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Short Communication

Molecular weight predicts critical temperature

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Abstract

The critical temperatures of hydrocarbons and related compounds are predicted by using molecular weights. The correlation.

$$T_c = A + B \log (M + C)$$

predicts the critical temperature with an average and maximum deviation of 0·34% and 2·1% respectively.

Key words: Critical temperature, hydrocarbon, mixture, molecular weight.

Several correlations to predict the critical properties, in particular the critical temperature are available in literature[1]. Grunberg and Nissan[2], and Mathur *et al*[3] have tried to correlate the critical temperature with the molecular weight. Grunberg *et al* have pointed out that T_c^3 of paraffins is proportional to the molecular weight. Mathur *et al* have proposed the correlation

$$T_c = A + B. \log M \tag{1}$$

for hydrocarbons and related compounds. The drawback of this correlation is that it predicts very low or high values for the critical temperature for the first few members of the homologs considered.

In the present correlation a third constant C is introduced. overcomes the drawback of the previous correlation and also predicts critical temperature better. The new correlation is

Table I

Values of the constants in the equation $T_o = A + B \log (M + C)$ for hydrocarbons and related compounds

Sl. No.	Series	Number of points	*A*	*B*	*C*	Present work		Mathur *et al*[3]	
						Av. Abs. devn. %	Max. devn. %	Av. Abs. devn. %	Max. devn. %
1.	*n*-Paraffins	20	—540·7207	531·8967	7·855	0·30	—2·06	0·68	—75·6*
2.	*n*-Monoolefins	19	—492·266	511·8547	4·551	0·46	1·20	0·73	—5·0*
3.	*n*-Alkynes	10	—384·720	469·165	4·497	0·53	—1·45	0·82	—6·91*
4.	*n*-Alkylbenzenes								
	(*a*) Up to C_{25}	20	—192·904	405·863	—6·087	0·26	0·64	0·67	1·73
	(*b*) Above C_{25}	14	738·165	55·505	—307·78	0·12	0·29	0·33	0·92
5.	Cyclopentanes								
	(*a*) Up to C_{25}	21	—365·651	467·057	2·492	0·44	—1·57	0·54	10·62*
	(*b*) Above C_{25}	13	653·486	89·182	—277·754	0·14	0·31	0·24	0·55
6.	Cyclohexanes								
	(*a*) Up to C_{25}	20	—450·395	505·897	8·115	0·54	—1·75	0·51	—3·50*
	(*b*) Above C_{25}	17	223·211	252·716	—84·918	0·24	0·59	0·27	0·66

* Not included in the calculation of average deviation.

$$T_c = A + B. \log (M + C) \quad (2)$$

The constants in the eqn. (2) are evaluated by the use of nonlinear least squares technique. The constants A,B,C for the various groups of compounds are presented in Table I along with the average percentage deviations obtained by the present equation and that of Mathur *et al*[3]. Experimental critical temperature data were taken from elsewhere[3-5]. Equation (2) predicts the critical temperature for hydrocarbons and related compounds* with an average absolute and maximum deviation of 0·34% and 2·1% respectively.

Extension to mixtures

Equation (2) is also applied to several mixtures. The constants A, B and C for mixtures are calculated using the constants of pure components by making use of the combining rule.

$$Y_{mixt} = X_1 Y_1 + X_2 Y_2 \quad (3)$$

Where X_1 and X_2 are the mole fractions ; Y_1, Y_2 and Y_{mixt} are the corresponding constants of pure components (1), (2) and the mixture respectively. Average molecular weight is used as the input data for mixtures. Table II gives the average

Table II

Average percentage deviations and maximum deviations of calculated T_c from experimental values for mixtures

Sl. No.	System	Reference	No. of compo-sitions	Average absolute Devn.%	Max. Devn. %
1.	*n*-Hexane-Benzene	6	6	1·02	1·23
2.	Benzene-Toluene	6	4	0·11	—0·18
3.	Ethylene-Propylene	10	7	1·53	—2·23
4.	Ethane-Butane	8	5	2·30	—2·88
5.	Butane-n-Heptane	9	5	0·77	—1·25
6.	Ethane-Propylene	7	10	1·22	—2·25
7.	*n*-Pentane-Cyclohexane	6	5	1·31	—1·76
8.	*n*-Pentane-Benzene	6	5	1·08	2·00
9.	*n*-Hexane-Toluene	6	3	0·42	0·57
10.	Cyclohexane-Benzene	6	6	0·61	—1·42
11.	Cyclohexane-Toluene	6	4	0·62	—1·08
12.	*n*-Pentane-Toluene	6	4	1·52	2·10
13.	*n*-Hexane-Cyclohexane	6	3	0·45	—0·95
14.	Propane-Pentane	11	4	0·33	—0·54
	Average			1·0	

* Detailed tabular material giving deviations for individual substances and for various compositions in the case of mixtures is available with the authors.

percentage deviations and the number of points considered for various mixtures. Equation (2) predicts critical temperature of 14 mixtures with average absolute and maximum deviations of 1·0% and 2·3% respectively.

References

1. Reid, R. C. and Sherwood, T. K. — *The properties of gases and liquids*, 2nd edition, McGraw-Hill Book Co., 1966.
2. Grumberg, L. and Nissan, A. H. — *Nature*, 1948, **161**, 170.
3. Mathur, B. C., Ibrahim, S. H. and Kuloor, N. R. — *Chem. Engng.*, March 24, 1964, 182.
4. Dreisbach, R. R. — *Physical properties of chemical compounds*, Vols. I and II Advances in Chemistry Series, A.C.S. Publications, 1955.
5. Kobe, K. A. and Lynn, R. E. — *Chem. Rev.*, 1953, **52**, 117.
6. Partington, E. J., Rowlinson, J. S. and Weston, J. F. — *Trans. Farad. Society*, 1960, **56**, 479.
7. Mokay, R. A., Reamer, H. H., Sage, B. H. and Lacey, W. N. — *Ind. Engng. Chem.*, 1951, **43**, 2112.
8. Kay, W. B. — *Ind. Engng. Chem.*, 1940, **32**, 353.
9. Kay, W. B. — *Ind. Engng. Chem.*, 1941, **33**, 590.
10. Haselden, G. G., Holland, F. A., King, M. B., and Strickland, R. F. — *Proc. Roy. Society (Lond.)*, 1957, **240A**, 1.
11. Sage, B. H. Lacey, W. N. — *Ind. Engng. Chem.*, 1940, **32**, 992.