acentric factor.

GENERALIZED CORRELATION

Pitzer (*13*) tabulated a set of values of ΔS_v^0, ΔS_v^1, ΔS_v^2 at reduced temperatures from 0.56 to 1.00 and proposed to calculate the entropy of vaporization by the following equation:

$$\Delta S_v = \Delta S_v^0 + \omega \Delta S_v^1 + \omega^2 \Delta S_v^2 \tag{1}$$

where ω is the acentric factor defined by

$$\omega = -(\log_{10} P_{r0.7} + 1) \tag{2}$$

where $P_{r0.7}$ is the reduced pressure at reduced temperature $T_r = 0.7$. Hence, Equation 1 shows that when the reduced temperature and the acentric factor are known, the total entropy of vaporization which is the ratio of latent heat of vaporization to temperature can then be calculated. Consequently, a plot can be made of the total entropy of vaporization *vs.* the acentric factor at different reduced temperatures, which are shown as broken lines in Figure 1.

In the same article, they also presented another equation as follows:

$$\log_{10} P_r = \log_{10} P_r^0 + \omega \left(\frac{\partial \log_{10} P_r}{\partial \omega}\right)_T \tag{3}$$

Another set of values for $\log_{10} P_r^0$ and $(\partial \log_{10} P_r / \partial \omega)_T$ was tabulated at different reduced temperatures, where P_r^0 is the reduced pressure for a simple fluid and $(\partial \log_{10} P_r / \partial \omega)_T$ is the partial derivative of the $\log_{10} P_r$ with respect to acentric factor at constant temperature. Now from Equation 3, by knowing the reduced temperature and acentric factor, the corresponding reduced pressure can be calculated. Then a similar plot can be made of $\log_{10} P_r$ *vs.* the acentric factor at different reduced temperatures which are shown as solid lines in Figure 1.

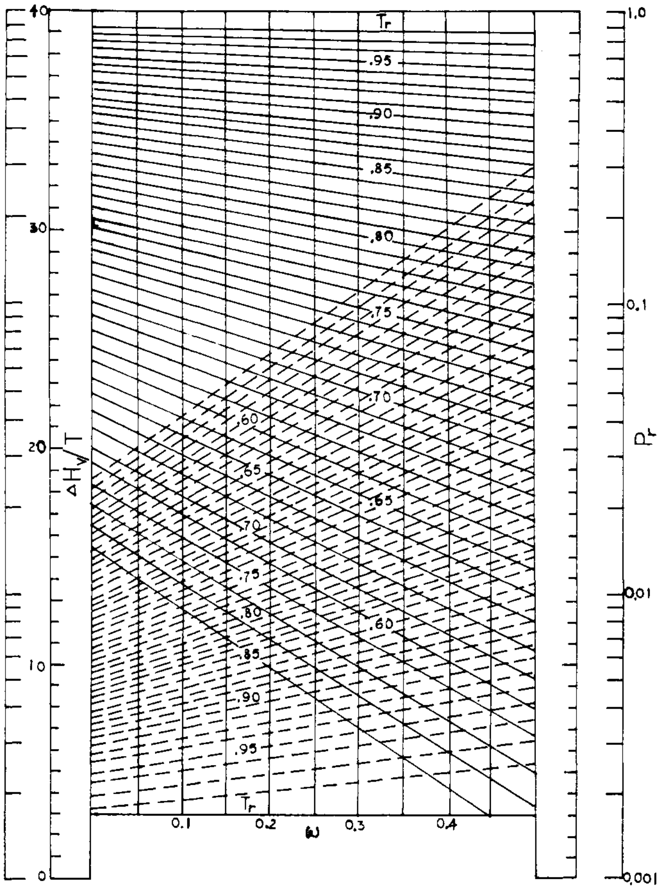


Figure 1. Generalized correlation chart

Figure 1 shows that the solid lines have the slopes of the partial derivative in Equation 3. Theoretically, the broken lines are not straight, which can be mathematically proved from Equation 1. However, at small values of acentric factor (usually less than one), inasmuch as the product of the squares of a small value of ΔS_v^2 would be very small, the last term in Equation 1 contributes very little to the total. Under this condition, the total entropy of vaporization is approximately linear with the acentric factor. This relationship is verified by the nearly straight lines which were plotted between small values of the acentric factor of zero to 0.5. In a manner perfectly analogous to that in Equation 3, these broken lines can be assumed to be represented to good approximation by

$$\Delta S_v = \frac{\Delta H_v}{T} = \left(\frac{\Delta H_v}{T}\right)^0 + \omega \left(\frac{\partial \Delta H_v / T}{\partial \omega}\right)_T \tag{4}$$

where $(\Delta H_v / T)^0$ may be defined as the entropy of vaporization of a simple fluid and is the value of $\Delta H_v / T$ when $\omega = 0$; that is, the intercept of the broken lines at $\omega = 0$. From Equation 1, it is seen that this value is equal to ΔS_v^0 in Pitzer's article. Evidently $[\partial(\Delta H_v / T) / \partial \omega]_T$ is the slope of the lines which can then be calculated.

Eliminating the acentric factor from Equations 3 and 4 gives:

$$\frac{(\Delta H_v / T) - (\Delta H_v / T)^0}{\log_{10} P_r - \log_{10} P_r^0} = \frac{\left(\dfrac{\partial \Delta H_v / T}{\partial \omega}\right)_T}{\left(\dfrac{\partial \log_{10} P_r}{\partial \omega}\right)_T} \tag{5}$$

The values of $(\Delta H_v / T)^0$, $\log_{10} P_r^0$, and $(\partial \log_{10} P_r / \partial \omega)_T$ were given in Pitzer's article. Those of $[\partial(\Delta H_v / T) / \partial \omega]_T$ are calculable. Hence Equation 5 can be simplified to

$$\log_{10} P_r = A\,(\Delta H_v / T) + B \tag{6}$$

where A and B are functions of reduced temperature. Figure 2 is such a plot which shows the linearity of the values of A and B with the reduced temperature. These two lines were then evaluated by the method of least squares. After substitution and simplification, Equation 6 becomes the proposed generalized correlation as follows:

$$\log_{10} P_r = (0.1406 T_r - 0.1504)(\Delta H_v / T) + (1.11 T_r - 1.1) \tag{7}$$

HEAT OF VAPORIZATION AT NORMAL BOILING POINT

Equation 7 can be rearranged to give the latent heat of vaporization at normal boiling point as

$$\Delta H_{vb} = \frac{T_b\,(7.11 \log_{10} P_c - 7.82 + 7.9\, T_{rb})}{1.07 - T_{rb}} \tag{8}$$

With the input data of normal boiling point, critical temperature, and critical pressure, values of latent heat of vaporization for 165 compounds were calculated by means of this proposed Equation 8, the Giacalone equation (*5*), the Riedel equation (*15*), and the modified Klein equation (*4, 8*). These calculated values were compared with the corresponding literature values (experimental or calculated) which were taken from reliable sources, (*6, 10-12*). The critical pressures and critical temperatures were taken from the article by Kobe and Lynn (*9*) which was considered reliable by many investigators. The boiling temperatures were taken from reliable sources (*2, 12*). The comparison of these results is found in Table I. The proposed correlation plot is shown in Figure 3. For 165 compounds, the deviations of the calculated from the literature values are 2.40% by the Giacalone, 2.02% by the Riedel, 1.85% by the modified Klein, and 1.82% by the proposed equation.

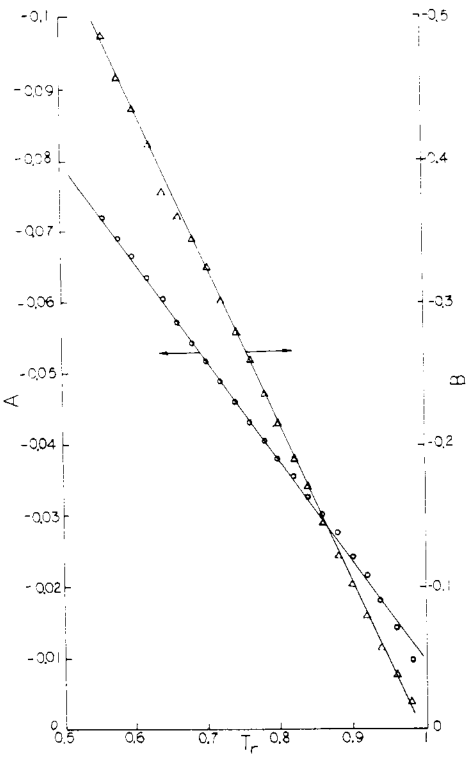


Figure 2. Linear plot of *A* and *B* vs. T_r

Table I. Latent Heat of Vaporization at Normal Boiling Point by Different Methods

Compound Group	No. of Substances Tested	Deviation, %			
		Giacalone	Riedel	Modified Klein	Proposed Eq. 8
Monoatomic gases	4	3.85	0.97	1.22	0.70
Diatomic gases	8	2.97	1.22	1.96	1.45
Inorganic halides	7	2.23	2.77	2.69	2.78
Inorganic oxides	4	3.55	2.04	2.24	1.71
Miscellaneous inorganics	8	2.44	2.08	1.82	2.15
Aliphatic hydrocarbons (satd.)	39	2.25	1.50	1.06	1.13
Aliphatic hydrocarbons (unsatd.)	11	3.02	1.40	1.43	0.98
Cycloparaffins	5	1.38	1.08	0.68	1.16
Aromatic hydrocarbons	15	1.51	1.61	1.55	1.60
Substituted aromatics	11	2.59	2.21	2.33	2.16
Alcohols	5	3.69	2.87	2.97	2.92
Amines	8	3.05	2.85	3.75	3.30
Esters	9	1.96	1.18	1.43	1.59
Ethers	4	0.62	1.22	1.45	1.58
Nitriles	5	7.88	8.31	7.60	7.12
Organic halides	13	1.10	2.80	1.50	1.62
Miscellaneous organics	9	1.20	2.00	1.35	1.85
Grand total	165	2.40	2.02	1.85	1.82

HEAT OF VAPORIZATION AT ANY TEMPERATURE AND ANY PRESSURE

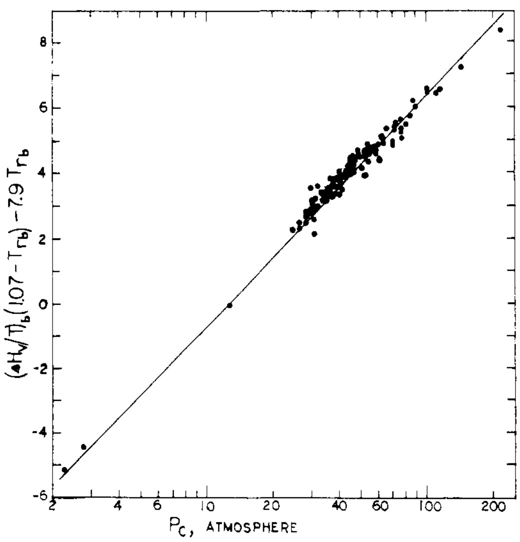
The proposed Equation 7 relates the latent heat of vaporization at any temperature with the corresponding reduced temperature and reduced vapor pressure. It is useful in checking the thermodynamic table in which the temperature and vapor pressure are usually given. For 12 compounds, Table II lists the ranges of the reduced temperature and the corresponding vapor pressures, the number of points within these ranges, and the average deviation from the literature values by different methods. Column 5 is the deviation by Equation 7. Column 6 is the deviation calculated by the combined equation of the Giacalone (*5*) and the Watson (*18*) as recommended by Reid and Sherwood (*12, 14*). For 58 point values, the average deviation is 2.55% by Equation 7 and 3.36% by the Giacalone-Watson correlation. With the given input data, T, T_b, T_c, and P_c, the values can also be found from Figure 1 or the nomogram Figure 4 which was constructed from Equation 7.

LATENT HEAT OF VAPORIZATION AT ANY TEMPERATURE

When the normal boiling point, the latent heat of vaporization at this temperature, and the critical temperature are given, the latent heats at any other temperature can be calculated. To this end, the Watson correlation (*18*) has been considered as the most accurate one for a great variety of compounds. However, it can also be accomplished by Equation 4 which can be rearranged as

$$(\Delta H_v/T)_T = (\Delta H_v/T)^0_T + \frac{[(\Delta H_v/T)_b - (\Delta H_v/T)^0_b]}{\left(\frac{\partial\,\Delta H_v/T}{\partial\omega}\right)_b}\left(\frac{\partial\,\Delta H_v/T}{\partial\omega}\right)_T \quad (9)$$

where the subscripts T and b denote the temperature in question and the boiling temperature, respectively. The values of the compounds in Table II calculated by the



← Figure 3. Correlation at normal boiling point

→ Figure 4. Generalized nomogram for latent heat of vaporization at any temperature and pressure

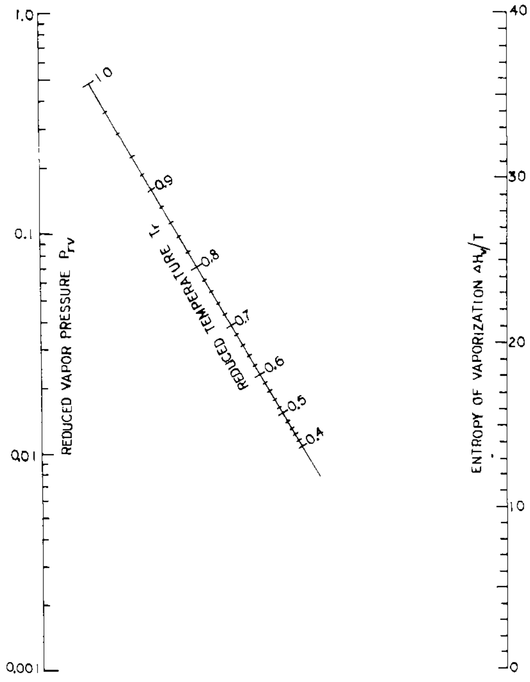


Table II. Latent Heat of Vaporization at Temperatures and Pressures other than Normal Boiling Point and Atmosphere by Different Methods

Compound	T_r	P_r	No. of Points	Eq. 7	Giacalone-Watson	Watson	Eq. 9	Fig. 1
Ammonia (*12*)[a]	0.549–0.803	0.0036 –0.20	5	0.81	2.18	0.27	0.61	0.41
Benzene (*17*)	0.771–0.978	0.14 –0.84	6	1.80	6.96	6.35	7.29	5.48
Ethylene (*12*)	0.512–0.985	0.00338–0.890	4	6.40	2.70	1.23	0.75	1.27
Ethyl alcohol (*17*)	0.792–0.970	0.108 –0.756	4	2.48	1.95	3.41	5.65	4.03
Ethyl ether (*16*)	0.63 –0.964	0.0167 –0.758	4	1.25	3.09	2.54	3.17	2.09
Methane (*1*)	0.523–0.941	0.00751–0.70	5	1.82	2.27	2.78	1.75	0.86
Methylamine (*12*)	0.6 –0.739	0.00925–0.0911	6	2.55	3.89	0.72	0.80	0.91
Methyl formate (*12*)	0.615–0.684	0.0138 –0.0442	4	1.51	2.78	1.76	2.61	2.41
Nitrogen (*1*)	0.567–0.95	0.0149 –0.745	4	4.48	2.07	2.86	3.15	3.43
Sulfur dioxide (*12*)	0.594–0.915	0.00897–0.528	6	2.08	4.93	1.43	1.69	2.08
Trichlorofluoromethane (*12*)	0.625–0.720	0.0211 –0.0832	5	0.77	0.32	0.98	1.26	1.26
Water (7)	0.566–0.91	0.0036 –0.482	5	5.56	5.54	1.66	1.82	1.11
	Grand total		58	2.55	3.36	2.18	2.52	2.20

[a] Numbers in parentheses designate the references at the end of the article.

Watson equation (*18*) and Equation 9 compare with the literature values in columns 7 and 8. For 58 point values, the average deviation is 2.18% by the Watson equation and 2.52% by Equation 9. Because the use of Equation 9 is not very convenient, and its accuracy is not as good as the Watson equation, its use is recommended only when the Watson equation is in doubt.

LATENT HEAT OF VAPORIZATION AT ANY PRESSURE

Sometimes it is necessary to find the latent heat of vaporization at pressures other than one atmosphere with the additional input data of critical temperature, critical pressure, and the normal boiling point. If we use Equations 3 and 4, the method of trial and error is required. With the input data, the acentric factor can be estimated from Equation 3. Then a value of T_r should be tried to satisfy Equation 3 for other pressures. With this value of reduced temperature, either the proposed Equation 7 or Equation 4 can be used to find the value of latent heat at the given reduced pressure. To provide a rough estimate and avoid this tedious trial and error method, Figure 1 can be used in a very convenient way. The procedures are: Locate the imaginary ω at the abscissa for the given T_c, P_c, and T_b (It is not necessary to record this value); For this value of ω, locate T_{r_1} corresponding to P_{r_1}; For this value of ω and T_{r_1}, then find $\Delta H_{v_1}/T_1$. For these same data, the Watson and the other three equations fail to give a result. Again for the same compounds in Table II, column 9 tabulates the values from Figure 1 for different pressure (assuming the corresponding temperatures are not given) with the input data thus described.

CONCLUSIONS

Inasmuch as the proposed equation was developed from a sound theoretical background, it is expected that the accuracy should be good. Table I shows that the accuracy of the proposed equation is better than those of the Giacalone and the Riedel equations; it is at least as good as the modified Klein equation which is more complicated. Table II shows that Equation 7 is better than the Giacalone-Watson equation. Besides, for the input data of T_b, P, P_c, and T_c, only the proposed Equation 7 can give the value of ΔH_v, whereas the Watson and the other three correlations cannot. With all of these advantages, the use of Equations 7 and 8, Figure 1, and the nomogram is recommended with an over-all uncertainty not greater than 2% which is believed to be within the experimental error.

NOMENCLATURE

A = function of reduced temperature in Equation 6
B = function of reduced temperature in Equation 6
ΔH_v = molal latent heat of vaporization, cal. per mole
P = pressure, atm.
P_c = critical pressure, atm.
P_r = reduced pressure
P_r^0 = reduced pressure for a simple fluid
ΔS_v = entropy of vaporization = $\Delta H_v/T$, cal. per mole per ° K.
T = temperature, ° K.
T_b = boiling temperature, ° K.
T_{rb} = reduced boiling temperature
T_c = critical temperature, ° K.
T_r = reduced temperature
ω = acentric factor
$(\Delta H_v/T)^0$ = entropy of vaporization for a simple fluid

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RECEIVED for review May 27, 1964. Accepted December 21, 1964.