

PART - A.

CHAPTER - 6

C O N C L U S I O N

Chapter 6C O N C L U S I O N .

6.1 The following conclusions have thus been arrived at:-

- (i) The necessity of theoretical estimation of thermodynamic properties exists even if sophisticated methods are now available for experimental determination. Theoretically estimated values are required not only for choosing the ranges of equipments and instruments required for experimental work and verification of experimentally obtained values, but also to estimate the property values at points beyond experimental ranges.
- (ii) Many investigators have suggested different equations of state for Freon refrigerants since 1930 but all of them have one short coming or another. The Martin-Hon equation of 1955 appear to give the best results upto one and a half times the critical value.
- (iii) Enthalpy measurement methods as described in Chapter 2 are likely to give more accurate results from engineering point of view.
- (iv) Theoretically estimated critical properties compare well with experimentally determined values. Hence it is expected that the critical properties given in chapter 3 for refrigerants whose critical properties have not yet

- been experimentally determined, can be safely used.
- (v) The theoretically calculated values of ideal gas heat capacities of many refrigerants, which have been given in Chapter 4, will be very useful to refrigeration design engineers. This method can also be safely used for estimating low pressure gas heat capacities of mixtures of refrigerants.
 - (vi) The generalised method, based on the theory of corresponding states with some modifications, gives sufficiently accurate results for Freon 12 and Freon 11 gases. It is expected that this method will also give accurate results for other Freon refrigerants, in saturated vapour and superheated gaseous states.
 - (vii) The experimental values rather than theoretical values for liquid enthalpy and liquid entropy of Freon refrigerants, are to be used for design calculations.
 - (viii) The p-h diagram and h-s diagram of Freon 11 as given in Chapter 5 will be useful for Freon turbine designers as these charts have been drawn well into the supercritical region.

Appendix No.1Table No. 1

Vowles's constants to be used in Eq.3.1

(From C.Vowles, S.M.Thesis in Chemical Engg., MIT, 1951)

Carbon	-0.5592
Hydrogen	0.2375
Fluorine	0.3042
Chlorine	0.2983
Double Bond(c=c)	0.5640

Table No. 2Reidel's & Lydersen's constants to be used in Eqs.3.2 & 3.3. → Tc → Tc

All bonds indicated with a dash are connected to atoms other than Hydrogen.

Group	ΔT	
	Riedel's*†	Lydersen's
-CH ₃ , -CH ₂ -	0.016	0.020
- $\begin{array}{c} \\ \text{CH} \\ \end{array}$ -----	0.013	0.012
- $\begin{array}{c} \\ \text{C} \\ \end{array}$ -----	0.003	0.00
H -----	0.00	0.00
- F -----	0.015	0.018
- Cl -----	0.013	0.017

* L.Riedel, Chem-Ing-Tech, 24; 353 (1952)

Ref No. 20.

Table No. 3Vowles' constants to be used in eq.3.4 (for ρ_c)

Carbon	1.02
Hydrogen	1.95
Fluorine	3.63
Chlorine	7.45
C = C	2.50

Table No. 4Riedel's constants to be used in eqn.3.5 (for ρ_c)

Hydrogen	0.00
Carbon	0.23
Fluorine	0.23
Chlorine	0.32
C = C	-0.06

Table No. 5Lydersen's constants to be used in eqn.3.6 (for ρ_c)

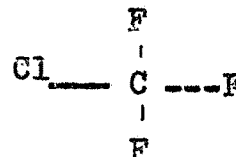
-CH ₃ and -CH ₂ -	0.227
-CH-	0.210
-C-	0.210
- F	0.224
- Cl	0.320

Table No. 6Vowles's constants to be used for calculating V_c .

	<u>Increment</u> <u>cm³/g.mole</u>
Carbon	23.0
Hydrogen	17.0
Fluorine	33.1
Chlorine	63.5
C = C	13.2

Table No. 7Lydersen's constants to be used for calculating V_c .

	<u>Increment</u> <u>cm³/g.mole</u>
Base value	40
- CH ₃ and - CH ₂ -	55
-OH	51
-C-	41
-F	18
-Cl	49

Appendix No. 2Sample calculations for the estimation of
Critical Properties of F 13, C Cl F₃.Critical Temperature:

(i) Vowles's method, Ref.No. [19]

$$T_c = \frac{T_b}{\theta}, \quad T_b = 192^\circ\text{K}$$

$$\begin{aligned} \theta &= 1(\text{C}) + 1(\text{Cl}) + 3(\text{F}) \\ &= (-0.5592) + (0.2983) + (3 \times 0.3042) \\ &= 0.6517 \end{aligned}$$

$$T_c = \frac{192}{0.6517} = 294.5^\circ\text{K}$$

(ii) Riedel's method, Ref. No. [19]

$$T_c = \frac{T_b}{\theta}$$

$$\begin{aligned} \theta &= 0.574 + \sum \Delta T \\ &= 0.574 + 0.003 + 0.013 + (3 \times 0.015) \\ &= 0.635 \end{aligned}$$

$$T_c = \frac{192}{0.635} = 302.5^\circ\text{K}$$

(iii) Lydersen's method, Ref. No. [20]

$$T_c = \frac{T_b}{\theta}$$

$$\begin{aligned} \text{where } \theta &= 0.567 + \sum \Delta T - [\sum \Delta T]^2 \\ &= 0.567 + 0.017 + (3 \times 0.018) - 0.005 \\ &= 0.633 \end{aligned}$$

$$T_c = \frac{192}{0.633} = 303.5^\circ\text{K}$$

Critical Pressure:

(i) Vokles's method, Ref. No. [19]

$$P_c = \left(\frac{T_c}{\gamma} \right)^{1.25}$$

where γ = sum of atomic and structural contributions.

$$\begin{aligned} T_c &= 294.5^\circ\text{K, calculated above} \\ &= 1.02 + 7.45 + (3 \times 3.63) \\ &= 19.36 \end{aligned}$$

$$\begin{aligned} P_c &= \left(\frac{294.5}{19.36} \right)^{1.25} \\ &= 39 \text{ atm.} \end{aligned}$$

(ii) Riedel's method, Ref. No. [19]

$$P_c = \frac{M}{(\phi + 0.33)^2}$$

where M = Mol. wt.

 ϕ = sum of atomic and structural constants.

$$M = 104.45$$

$$\phi = (0.23) + (0.32) + (3 \times 0.23) = 1.24$$

$$P_c = \frac{104.45}{(1.24 + 0.33)^2} = 42.3 \text{ atm.}$$

(iii) Lydersen's method, Ref. No. [20]

$$P_c = \frac{M}{(\phi + 0.34)^2}$$

where ϕ has different values from those of Riedel's method

$$\begin{aligned} \phi &= (0.21) + (0.32) + (3 \times 0.224) \\ &= 1.202 \end{aligned}$$

$$P_c = \frac{104.45}{(1.202 \times 0.34)^2}$$

$$= 51.45 \text{ atm.}$$

Critical Volume:

(i) Vowles's method, Ref. No. [19]

$$V_c = 1(C) + 1(Cl) + 3(F)$$

$$= 23 + 63.5 + (3 \times 33.1)$$

$$= 188.8 \text{ cubic centimeters/gm.mole}$$

(ii) Lydersen's method, Ref. No. [20]

$$V_c = 40 + 41 + 49 + (3 \times 18)$$

$$= 184 \text{ cubic centimeters/gm. mole.}$$

Appendix No. 3

Table No. 1.

Bond frequencies and constants used for evaluating C_p^* .

Bond	Stretching vibrations			Bending vibrations				
	δ -wave number cm^{-1}	A	B x 10^3	C x 10^6	δ -wave number cm^{-1}	A	B x 10^3	C x 10^6
C - I, S - S	500	0.181	4.664	-3.338	260	1.461	1.730	-1.272
C - Br	560	-0.073	5.158	-3.591	280	1.242	2.046	-1.501
C - Cl, C - S	650	-0.562	6.385	-4.495	330	1.023	2.590	-1.874
C-C, C-N, N-N	990	-1.090	6.000	-3.441	390	0.730	3.414	-2.577
C-O, N-O	1,030	-1.173	6.132	-3.555	205	1.461	1.633	-1.414
C-F, C=S	1,050	-1.123	5.845	-3.253	530	0.011	5.119	-3.699
C=C, C=N	1,620	-0.432	1.233	0.935	345	-1.140	7.254	-4.936
C=O, N=O	1,700	-0.324	0.724	1.308	390	0.730	3.414	-2.577
S - H	2,570	0.129	-1.333	2.263	1,050	-1.128	5.845	-3.253
C-H, N-H	2,920	0.229	-1.224	1.658	1,320	-0.938	3.900	-1.342
O - H	3,420	0.150	-0.810	1.055	1,150	-1.135	5.363	-2.749

*From C.J. Dobratz, Ind. Eng. Chem., 33:759 (1941).

Appendix No. 4.Sample calculations of thermodynamic properties.

The thermodynamic properties of Freon 12 have been calculated at the following five state points, to show the use of the equations given in chapter No.5.

- (i) Saturated liquid at 233°K (-40°F);
- (ii) Saturated vapour at 233°K;
- (iii) Ideal gas at 233°K;
- (iv) Ideal gas at 350°K; and
- (v) Gas at 350°K, 10 atmosphere pressure.

The points have been shown numbered in Fig.5.1. The available data for Freon 12 are:

$$\begin{aligned} \lambda_b &= 70.9 \text{ Btu/lb} \\ T_b &= 244^\circ\text{K} \\ T_c &= 384.7^\circ\text{K}, \\ P_c &= 40.86 \text{ atmospheres} \\ Z_c &= 0.278 \end{aligned}$$

Point 1:

$$T_1 = 233^\circ\text{K.}, \quad T_r = \frac{233}{384.7} = 0.605$$

Equation (5.7) has to be used for finding the vapour pressure at this temperature. For normal boiling point,

$$\begin{aligned} P_r &= \frac{1 \text{ atmosphere}}{40.86 \text{ atmospheres}} \\ T_r &= \frac{244}{384.7} = 0.634 \end{aligned}$$

The values of ϕ and ψ for this value of T_r are 1.69 and 0.292 respectively. [19.7]

$$\begin{aligned}\log_{10} 40.86 &= 1.69 + (\alpha_c - 7) \times 0.292 \\ (\alpha_c - 7) &= -0.274\end{aligned}$$

Substituting the value of $(\alpha_c - 7)$ and the corresponding values of ϕ and ψ for $T_{r1} = 0.605$ we get

$$\log_{10} \frac{1}{p_{r1}} = 1.924 - 0.274 \times 0.34$$

$$p_{r1} = \frac{p_1}{p_c} = 0.01476$$

$$p_1 = 0.603 \text{ atmosphere} = 8.85 \text{ lb per sq. in.}$$

The data given in Reference 1 indicates the value of 9.3076 lb. per sq. in. at -40°F . Since p_{r1} is less than 0.1, Watson's equation (5.8) has to be used to find the latent heat:

$$T_b = 244^\circ\text{K.}, T_{rb} = \frac{244}{384.7} = 0.634$$

$$\lambda_b = 70.9 \text{ B.Th.U. per lb.} = 4,760 \text{ calories per gm. molecule}$$

$$\begin{aligned}\lambda_1 &= 4,760 \times \left(\frac{1 - 0.605}{1 - 0.634} \right)^{0.38} \\ &\approx 4,900 \text{ calorie per gm. molecule} \\ &= 73 \text{ B.Th.U. per lb.}\end{aligned}$$

$$\text{From Ref. No. 1, } \lambda_1 = 72.913 \text{ Btu/lb.}$$

For the datum at -40°F. ,

$$H_1 = 0, S_1 = 0$$

Point 2

$$H_2 = H_1 + \lambda_1 = 4,900 \text{ calorie per gm.-molecule}$$

$$S_2 = \frac{4,900}{293} = 21.05 \text{ calorie per gm. molecule per } ^\circ\text{K.}$$

Point 3

From Table 3 in Reference 24, for $p_{r3} = 0.01422$
and $T_{r3} = 0.605$,

$$\frac{H_3^* - H_2}{T_c} \text{ at saturation (for vapour)} = 0.04$$

$$H_3^* - H_2 = 0.04 \times 384.7 = 15.4$$

$$H_3^* = 15.4 + 4,900 = 4915.4 \text{ calorie per gm.-molecule}$$

From Reference 24 (Table 3)

$$S_3^* - S_2 = 0.0508$$

$$S_3^* = 21.05 + 0.0508 = 21.1 \text{ calorie per gm.-molecule per } ^\circ\text{K.}$$

Point 4

$$\Delta H^* = H_4^* - H_3^* = \int_3^4 C_p^* dT = \int_{233}^{350} (7.153 + 43.73 \times 10^{-3} T - 29.416 \times 10^{-6} T^2) dT$$

$$= 2,046$$

$$H_4^* = 6,961.4 \text{ calorie per gm.-molecule}$$

$$S_4^* - S_3^* = \int_3^4 C_p^* \frac{dT}{T} = 7.153 \times 2.303 \times \log_{10} \frac{350}{233} + 43.73 \times 10^{-3} (350 - 233) - \frac{29.416}{2} \times 10^{-6} (350^2 - 233^2) = 7.1$$

$$S_4^* = S_3^* + 7.1 = 28.2 \text{ calorie per gm.-molecule per } ^\circ\text{K.}$$

Point 5

$$T_{r5} = \frac{350}{384.7} = 0.91, \quad p_{r5} = \frac{10}{40.86}$$

$$= 0.242 \text{ as } p_5 = 10 \text{ atm.}$$

From Table 3 in Reference 24,

$$\frac{H_4^* - H_5}{T_c} = 0.767$$

Therefore

$$H_5 = H_4^* - 0.067 \times 384.7 = 6,666.4 \text{ calories per gm-molecule}$$

$$S_5 = S_3^* + \int_{233}^{350} c_p \frac{dT}{T} - (S_4^* - S_5^*)_T - (S_5^* - S_5)$$

where $S_3^* = 21.1 \text{ Cal/gm.mole } ^\circ\text{K}$ (already found)

$$\int_{233}^{350} c_p \frac{dT}{T} = 7.1 \text{ Cal/gm.mole } ^\circ\text{K}$$

$$(S_4^* - S_5^*)_T = R \ln \frac{p_5}{p_1} = 5.64$$

(R being 1.986 Cal/gm.mole $^\circ\text{K}$)

$$S_5^* - S_5 = 0.6616 \text{ (Table No.11, Ref. 24)}$$

$$\begin{aligned} \therefore S_5 &= 21.1 + 7.1 - 5.64 - 0.6616 \\ &= 21.9 \text{ Cal/gm.mole } ^\circ\text{K.} \end{aligned}$$
