Critical Constants of *n*-Pentane

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A universal demand exists for precise thermophysical property data to minimize costs of investment in various areas of engineering. The principle of corresponding states often provides good information when the critical constants of pure fluids are well known. This note is concerned with the critical constants of *n*-pentane. The experimental investigations known from literature have been carried out carefully. Nevertheless, the various results disagree by more than the individually estimated experimental uncertainty. No result can be preferred for obvious reasons. Comparing the thermal properties of *n*-pentane with those of the lower *n*-alkanes, we are able to evaluate a consistent set of data for T_c, p_c, and ρ_c that seems to be very reliable.

CRITICAL TEMPERATURE AND PRESSURE

The most accurate measurements have been performed by Beattie et al. (1951), Ambrose et al. (1960), and Partington et al. (1960) (see Table 1), Beattie et al. (1951) carried out a series of isothermal P,V measurements. From a P,V plot they selected that isotherm for the critical temperature that showed a point of horizontal inflection. The critical pressure and volume were then obtained from the coordinates. Some impurity of the sample is indicated by the fact that the vapor pressure varied at $T = 373.15$ K by about 0.15%, depending on the vapor-liquid ratio. Ambrose et al. (1960) made observations of the disappearance of the meniscus as the temperature rose and of the reappearance as the temperature fell. The temperatures of disappearence and reappearance agreed within 0.004 K. Partington et al. (1960) observed the critical point by twice raising and lowering the temperature of the sample. The critical temperature was reproducible within 0.1 K.

The various stated critical temperatures differ by nearly 0.3 K. The agreement is far outside the individually estimated experimental uncertainty. For the critical temperature, Kudchadker et al. (1968) selected the mean value $T_c = 469.69$ K, which we have converted to IPTS-68. The critical pressure $p_c = 3.364$ MPa follows from our vapor-pressure measurements with liquid *n*-pentane (Kratzke, 1983).

CRITICAL DENSITY

The critical density of *n*-pentane was obtained from the law of rectilinear diameters by Young (1897) and Sage and Lacey (1942). The difference is only slightly above 1%. However, Beattie et al. (1951) determined the critical density to be about 5% above. Kudchadker et al. (1968) have evaluated $\rho_c = 237.0$ kg·m^{-3} graphically. This corresponds almost to the average of the various results.

We have some reason to assume that this value for the critical density in inapplicable. Therefore, we have compared the *n*-alkanes containing two to five C atoms with each other. These substances have similar mechanisms of molecular interactions; differences should be only a function of different chain length.

The principle of corresponding states has been extended by Riedel (1954). The additional correspondence parameters α_{kr} can be calculated from the slope of the vapor-pressure curve directly at the critical point:

TABLE 1. INVESTIGATIONS OF THE CRITICAL POINT OF n-PENTANE

Authors	Purity of the sample, moles %	T_c/K	p_c/MPa	ρ_c/kg m^{-3}
Young (1897)	—	470.4	3.347	232.4
Sage and Lacey (1942)	99.7	470.41	3.346	229.1
Beattie et al. (1951)	99.85	469.81	3.375	244.0
Ambrose et al. (1960)	99.95	469.53	—	—
Partington et al. (1960)	99.8 to 99.99	469.59	—	—
Present Study	—	469.69	3.364	232.0

TABLE 2. COMPARISON OF CALCULATED CRITICAL DENSITIES $\rho_{c,\text{calc}}$ WITH VALUES ρ_c FROM LITERATURE

	Ethane	Propane	*n*-Butane	*n*-Pentane
T_c/K	305.33	369.85	425.14	469.69
p_c/MPa	4.8714	4.246	3.7839	3.364
T_b/K	184.574	231.04	272.63	309.21
α_{kr}	*6.278*	*6.543*	*6.773*	*7.032*
Z_c	0.283	0.278	0.273	0.268
$\rho_{c,\text{calc}}$/kg·m^{-3}	204.0	219.0	228.0	232.0
ρ_c/kg·m^{-3}	204.5	220.5	227.85	—
$100\lvert\Delta\rho_c/\rho_c\rvert$	0.2	0.7	0.07	—

TABLE 3. ACENTRIC FACTORS ω OF ARGON AND LOW n-ALKANES

Substance	ω
Argon	−0.002
Ethane	0.105
Propane	0.152
n-Butane	0.199
n-Pentane	0.251

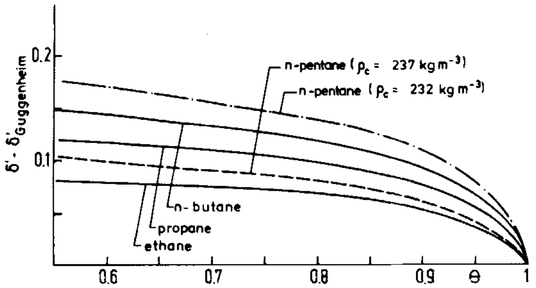

Figure 1. Differences of the reduced orthobaric liquid densities δ' from Guggenheim's equation as a function of reduced temperature θ.

$$\alpha_{kr} = \frac{T_c}{p_c}\left(\frac{dp_\sigma}{dT}\right)_{T=T_c} \tag{1}$$

According to Riedel (1954a) α_{kr} can be calculated when the critical temperature and pressure are known and an additional value of the vapor-pressure curve, for example, the normal boiling point. Then α_{kr} follows from

$$\alpha_{kr} = 7 + \frac{\lg(p_c/p_0) - \phi(T_b/T_c)}{\psi(T_b/T_c)} \tag{2}$$

where p_o = 0.101324 MPa. The reduced temperature functions ϕ and ψ are given by Riedel (1954a). For the critical compressibility factor Z_c of n-alkanes, Riedel (1954b) gives an empirical relation:

$$\frac{1}{Z_c} = 3.72 + 0.26\,(\alpha_{kr} - 7) \tag{3}$$

The critical density ρ_c follows, as T_c and p_c are known.

$$\rho_c = \frac{p_c}{RT_cZ_c} \tag{4}$$

Comparison of these calculated values for the critical density with selected literature values for ethane (Goodwin et al., 1976), propane (Goodwin and Haynes, 1982), and n-butane (Haynes and Goodwin, 1982) indicates a satisfactory agreement (see Table 2). So it is expected that the critical density of n-pentane (ρ_c = 232.0 kg·m^{-3}), calculated in this manner, should also be very reliable. This is indicated by another fact. Guggenheim (1945) proposed a simple equation for the reduced orthobaric liquid density of argon as a function of reduced temperature:

$$\delta' = 1 + 0.75\,(1 - \theta) + 1.75\,(1 - \theta)^{1/3} \tag{5}$$

Argon is regarded as a spherical nonpolar molecule. The more the molecular interactions of various substances differ from those of argon, the more the reduced orthobaric liquid densities differ from those of argon. The acentric factor ω gives a good estimate for the magnitude of these differences (see Table 3). The differences $\delta' - \delta_{Guggenheim}$ of the reduced orthobaric liquid densities of the n-alkanes from those predicted by Guggenheim's equation have been plotted as a function of reduced temperature (see Figure 1). As expected from the acentric factors, these differences increase systematically from ethane to n-butane. If the critical density of n-pentane is chosen to be ρ_c = 237.0 kg·m^{-3}, as proposed by Kudchadker et al. (1968), the dashed line for n-pentane seems to be doubtful. A more meaningful slope is given by the dashed-dotted line with ρ_c = 232.0 kg·m^{-3}. This demonstrates consistency of the selected values for the critical point of n-pentane.

NOTATION

p_c = critical pressure
p_σ = vapor pressure
R = gas constant
T = absolute temperature
T_b = normal boiling temperature
T_c = critical temperature
Z_c = critical compressibility factor
α_{kr} = Riedel's factor
δ' = reduced orthobaric liquid density
ω = acentric factor
θ = reduced temperature
ϕ,ψ = functions of reduced temperature, given by Riedel

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