Isothermal Changes of Enthalpy, Entropy, and Heat Capacity Based on Modified Reduced Berthelot Equation

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Methods (*5, 6, 7, 8, 11, 16, 19*) proposed to date for the calculation of pressure effect on thermodynamic properties of gases based on the corresponding states are, in general, susceptible to appreciable errors because of the graphical or numerical differentiation and integration involved. These errors may be avoided if adequate generalized equations of state are available to make analytical solutions feasible.

Presented in the communication are generalized equations for the calculation of isothermal changes of enthalpy, entropy, and heat capacity under relatively moderate pressures. Work is being continued to determine if generalized equations applicable in the high-pressure regions can be formulated.

GENERALIZED P-V-T RELATIONS

The left-hand section of the reduced isotherms in compressibility charts are, to a limited extent, nearly linear in reduced pressure p_R and can be represented by the Berthelot-type reduced equation of state (*2*). Using the latest compressibility factor chart (*14*) as a basis of comparison, the reduced isotherms at low values of p_R may be expressed by the following equation:

$$Z = \frac{pV}{RT} = 1 + \frac{0.076}{T_R}\left(1 - \frac{6}{T_R^2}\right) p_R \tag{1}$$

The linear isotherms represented by both Equation (1) and the reduced Berthelot equation are shown in Figure 1.

Figure 1 indicates that, with the exception of $T_R = 1.6$, Equation (1) in general agrees better with the mean experimental values than does the reduced Berthelot equation. This trend is upheld by more recent compressibility data (*4, 9, 18*). For T_R greater than 1.8, the difference between Equation (1) and the Berthelot equation continuously diminishes. Figure 1 also indicates the applicable p_R range for the different isotherms above which the deviation between the mean values of Z and those calculated by Equation (1) will increase rapidly.

For different reduced temperatures, the maximum reduced pressures at which Equation (1) is applicable are recommended below:

T_R: 0.7 0.8 0.9 1.0 1.1 1.2
0.06 0.15 0.38 0.46 0.56 0.75

T_R: 1.3 1.4 1.6 1.8 2.0 2.5 3.5
p_R: 1.0 1.2 1.4 1.6 1.8 2.0 2.4

GENERALIZED EQUATIONS FOR ISOTHERMAL CHANGES OF ENTHALPY, ENTROPY AND HEAT CAPACITY

For the isothermal enthalpy change referred to the ideal state

$$(H_o - H_P)_T = RT\,T_R \int_{p_o}^{p_R} \left(\frac{\partial Z}{\partial T_R}\right)_{p_R} \frac{dp_R}{p_R} \tag{2}$$

Similarly, for the corresponding changes in entropy and heat capacity we have

$$(S_o - S_P)_T = R\left[\int_{p_o}^{p_R} (Z-1)\,\frac{dp_R}{p_R} + T_R \int_{p_o}^{p_R} \left(\frac{\partial Z}{\partial T_R}\right)_{p_R} \frac{dp_R}{p_R} + \ln\frac{p_R}{p_o}\right] \tag{3}$$

$$(C_o - C_P)_T = \int_{p_o}^{p_R} \frac{RT_R^2}{p_R}\left(\frac{\partial^2 Z}{\partial T_R^2}\right)_{p_R} dp_R + 2\int_{p_o}^{p_R} \frac{RT_R}{p_R}\left(\frac{\partial Z}{\partial T_R}\right)_{p_R} dp_R \tag{4}$$

When the compressibility factor Z is replaced by Equation (1) and solved, Equations (2), (3), and (4) become, respectively

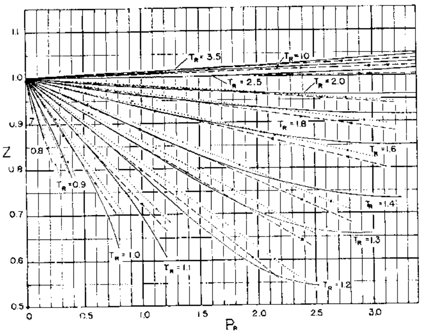

Fig. 1. Compressibility factor at low values of p_R.
— — — — Equation (1)
. . . . Reduced Berthelot equation
———— Mean experimental value (*14*)

$$(H_o - H_P)_T = T_c\left(\frac{2.72}{T_R^2} - 0.152\right)(p_R - p_o) \tag{5}$$

$$(S_o - S_P)_T = \frac{1.815}{T_R^3}(p_R - p_o) + R\ln\frac{p_R}{p_o} \tag{6}$$

$$(C_P - C_o)_T = \frac{5.44(p_R - p_o)}{T_R^3} \tag{7}$$

VALIDITY OF THE GENERALIZED EQUATIONS

The isothermal enthalpy changes calculated by Equation (5) have been compared with the experimentally derived values for nitrogen (*10*), methane (*12*), ethylene (21), benzene (*15*) and Freon 13 (*1*) at a range of reduced temperatures and pressures. As would be expected, the enthalpy changes calculated by Equation (5) may be slightly greater or smaller than the corresponding experimental values depending on whether the compressibility factor calculated by Equation (1) is smaller or greater than the experimental value of Z (Figure 1). Within the p_R range recommended above for various values of T_R, the maximum and average deviations between the experimentally derived enthalpy values and those calculated by Equation (5) are, respectively, less than 5% and 2%.

The agreement between the experimentally derived values and those calculated by Equation (5) is in general better than that between the former and those calculated by other generalized methods (*5, 11, 20*). This is attributable to the fact that transformation of Equation (2) to Equation (5) does not involve cross-plotting and graphical differentiation and integration.

Similar comparisons have been made between the experimentally derived values and those calculated by Equations (6) and (7) for isothermal changes of entropy and heat capacity. Because the pressure effect on entropy changes due to nonideality is relatively small under moderate pressures, the entropy change calculated by Equation (6) agrees remarkably well with the cor-

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responding literature values for a variety of gases [nitrogen (*10*), ethylene (*21*), methane (*12*) and Freon 13 (*1*)].

On the other hand, appreciable deviations between the $(C_p - C_o)_T$ values calculated by Equation (7) and those available in the literature have been noted, the gases used in the comparison being methane (*12*), ethane (*3*), nitrogen (*10*) and carbon dioxide (*17*). The relatively large deviations among the values derived from different methods are probably due mainly to the errors inherent in Equation (4), which involves the vulnerable second-order differentiation operation. Heat capacity values of gases at elevated pressures derived from Joule-Thomson expansion measurements too are subject to relatively large errors.

Within the applicable p_R range the fugacity coefficient f/p of gases can be calculated by the generalized equation derived in the same manner as Equations (5) to (7).

$$\log \frac{f}{p} = \left(\frac{0.0380}{T_R} - \frac{0.198}{T_R^3} \right) (p_R - p_o) \quad (8)$$

As no differentiation is needed in arriving at Equation (8), there is close agreement, as expected, among the values obtained by Equation (8) and those available in the literature (*4, 5, 11, 12, 13, 15*) for different gases and by different methods.

NOTATION

C = heap capacity
f = fugacity
H = enthalpy
p = pressure
p_R = reduced pressure
R = universal gas constant
S = entropy
T = temperature
T_c = critical temperature
T_R = reduced temperature
V = volume
Z = compressibility factor

Subscripts

o = property at ideal state
p = property under pressure p

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INFORMATION RETRIEVAL

Thermodynamic properties of methyl chloride, Hsu, C. C., and J. J. McKetta, **A.I.Ch.E. Journal, 9,** No. 6, p. 794 (November, 1963).

Key Words: Densities-7, Enthalpy-7, Entropy-7, Heat Capacities-7, Latent Heat-7, Liquid-5, Methyl Chloride-5, Mollier-9, Pressure-6, Temperature-6, Thermodynamics-9, Vapor-5, Vapor Pressure-7, Volume-7.

Abstract: The thermodynamic properties of methyl chloride have been calculated from experimental data and presented in tabular form, and as Mollier diagram, at pressures from 5 to 4,500 lb./sq. in. abs. and temperatures from —40° to 420°F.

Laminar flow of a heat-generating fluid in a parallel-plate channel, Sparrow, E. M., J. L. Novotny, and S. H. Lin, **A.I.Ch.E. Journal, 9,** No. 6, p. 797 (November, 1963).

Key Words: Parallel-Plate Channel-10, Forced Convection-8, Internal Heat Generation-6, Heat Transfer-8, Temperature-8, Laminar Flow-10, Wall Temperature-7, Wall Heat Flux-7, Bulk Temperature-7, Thermally Developed Region-9, Thermal Entrance Region-9.

Abstract: Heat transfer results for laminar flow of a heat-generating fluid in a parallel-plate channel have been determined analytically and verified by experiment. The analysis was carried out for very general conditions which included either arbitrary longitudinal variations of wall temperature or wall heat flux along with arbitrary variations of the internal heat generation. The analytical results apply both in the thermal entrance region and the fully-developed region. Experiments carried out with an electrolyte heated internally by ohmic heating agreed well with the theory.

Behavior of non-Newtonian fluids in the entry region of a pipe, Collins, Morton, and W. R. Schowalter, **A.I.Ch.E. Journal, 9,** No. 6, p. 804 (November, 1963).

Key Words: Boundary-Layer Theory-10, Non-Newtonian Flow-8, Fluid Mechanics-8, Rheology-8, Entry Length-9, Pipe Flow-8, Pseudoplastic Fluid-8, Power Law-6, Velocity Profiles-9, Computers-10, Pressure Drop-9.

Abstract: Boundary-layer theory has been applied to axisymmetric flow of non-Newtonian fluids in the entry region of a pipe. The analysis considers pseudoplastic fluids which can be described by a power-law relationship between the stress tensor and rate of deformation tensor. Results include estimates of entry length, pressure loss, and velocity profiles for such fluids. The results compare favorably with existing experimental data.

Characterization of multiple variable linear systems from random inputs, Angus, R. M., and Leon Lapidus, **A.I.Ch.E. Journal, 9,** No. 6, p. 810 (November, 1963).

Key Words: Random Inputs-1, Random Outputs-2, Perfectly Mixed Reactor-5, Concentrations-6, Temperatures-6, System Response-7, Transfer Functions-8, Computer-10.

Abstract: The technique of power spectral analysis is satisfactorily used to determine the transfer functions of multiple variable linear systems. A technique of sampling is developed so that nonstationary random signals can be used as input to the system under study. Application of this technique is made to a second-order system with two random inputs and to a fifth-order system. The results show that the limits of accuracy to be expected from such an analysis may be predicted by theoretical equations.

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ERRATA

Equation (32) of the article "The Laminar Nonisothermal Flow of Non-Newtonian Fluids" by Richard W. Hanks and Ernest B. Christiansen, which appeared on page 519 of the September, 1961, issue of the *A.I.Ch.E. Journal*, should read

$$\nu_0 = \frac{1 + 3n}{n} - \frac{\Delta\Phi}{\text{Ln}\lambda(Z)}$$

Equation (16) of the article "The Laminar Turbulent Transition in Nonisothermal Flow of Pseudoplastic Fluids in Tubes" by Richard W. Hanks and Ernest B. Christiansen, which appeared on page 467 of the September, 1962, issue of the *A.I.Ch.E. Journal*, should read

$$X_{ch} = \left[\frac{f(n)}{1 + 2f(n)}\right]\frac{1}{1 + f(n)}$$