Estimation of Vapor and Liquid Enthalpies

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The Lydersen-Greenkorn-Hougen (L-G-H) charts correlating the isothermal pressure effects on enthalpy for pure compounds based on a modified corresponding states principle have been improved with the aid of reliable literature data. To facilitate machine computations, the improved charts, divided into the superheated vapor region, the subcooled liquid region, the saturated vapor, and the saturated liquid lines, have been expressed in analytical forms. This correlation reproduces the literature enthalpy data including those in the critical region for pure compounds with an average deviation of about 5 B.t.u./lb. It can also be used for the estimation of enthalpies of nonpolar mixtures with satisfactory results.

The enthalpy of a pure compound is a function of both temperature and pressure. At zero pressure all gases behave ideally, and the enthalpy becomes independent of pressure. The calculation of vapor enthalpy at zero pressure can be easily made from ideal gas heat capacities which are available in the literature (*23, 37*) for many compounds. At elevated pressures the enthalpy of a fluid relative to its enthalpy as an ideal gas can be calculated from the pressure-volume-temperature data by using thermodynamic relationships. In the absence of P-V-T data for the compound of interest, or if the data do not cover the condition under which engineering calculations are to be made, generalized correlations have been found of great value in estimating enthalpies. Lydersen, Greenkorn, and Hougen (*26*) presented in both graphical and tabular form a correlation of the enthalpy departure from ideal gas behavior based on a modified theory of corresponding states. Although their values of $(H^\circ - H)/T_c$ were obtained from a general correlation which represents the P-V-T data of eighty-two compounds within 3%, the accuracy of their enthalpy correlation has not been well established, as their values of $(H^\circ - H)/T_c$ were compared with literature enthalpy data for only three compounds. In addition. their graphical and tabular forms of correlation are convenient only for manual calculations. With the increasing use of digital computers in process design calculations, it is desirable to express the correlation in analytical forms. It is the purpose of this paper to improve and establish the accuracy of L-G-H charts with the aid of reliable enthalpy data of pure compounds from the literature, to convert the graphical correlations in analytical forms for machine computations, and to apply them to the estimation of mixture enthalpies.

TABLE 1. SOURCES OF ENTHALPY DATA

Compound	Z_c group	Temp. range, °F.	Pressure range, lb./sq. in. abs.	Source
Methane	0.29	—260 to 500	10 to 1,500	(*28*)
Ethane	0.29	—140 to 500	10 to 1,500	(*1*)
Isobutane	0.29	60 to 280	14.7 to 400	(*39*)
Hydrogen	0.29	—440 to 1,100	14.7 to 7,000	(*34, 49*)
Nitrogen	0.29	—320 to 500	10 to 1,500	(*3*)
Oxygen	0.29	—300 to 300	14.7 to 4,000	(*22*)
Air	0.29	—320 to 540	25 to 10,000	(*17, 25, 48*)
Carbon disulfide	0.29	30 to 1,500	2.46 to 1,000	(*31*)
n-butane	0.27	40 to 540	14.7 to 1,500	(*35*)
n-pentane	0.27	100 to 570	10 to 3,000	(*5*)
n-hexane	0.27	30 to 540	14.7 to 600	(*46*)
n-heptane	0.27	210 to 1,040	1 to 150 atm.	(*42*)
Ethylene	0.27	—160 to 500	14.7 to 4,000	(*50*)
Propylene	0.27	—60 to 480	14.7 to 3,000	(*6*)
i-butene	0.27	30 to 480	14.7 to 1,000	(*45*)
Acetylene	0.27	30 to 5,000	14.7 to 2,000	(*47*)
Benzene	0.27	100 to 1,800	14.7 to 3,000	(*32*)
Chlorine	0.27	—130 to 540	1 to 1,400	(*20*)
Carbon dioxide	0.27	—140 to 1,840	1 to 20,000	(*43*)
Sulfur dioxide	0.27	—20 to 500	10 to 4,600	(*19, 38*)
Diethyl ether	0.27	30 to 600	14.7 to 1,000	(*40*)
Freon-12	0.27	—160 to 500	0.14 to 600	(*16*)
Ammonia	0.25	—40 to 400	14.7 to 300	(*44*)
Nitric oxide	0.25	—80 to 920	10 to 3,000	(*33*)
Ethylene oxide	0.25	120 to 300	0 to 540	(*29*)
Ethyl alcohol	0.25	30 to 470	14.7 to 800	(*36*)
Water	0.23	32 to 1,600	0.25 to 5,500	(*21*)
Acetone	0.23	150 to 750	14.7 to 2,000	(*30*)

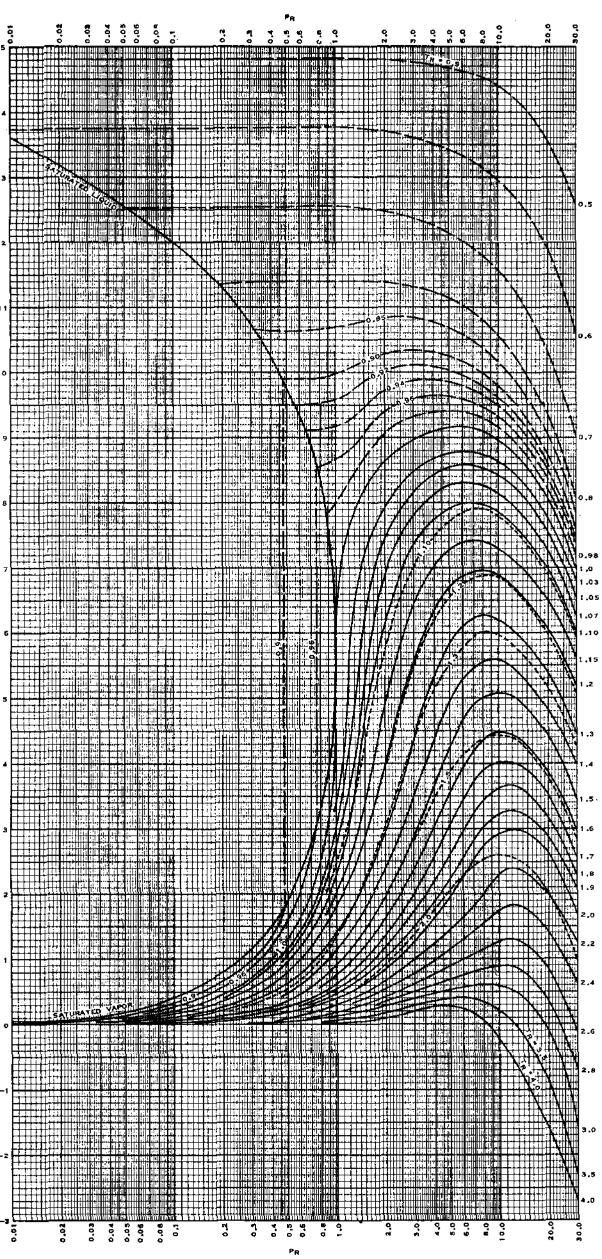

Fig. 1. Enthalpy departure from ideal gas behavior for fluids, $z_c = 0.27$. — — — — liquid, ———— vapor, - - - - - - - - - Lydersen-Greenkorn-Hougen.

IMPROVEMENT OF LYDERSEN-GREENKORN-HOUGEN CHARTS

Reliable enthalpy data for twenty-eight compounds from the literature were collected. The compounds, temperature and pressure ranges, and data sources are listed in Table 1. The compounds are classified into four groups according to their Z_c values: 0.29, 0.27, 0.25, and 0.23. Values of $(H^\circ - H)/T_c$ calculated as a function of P_r and T_r for each Z_c group were superimposed on the L-G-H charts. The L-G-H charts were then modified or extended, wherever necessary, to better represent the literature enthalpy data.

Among the four L-G-H charts, only the one for $Z_c = 0.27$ covers a reduced pressure range of 0.01 up to 30 as the reduced temperature ranges from 0.5 to 15. There are very little enthalpy data in the literature for the liquid region except those along the saturated liquid lines. The original correlation of Lydersen, Greenkorn, and Hougen was therefore adopted without any modification. In the vapor region, there was a definite discrepancy between the majority of the literature data selected and the L-G-H charts at high reduced pressures. These lines were modified in order to better represent the literature data, and the final graphical correlation is shown in Figure 1. Several lines from the original L-G-H charts are also given for comparison. The isotherms at reduced temperatures above 4, as given by Lydersen et al., could not be verified owing to the lack of enthalpy data. They are not included in this work.

For Z_c of 0.29, the highest reduced pressure covered in the L-G-H chart is 1.2. Literature data were used extensively to extend the L-G-H chart to a reduced pressure of 30 and a reduced temperature of 25. The results are shown in Figure 2. The charts for Z_c of 0.25 and 0.23 (Figures 3 and 4) were developed in a similar manner. Where no literature data were available, isotherms were extended to high pressures with the aid of the chart for Z_c of 0.27.

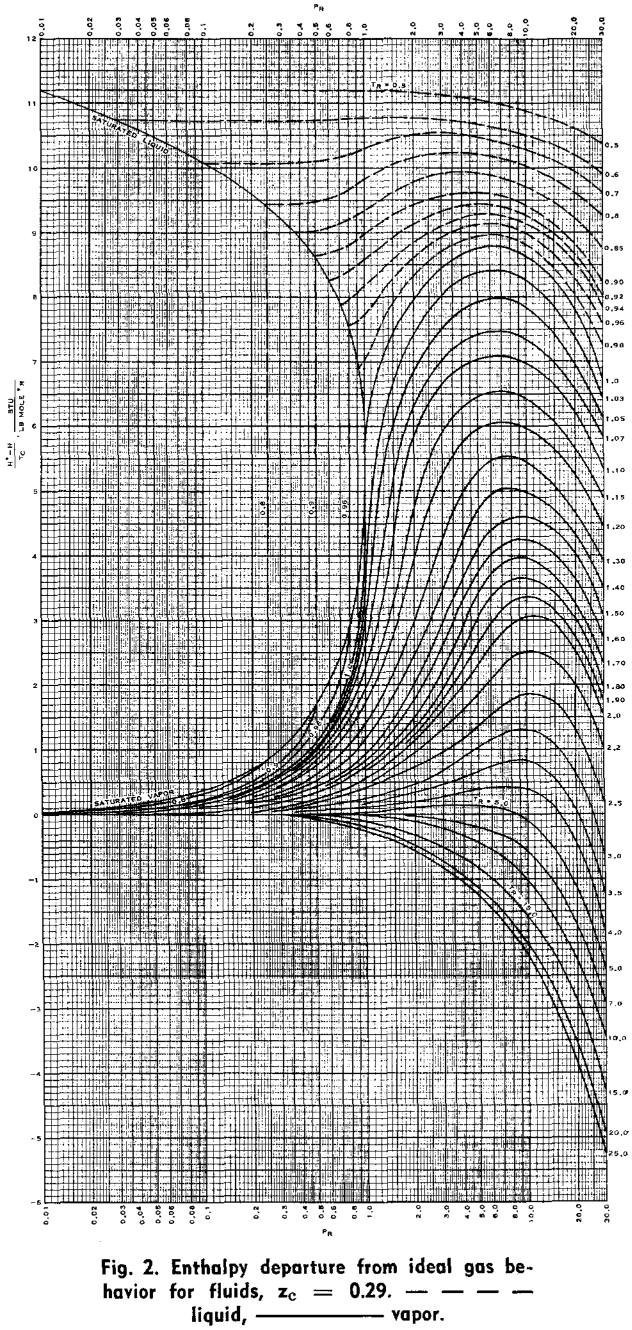

Fig. 2. Enthalpy departure from ideal gas behavior for fluids, $z_c = 0.29$. — — — — liquid, ———— vapor.

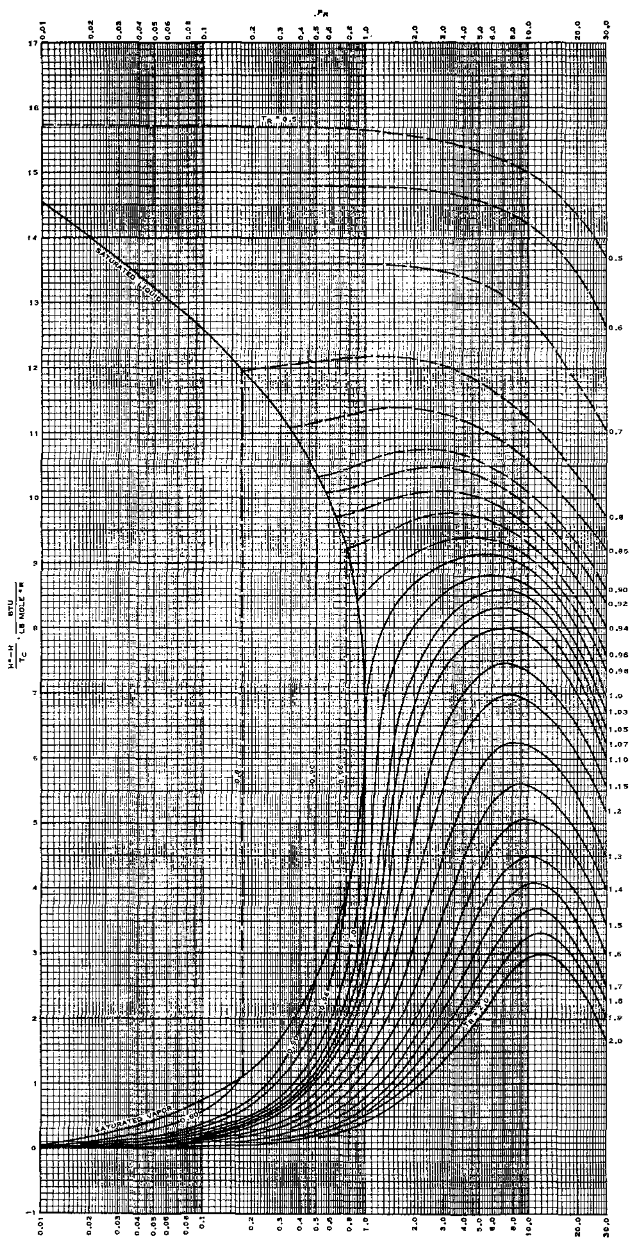

Fig. 3. Enthalpy departure from ideal gas behavior for fluids, z_C = 0.25. — — — — liquid, ———— vapor.

Owing to the limited amount of data, the highest reduced temperature is 2.0 and 1.7 in the charts for Z_c of 0.25 and of 0.23, respectively.

The four improved charts* reproduce the literature data listed in Table 1 with an average deviation of about 5 B.t.u./lb. including the critical region where the deviation can be as high as 15 B.t.u/lb. The deviation around the critical region is generally the highest among the deviations found in this work. This is partially due to the uncertainties of the literature enthalpy data calculated from equations of state, and partially due to the approximate nature of the corresponding states theorem.

To further check the reliability of these charts, calculated results were compared with some recently published data which were not used in the construction of the charts. In order to have a severe test of the correlation, points selected for comparison were at the highest pressure and extreme temperatures available. Data at temperatures around critical were also included. This test provides a good indication of possible errors one would expect in using these improved charts for the estimation of vapor and liquid enthalpies of various pure compounds. For thirty-six points tested, as shown in Table 2, the average deviation is 5.5 B.t.u./lb., quite close to the deviation found for the compounds listed in Table 1.

When T_r is above 1.2 and P_r is above 3, where major modification was made on the L-G-H charts, it can be seen from Table 2 that the improved charts give better results than those obtained from the original L-G-H charts. The L-G-H charts can not be used to calculate the values of $(H^\circ - H)/M$ in Table 2 for compounds in the group of $Z_c = 0.29$, since the pressures are higher than the highest pressure available in the L-G-H charts.

Generally, the Z_c value of a given compound is not exactly 0.29, 0.27, 0.25, or 0.23. The one chart for the

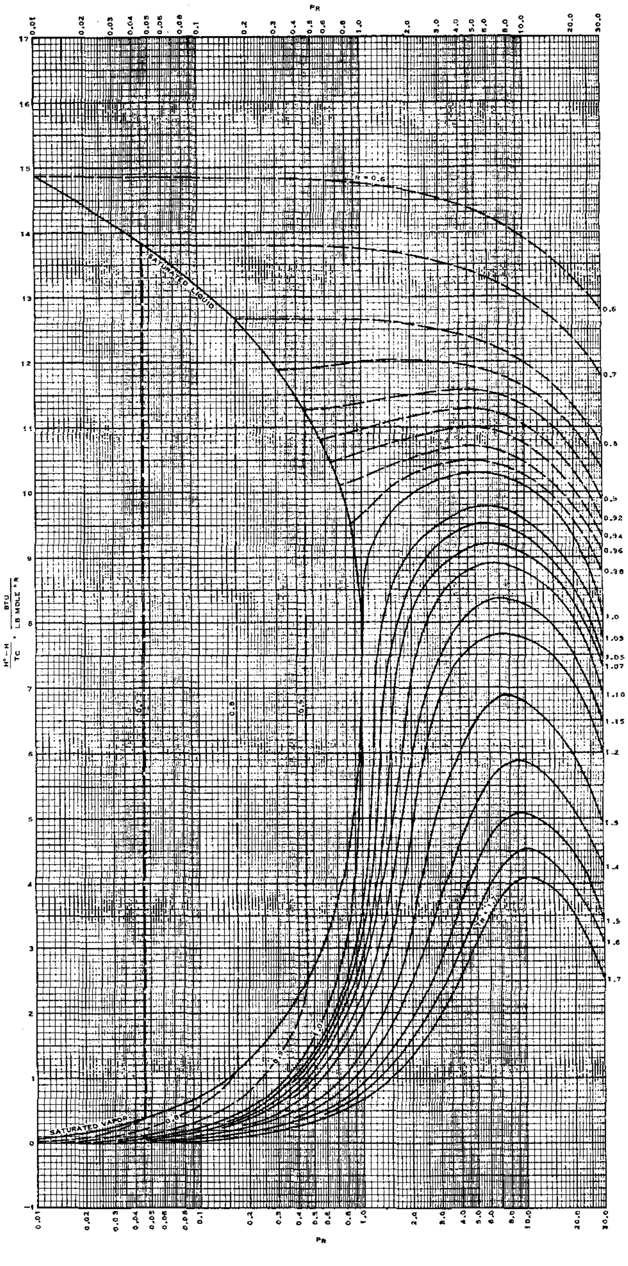

Fig. 4. Enthalpy departure from ideal gas behavior for fluids, z_C = 0.23. — — — — liquids, ———— vapor.

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* Large size charts are available from the authors and will be sent to the reader upon request.

nearest Z_c value is used in the calculations presented in this paper. For most engineering applications, this procedure has been found to offer sufficient accuracy as shown in Table 2.

ANALYTICAL EXPRESSIONS OF IMPROVED CHARTS

To facilitate machine computations, the values of $(H^\circ - H)/T_c$ were read from the four improved charts and converted into analytical expressions representing the superheated vapor region, the subcooled liquid region, the saturated vapor, and the saturated liquid lines. The process of curve fitting was done by trial and error with the aid of a computer program on nonlinear estimation. The final equations were developed according to the least-squares criterion and represent the charts to within ±0.1 B.t.u./lb.-mole/°R. in $(H^\circ - H)/T_c$, an accuracy much better than that of the curves in representing the literature enthalpy data. These equations, given in Table 3*, are used to calculate the values of $(H^\circ - H)/M$ in the comparison with recent enthalpy data as given in Table 2. It can be seen that the results obtained from the charts and those from the equations agree well.

The analytical expression for the saturated vapor and saturated liquid lines based on the original L-G-H charts have been given by Stevens and Thodos (*41*). Calculated results from their equations, however, do not reproduce the values given by Lydersen et al, over the entire saturated line. At $T_r = 1.0$, $(H^\circ - H)/T_c$ calculated from the equations of Stevens and Thodos as saturated vapor is 4.03 B.t.u./lb.-mole/°R. for $Z_c = 0.27$ compared with 5.80 by Lydersen et al. In addition, the saturated vapor and saturated liquid lines with their equations do not meet at $T_r = 1$. Therefore, analytical expressions developed in this work are presented and included in Table 3.

ESTIMATION OF MIXTURE ENTHALPIES

Stevens and Thodos (*41*) demonstrated the application of the L-G-H charts for pure compounds to the estimation of mixture enthalpies at the saturated states using pseudocritical constants. The same application can be made in the estimation of mixture enthalpies in the superheated vapor state. A nonpolar system of nitrogen and methane is selected, since reliable data for this system are available from the Institute of Gas Technology (IGT) (*2*). The calculated values of $(H^\circ - H)/M$ for two-vapor mixtures of nitrogen and methane, 10% nitrogen and 90% methane and 30% nitrogen and 70% methane, at −100°F. and

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* Tabular material has been deposited as document 8256 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or $1.25 for 35-mm. microfilm.

TABLE 2. COMPARISON OF CORRELATION WITH LITERATURE DATA

				$(H^\circ - H)/M$, B.t.u./lb.				
					This work			
Compound	P_r	T_r	Phase	Lydersen et al.	Chart	Equation	Literature	Reference
Nitrogen	6.10	2.240	Vapor		16.2	16.9	17.5	*27*
($Z_c = 0.291$)		1.011	Vapor		70.3	69.9	61.9	
		0.660	Liquid		85.2	87.1	77.4	
Methane	14.87	1.921	Vapor		67.0	70.5	69.5	*7*
($Z_c = 0.290$)		1.339	Vapor		105.1	104.7	109.0	
	7.43	1.921	Vapor		67.7	69.7	66.1	
		1.339	Vapor		113.7	110.7	118.0	
		0.582	Liquid		227.0	231.5	195.3	
Ethane	9.861	1.673	Vapor		74.1	75.7	77.0	*8*
($Z_c = 0.284$)		1.018	Vapor		154.0	152.5	136.6	
		0.655	Liquid		189.7	193.5	182.0	
	4.226	1.673	Vapor		58.5	56.7	54.0	
		1.018	Vapor		154.4	153.1	143.6	
		0.655	Liquid		193.7	197.3	199.0	
i-butane	5.670	1.442	Vapor		58.6	56.7	62.6	*12*
($Z_c = 0.283$)		1.170	Vapor		79.4	80.1	93.5	
		0.762	Liquid		130.0	131.9	134.5	
Carbon monoxide	2.899	3.550	Vapor		4.1	4.1	3.4	*22*
($Z_c = 0.294$)								
Propane	4.859	1.530	Vapor	54.5	59.2	59.8	60.9	*9*
($Z_c = 0.277$)		1.171	Vapor	104.3	105.8	105.0	105.0	
		0.690	Liquid	185.4	185.4	186.1	170.5	
n-butane	5.448	1.319	Vapor	72.4	75.7	76.1	77.5	*10*
($Z_c = 0.274$)		1.058	Vapor	111.2	111.2	110.4	108.3	
		0.718	Liquid	156.4	156.4	157.5	150.0	
n-pentane	8.171	1.347	Vapor	66.6	69.2	68.1	75.2	*11*
($Z_c = 0.269$)		1.017	Vapor	105.1	103.9	104.2	105.8	
		0.662	Liquid	144.0	144.0	142.3	145.7	
Carbon dioxide	3.740	2.738	Vapor	4.0	3.6	2.8	3.4	*13*
($Z_c = 0.275$)		1.752	Vapor	27.4	28.3	28.5	33.4	
	1.122	1.059	Vapor	44.9	44.8	49.3	44.9	*24*
		1.004	Vapor	87.8	89.4	86.0	97.0	
		0.958	Liquid	109.5	109.5	111.9	114.4	
Methyl chloride	4.648	1.174	Vapor	101.0	102.1	102.1	99.7	*18*
($Z_c = 0.276$)		1.014	Vapor	133.0	132.6	133.1	138.4	
n-propyl alcohol	0.9485	1.034	Vapor	51.2	51.2	51.8	51.2	*14*
($Z_c = 0.251$)	0.5420	1.034	Vapor	21.1	22.5	22.8	23.5	
				Absolute deviation	5.5	5.7		

pressures of 100 to 1,500 lb./sq. in. abs. show an average deviation from the IGT data of less than 2 B.t.u./lb., with either the charts or the equations used.

Pseudocritical constants of the mixture are obtained by using Kay's rule which combines the critical constants of the components as follows:

$$Z_c' = \sum_{i=1}^{N} n_i Z_{ci} \tag{1}$$

$$T_c' = \sum_{i=1}^{N} n_i T_{ci} \tag{2}$$

$$P_c' = \sum_{i=1}^{N} n_i P_{ci} \tag{3}$$

Brewer and Geist (*4*) compared different methods for calculating vapor mixture enthalpies with reference to the IGT data for the nitrogen-methane system. They found that the method of Hougen and Watson was not as satisfactory as some of the other methods. It should be noted that the method of Hougen and Watson they used was the one based on the reduced temperature and reduced pressure only before the introduction of Z_c as the third parameter. With the present method used, the calculated results are much improved and indeed as good as those obtained from other methods.

Stevens and Thodos (*41*) pointed out that better results could be obtained from the use of the actual critical constants of the mixture, when such information is available. For the nitrogen-methane mixture studied here, the pseudocritical constants are not much different from the actual critical constants. The calculated results would not be significantly improved even if the actual critical constants were used.

The same method can be applied to the estimation of mixture enthalpy in the subcooled liquid region, but no reliable literature data are available to check the calculated results.

Vapor or liquid mixtures involving polar compounds are not expected to obey Kay's rule very well, although many pure polar compounds are correlated well individually by Figures 1, 2, 3, and 4. Costa and Smith (*15*) reported enthalpy data for mixtures of benzene and *n*-propanol. As pure compounds, the enthalpy deviation from ideal gas for benzene and *n*-propanol can be predicted reasonably well by the present method. However, for their mixtures, the deviation of calculated results from the literature data become much higher than that for each pure compound, even if the actual critical constants are used. For example, in the superheated vapor region at 380°F. and 200 lb./sq. in. abs. for a mixture of 48 mole % benzene and 52% *n*-propanol, the calculated value of $(H^\circ - H)/M$ is 34 B.t.u./lb. compared with 53 B.t.u./lb. measured by Costa and Smith. The use of the charts presented in this work and Kay's rule to mixture enthalpy calculations should therefore be limited to nonpolar systems.

CONCLUSION

The Lydersen-Greenkorn-Hougen charts correlating the enthalpy departure from ideal gas have been improved to better represent the literature enthalpy data for pure compounds. The analytical expressions developed for the improved charts should be useful for machine computations in the supply of enthalpy values to process calculations. Comparisons made show that the calculated results are in good agreement with the literature enthalpy data. The correlation, although developed for pure compounds, can be used to estimate enthalpies for mixtures of nonpolar compounds.

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NOTATION

C = coefficient
H = enthalpy, B.t.u./lb.-mole
H° = enthalpy of ideal gas, B.t.u./lb.-mole
M = molecular weight
m = coefficient
N = number of components in a mixture
n = mole fraction
P = pressure, lb./sq. in. abs.
P_c = critical pressure, lb./sq. in. abs.
P_c' = pseudocritical pressure, lb./sq. in. abs.
P_r = reduced pressure
T = temperature, °R.
T_c = critical temperature, °R.
T_c' = pseudocritical temperature, °R.
T_r = reduced temperature
X_o = coefficient
Z_c = critical compressibility factor
Z_c' = pseudocritical compressibility factor

Subscript

i = ith component

LITERATURE CITED

1. Barkelew, C. H., J. L. Valentine, and C. O. Hurd, *Trans. Am. Inst. Chem. Engrs.*, **43**, 25 (1947).
2. Bloomer, O. T., B. E. Eakin, R. T. Ellington, and D. C. Gami, *Res. Bull. 21,* Inst. of Gas Technol., Chicago, Illinois (1955).
3. Bloomer, O. T., and K. N. Rao, *Res. Bull. 18,* Inst. of Gas Technol., Chicago, Illinois (1952).
4. Brewer, J., and J. M. Geist, *J. Chem. Eng. Data,* **6**, 405 (1961).
5. Brydon, J. W., N. Walen, and L. N. Canjar, *Chem. Eng. Progr. Symposium Ser. No. 7,* **49**, 151 (1953).
6. Canjar, L. N., M. Goldman, and H. Marchman, *Ind. Eng. Chem.*, **43**, 1186 (1951).
7. Canjar, L. N., and F. S. Manning, *Hydrocarbon Process. Petrol. Refiner,* **41**, No. 9, 253 (1962).
8. ———, V. M. Tejada, and F. S. Manning, *ibid.*, No. 10, 149 (1962).
9. ———, N. R. Patel, and F. S. Manning, *ibid.*, No. 11, 203 (1962).
10. ———, F. D. Gensini, and F. S. Manning, *ibid.*, No. 12, 115 (1962).
11. —————, *ibid.*, **42**, No. 1, 129 (1963).
12. Canjar, L. N., D. Nahmias, and F. S. Manning, *ibid.*, No. 8, 127 (1963).
13. Chen, L. H., "Thermodynamic and Transport Properties of Gases, Liquids and Solids," p. 358, Am. Soc. Mech. Engrs., New York (1959).
14. Cosner, J. L., J. E. Gagliardo, and T. S. Storvick, *J. Chem. Eng. Data*, **6**, 360 (1961).
15. Costa, E. C., and J. M. Smith, *ibid.*, **8**, 289 (1963).
16. E. I. Dupont de Nemour and Co., "Thermodynamic Properties of Freon-12," (1955 and 1956).
17. Gerhart, R. V., F. C. Brunner, H. S. Mickley, B. H. Sage, and W. N. Lacey, *Mech. Engr.*, **64**, 270 (1942).
18. Hsu, C. C., Ph.D. dissertation, Univ. of Texas, Austin, Texas (1963).
19. Kang, T. L., and J. J. McKetta, *A.I.Ch.E. Journal*, **7**, 418 (1961).
20. Kapoor, R. M., and J. J. Martin, "Thermodynamic Properties of Chlorine," Engr. Res. Inst., Univ. of Mich., Ann Arbor, Michigan (1957).

21. Keenan, J. H., and F. G. Keyes, "Thermodynamic Properties of Steam," Wiley, New York (1936).
22. Keesom, W. H., A. Bijl, and J. F. A. A. Van Ireland, *Appl. Sci. Res. Section A*, **5**, 349 (1955).
23. Kobe, K. A., and Associates, "Thermochemistry of Petrochemicals," Bur. of Eng. Res., Univ. of Texas, Reprint No. 44, Austin, Texas.
24. Koppel, L. B., and J. M. Smith, *J. Chem. Eng. Data,* **5**, 437 (1960).
25. Landsbaum, E. M., W. S. Dodds, W. F. Stevens, B. J. Sollami, and L. F. Stutzman, *A.I.Ch.E. Journal,* **1**, 302 (1955).
26. Lydersen, A. L., R. A. Greenkorn, and O. A. Hougen, *Wisc. Univ. Eng. Exp. Sta. Rept. No. 4* (October, 1955).
27. Mage, D. T., M. L. Jones, Jr., D. L. Katz, and J. R. Roebuck, Paper presented at 48th National A.I.Ch.E. Meeting, Denver (August 26-29, 1962).
28. Matthews, C. S., and C. O. Hurd, *Trans. Am. Inst. Chem. Engrs.*, **42**, 55 (1946).
29. Mock, J. E., and J. M. Smith, *Ind. Eng. Chem.*, **42**, 2125 (1950).
30. Moore, D. A., Ph.D. thesis, Univ. of Mich., Ann Arbor, Michigan (1952).
31. O'brien, L. J., and W. J. Alford, *Ind. Eng. Chem.*, **43**, 506 (1951).
32. Organick, E. I., and W. R. Studhalter, *Chem. Eng. Progr.*, **44**, 847 (1948).
33. Opfell, J. B., W. G. Schlinger, and B. H. Sage, *Ind. Eng. Chem.*, **46**, 189 (1954).
34. Phillips Petroleum Company, unpublished data.
35. Prengle, H. W., L. R. Greenhaus, and R. York, *Chem. Eng. Progr.*, **44**, 863 (1948).
36. Reid, R. C., and J. M. Smith, *ibid.*, **47**, 415 (1951).
37. Rossini, F. D., K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Project 44, Carnegie Press, Pittsburgh, Pennsylvania (1953).
38. Rynning, D. F., and C. O. Hurd, *Trans. Am. Inst. Chem. Engrs.*, **41**, 265 (1945).
39. Sage, B. H., and W. N. Lacey, *Ind. Eng. Chem.*, **30**, 873 (1938).
40. Schnaibal, H. C., and J. M. Smith, *Chem. Eng. Progr. Symposium Ser. No. 7,* **49**, 159 (1953).
41. Stevens, W. F., and George Thodos, *A.I.Ch.E. Journal,* **9**, 293 (1963).
42. Stuart, E. B., K. T. Yu, and J. Coull, *Chem. Eng. Progr.*, **46**, 311 (1950).
43. Sweigert, R. L., P. Weber, and R. L. Allen, *Ind. Eng. Chem.*, **38**, 185 (1946).
44. *U. S. Natl. Bureau Standards Circ. 142* (1923).
45. Weber, J. H., *A.I.Ch.E. Journal,* **1**, 210 (1955).
46. *Ibid.*, **2**, 514 (1956).
47. *Ibid.*, **5**, 17 (1959).
48. Williams, V. C., *Trans. Am. Inst. Chem. Engrs.*, **39**, 93 (1943).
49. Woolley, H. W., R. B. Scott, and F. G. Brickwedde, *J. Res. Natl. Bureau Standards,* **41**, 379 (1948).
50. York, R., and E. F. White, *Trans. Am. Inst. Chem. Engrs.*, **40**, 227 (1944).

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Stability in Distributed Parameter Systems

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Three models of a catalyst particle are examined for existence of multiple steady states depending upon whether intraparticle heat conduction or diffusion is important. The particle with constant temperature but with intraparticle diffusion is examined in detail and a necessary and sufficient condition for the stability of the steady state is obtained. Calculations are made for a particle with both intraparticle diffusion and conduction and it is shown that there may be multiple steady states some of which are unstable to small perturbations.

In recent papers the problem of stability in systems in which chemical reactions are coupled with heat transfer and mass transfer has been treated in great detail. These systems all had the common characteristic that they were lumped constant systems in the sense that there were no distributed effects such as diffusion or conduction, and their mathematical formulation was as ordinary nonlinear differential equations for the transient state and algebraic equations in the steady state. There is little published literature on stability in distributed parameter systems, and it is the purpose of this paper to consider three mathematical models of essentially the same physical problem. The problem is related to the single catalyst particle but a gross idealization will be treated here. While this model may be grossly oversimplified, it is felt and hoped that it should give some insight into more complicated situations. For the purposes of this paper a catalyst particle in the form of a one-dimensional slab will be considered in which a simple first-order chemical reaction $A \rightarrow B$, irreversible, is assumed to take place. Heat may be generated or absorbed in the reaction, and hence the possibility of a temperature gradient within the particle exists. Three different models will be treated, one in more detail than the others. The lack of detail in the others is not to save space but rather because no rational approach other than that given here seems to be available at the moment.

The authors consider a slab catalyst particle of thickness l impervious at $x = 0$ and exposed to reactant at $x = l$. The three models may be briefly described as follows.

1. The temperature of the catalyst particle is uniform, and therefore conduction within it is neglected. The resistance to heat transfer is lumped at the particle surface at $x = l$. Knudsen diffusion of the reactant is the prevailing mode of mass transfer within the particle, and the Knudsen diffusion coefficient is assumed to be a constant. It is assumed that there is no mass transfer resistance at the particle surface, but relaxation of this restriction presents no difficulty. It is assumed in this model as well as the others that the chemical reaction can be expressed by means of a simple first-order rate law on the local partial pressure of reactant in the interstitial volume of the particle.