Compressibility of *n*-Hexane

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Although a considerable amount of work has been done on the compressibility of *n*-hexane, it has been impossible until now to compare or evaluate the work of the various investigators. There has also been a serious lack of information in the region above the critical temperature. It is the purpose of this work to make an extensive study of temperatures of 240° to 300°C. and of pressures up to 225 atm. in order to provide the lacking information and to overlap with the work of other investigators so that a proper evaluation of their work may be made.

Thomas and Young (*10*) studied the volumetric properties of *n*-hexane in the superheated vapor region from 240° to 280.45°C. up to a pressure of 37.19 atm. using the capillary-glass method. The highest density investigated was 1.4193 g.-mole/liter. Higher density data was obtained by Kelso and Felsing (*6*); however their lowest measured density was 2.5 g.-mole/liter, leaving a considerable gap between their results and the earlier work of Thomas and Young (*10*) and making a comparison impossible. Furthermore Kelso and Felsing measured only two isotherms, 250° and 275°C., in the region above the critical temperature, with the result that the temperature coefficient of isometrics could not be determined for the purpose of fitting an equation or state. Stewart, Sage, and Lacey (*9*) more recently turned their attention to the volumetric behavior of *n*-hexane in the liquid phase. Comparison between their work and that of Kelso and Felsing (*6*) can be made only at temperatures below 238°C. This comparison indicates that in general Kelso and Felsing measured smaller densities in the high-pressure region and that the discrepancy increases with increasing temperature. Eduljee, Newitt, and Weale (*4*) also measured liquid volumes of *n*-hexane in the region 0° to 60°C. This investigation bridges the gap in the measurements of the earlier investigators. The densities measured in this work ranged from 1.3 to 5.8 g.-moles/liter for isotherms of 240°, 252°, 264°, 276°, 288°, and 300°C.

The apparatus used in this investigation is a modification of the design of Keyes (*7*) and Beattie (*1*). Except for certain changes, which have been described by Li and Canjar (*8*), a detailed description of the equipment was published by Cherney, Marchman, and York (*3*). A sample of *n*-hexane with a purity of 99.99 ± 0.01 mole % was made available for this investigation by the American Petroleum Research Project 44 at the Carnegie Institute of Technology from the series of samples of hydrocarbons purified by the American Petroleum Institute Research Project 6.

To determine whether appreciable decomposition had taken place at higher temperatures, the pressure at a density of 4.869 g.-moles/liter and a temperature of 276°C. was remeasured after all the data had been obtained and the sample exposed to temperatures of 300°C. The pressure measured originally was 117.789 atm., compared with a pressure of 117.839 atm. measured at the end of the 300°C. run, an indication of negligible decomposition.

A summary of experimental data is presented in Table 1. The over-all uncertainty of the measurements is estimated to vary from 0.12% at low pressures to 0.21% for the high-pressure measurements. Figure 1, a plot of the superheated vapor isotherms of Thomas and Young (*10*) and the low-density data of the present investigation, shows that the data of the present work exhibit somewhat higher pressures than the data of Thomas and Young at the same temperature and density. This same discrepancy was noted earlier in the work on isopentane (*5*). Figure 2 compares the 252° and 276°C. isotherms of the present work with the 250° and 275°C. isotherms of Kelso and Felsing. At the medium densities the data seem to be in fair agreement; however at the higher densities the data of Kelso and Felsing show higher pressures than those of the present work, which is

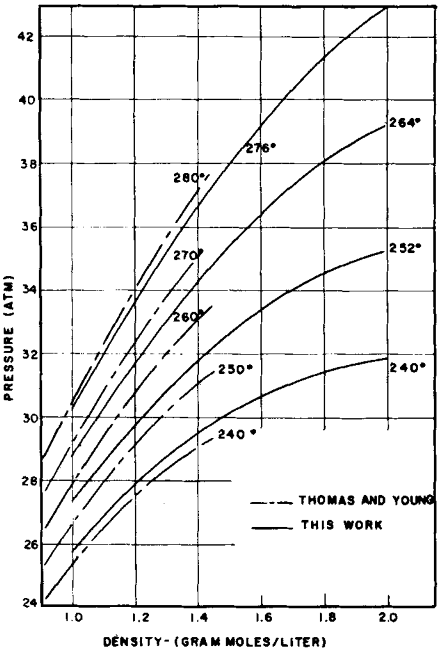

Fig. 1.

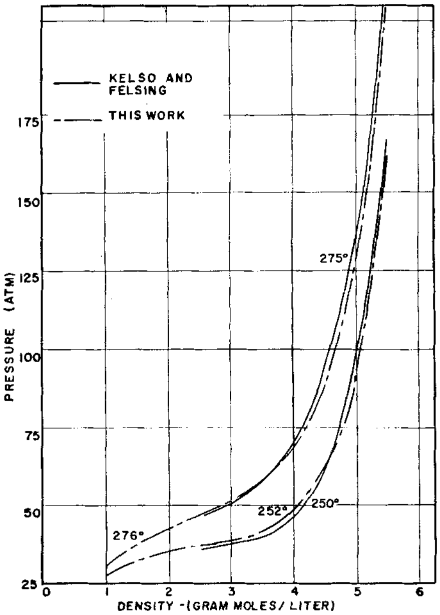

Fig. 2.

Table 1. P-V-T Data for *n*-Hexane

	P, atm.					
d, g.-mole/liter	240°C.	252°C.	264°C.	276°C.	288°C.	300°C.
1.0	25.689	27.275	28.739	30.256	31.747	33.222
1.5	30.110	32.583	35.264	37.812	40.326	42.840
2.0	31.842	35.245	39.337	42.943	46.644	50.329
2.5	32.461	37.644	42.468	47.381	52.399	56.955
3.0	32.925	39.192	45.959	51.988	58.788	65.321
3.5	34.009	41.821	49.988	58.249	67.138	75.852
4.0	37.606	48.312	58.765	68.912	82.247	91.994
4.5	47.575	65.012	76.914	89.730	105.148	119.449
5.0	74.575	94.623	114.597	131.356	147.064	172.273
5.5	135.695	161.980	186.657	210.277	228.277	

just the opposite of the situation when the work of Thomas and Young is considered.

The discrepancies among the various investigators are outside the limits of estimated experimental uncertainty. Critical analysis and selection of the most reliable data are in the province of another laboratory, where the system is now under study (*2*).

ACKNOWLEDGMENT

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Control-System Design for a Chemical Process by the Root-Locus Method

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This paper illustrates the application of the root-locus method in the design of a control system for a theoretical stirred-tank reactor. The merits of control by measuring reactor concentration or temperature were considered at both an unstable and stable steady state reactor condition. The modes of control studied were proportional, proportional-integral, and proportional-integral-rate.

The primary concern in the design of all control systems is the time response of a given system to a prescribed input or set of inputs. The dynamics of a system is analyzed experimentally and/or analytically by one or a combination of several methods. Most of the standard methods utilize the Laplace transform since it transforms a differential equation in time into an algebraic equation in S, and in addition the transform permits the consideration of analysis and design problems in terms of the complex frequency $S = \sigma + i\omega$, rather than in terms of the time functions.

The frequency-response analysis is the conventional method of obtaining time-response information. It provides such information as system stability, frequency of damped oscillation, damping, and steady state error. The method is simple to apply, and the frequency response of a component or system may be obtained mathematically or by laboratory measurement. The inherent reasons for the simplicity of this method, however, result in limiting its usefulness. At the outset of a design the complex frequency S is replaced only by $i\omega$, and thus the analysis is narrowed to the $i\omega$ axis of the S plane. Since the real part of S, (σ), is not considered, the opportunity of maintaining control over both frequency and transient responses is discarded.

The more recent design methods, such as the root-locus (*1*) and Guilleman's (*1*) methods, take into account the entire S plane. This is achieved by working through the poles and zeros of various transfer functions and thus simultaneously controlling the frequency and transient responses. A detailed description of the root-locus method (which is used in this paper) may be found in most recent texts on automatic control (*1*).

It should be pointed out that the control-system design is not for any specific stirred-tank chemical reactor but is concerned with the fundamental variables of a theoretical stirred-tank reactor. The calculated results have not been verified experimentally.

The basic continuous stirred-tank reactor process used in this paper was originally described by Aris and Amundson (*2*).

GENERAL CONTROL PROBELM

Description of Control-System Process

The process to be controlled is the continuous stirred-tank chemical reactor shown in Figure 1. The influent consists of a reactant A and an inert carrier. The reaction occurring in the reactor is

$$2A \longrightarrow \text{products}$$

The reaction is assumed to be exothermic, irreversible, and second order. The material balance around the reactor may be written

$$\frac{VdA}{dt} = Q(A_0 - A) - kVA^2 \qquad (1)$$

Equation (1) states that the rate of accumulation of A in the reactor is equal to the difference between the amount of A entering minus the amount of A leaving and the amount that has disappeared owing to the reaction.

The energy balance is

$$Vc\rho \frac{dT}{dt} = Qc\rho(T_0 - T) - ha(T - T_c) + kVA^2(-\Delta H) \qquad (2)$$

Thus the accumulation of heat in the reactor is equal to the difference in the total heat removed (by warming the influent and by the cooling coil) and the heat generated by the reaction.

The average coolant temperature and the inlet coolant temperature are related by

$$T_c = \frac{(\alpha/Q_c)T + T_{ec}}{(\alpha/Q_c) + 1} \qquad (3)$$

where α is defined as

$$\alpha = \frac{ha}{2c_c\rho_c} \qquad (4)$$

Equation (5) is then obtained by substituting Equations (3) and (4) into Equation (2):

$$Vc\rho \frac{dT}{dt} = Qc\rho(T_0 - T) - \frac{Q_c ha}{\alpha + Q_c} \cdot (T - T_{ec}) - kVA^2(\Delta H) \qquad (5)$$

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