Density: Reduced-State Correlations for the Inert Gases

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The principle of corresponding states has been adopted to the correlation of densities and found to be applicable for nonpolar substances when the critical compressibility factor is introduced as an independent parameter. For the inert gases, densities available in the literature for the gaseous and liquid states have been referred to their critical densities to produce reduced-state correlations which are identical only when their corresponding critical compressibility factors are the same. As a result, a consolidated reduced density correlation for $z_c = 0.291$ has been developed from experimental data for argon, krypton, and xenon. Although the z_c values for helium and neon are essentially alike, different reduced-state correlations for these substances were found to exist. This behavior is expected in view of the radical nature of helium, which can be accounted for by its excessive quantum deviation. Therefore the reduced density correlation for neon ($z_c = 0.307$) is selected as representative of that class of substances having similar z_c values.

The validity of both correlations has been extended beyond the monatomic gases to include substances having comparable critical compressibility factors. With the generalized chart for $z_c = 0.291$ gaseous densities at elevated temperatures and pressures have been calculated for nitrogen, oxygen, carbon monoxide, and methane to produce an average deviation of 1.4% from reported values in the literature. For these substances the average deviation becomes 1.5% for densities in the liquid state. With the reduced density chart for neon ($z_c = 0.307$) densities calculated for hydrogen ($z_c = 0.305$) in the gaseous region produced an average deviation of 2.5% and covered pressures in excess of 500 atm. and temperatures as high as 500°C.

Several equations of state have been proposed for the calculation of densities of gases. In this connection the van der Waals' equation represents the initial attempt to account for nonideal behavior of real gases. Several investigators have proposed equations of state (*4, 9, 42, 58*) that are capable of representing experimental results accurately; however in some cases their application requires as many as twelve arbitrary constants which ordinarily are not available. In addition the use of these equations is unwieldy and impractical for conventional engineering calculations. Edmister (*20*) obtains fair agreement with experimental values for hydrocarbons by introducing the residual volume

$$\alpha = \frac{RT}{P} - V \qquad (1)$$

The calculation of densities in the gaseous state by using compressibility-factor charts is limited in accuracy, particularly near the critical-point region. Furthermore the direct evaluation of liquid densities with the expansion-factor correlation of Watson (*65*) under isobaric conditions produces values that are not compatible with those resulting from a compressibility-factor correlation for gases. In addition, both compressibility- (*53*) and expansion-factor (*65*) plots are limited up to pressures of $P_R = 40$ $P_R = 5$, respectively.

The introduction of the critical compressibility factor as a necessary parameter for the correlation of fluid properties has been used by Meissner and Seferian (*47*) for the correlation of exacting gas-compressibility factors. Brock and Bird (*13*) extend this approach for the generalized correlation of surface tension, and Lydersen, Greenkorn, and Hougen (*41*) utilize z_c for the correlation of thermodynamic properties of eighty-two substances. The adaptability of z_c for the establishment of the saturated compressibility-factor envelope is presented by Hobson and Weber (*25*). These investigators show that a unique saturation envelope results from substances having similar z_c values. Their conclusions are well demonstrated for a number of substances having z_c values ranging from 0.220 for methanol to 0.291 for nitrogen.

The present investigation considers the development of reduced-state correlations capable of predicting densities in the gaseous and liquid regions. Such a correlation eliminates the discontinuities of density resulting from existing compressibility-factor charts for gases and the expansion-factor correlation for liquids. The inert gases have been arbitrarily selected for study because of their molecular simplicity and consequent adaptability to kinetic-theory considerations.

REDUCED DENSITY CORRELATIONS

An exhaustive literature search was conducted to compile experimental density data for helium, neon, argon, krypton, and xenon. In this search experimental densities for the liquid and gaseous states were considered, including the critical region. The critical constants presented in Table 1 were used to develop the reduced-state corre-

TABLE 1. CRITICAL CONSTANTS OF THE INERT GASES

	M	T_c, °K.	P_c, atm.	ρ_c, g./cc.	z_c
Helium	4.003	5.206 (*10*)	2.26 (*33*)	0.0693 (*40*)	0.306
Neon	20.183	44.45 (*17*)	26.86 (*37*)	0.484 (*44*)	0.307
Argon	39.944	151.2 (*40*)	48.00 (*16*)	0.531 (*37*)	0.291
Krypton	83.80	209.4 (*46*)	54.18 (*46*)	0.908 (*40*)	0.292
Xenon	131.3	289.75 (*21*)	57.64 (*21*)	1.099 (*21*)	0.290

0°C. = 273.16°K. R = 82.055 (cc.)(atm.)/(g. mole)(°K.)

lations of this study. With the exception of a limited number of density measurements (*3, 5, 21*) nearly all available experimental data are reported in terms of the relative quantities: the amagat density and the amagat unit. To convert this information into conventional units the following reference densities of the inert gases have been used:

	Density, g./cc. (0°C. and 1 atm.)
Helium	0.00017847 (*36*)
Neon	0.00089990 (*2*)
Argon	0.0017839 (*6*)
Krypton	0.003745 (*2*)
Xenon	0.0058989 (*50*)

TABLE 2. COMPARISON OF EXPERIMENTAL REDUCED DENSITIES FOR SEVERAL NON-INERT GASES WITH VALUES OBTAINED FROM FIGURE 4.

Gas	z_c	ρ_c, g./cc.	Range Investigated* T_R	P_R	Number of Experimental Points	% Deviation Maximum	Average
Oxygen	0.290	0.430	0.6–0.9	saturated	4	2.3	1.9
			1.0–3.0	0.5–2.0	23	3.6	1.2
Nitrogen	0.291	0.311	0.6–1.0	saturated-40	16	3.1	1.6
			1.0–1.5	0.4–40	32	2.9	1.1
Carbon Monoxide	0.294	0.301	0.6–0.95	saturated	4	3.9	1.7
			2.0–7.5	1.2–2.9	11	3.8	1.9
Methane	0.290	0.162	0.5–0.6	saturated	4	0.8	0.6
			1.1–4.8	1.2–45	16	7.1	1.8

*Values in upper line refer to the liquid state while those in lower line refer to the gaseous state only.

In addition to these amagat quantities a number of investigators (*3, 5, 23, 67, 68, 69*) fit their data to virial type equations. The application of equations of this type becomes too laborious for ordinary use and can prove practical only with the use of high speed computers.

Helium ($z_c = 0.306$)

The density data for helium presented in the literature (*10, 11, 26, 28, 30, 31, 32, 34, 38, 39, 52, 56, 62, 63, 70*) were used as the basis to construct Figure 1. Overlapping points from different sources were carefully examined, and only those considered most reliable are presented in this figure. To develop Figure 1 the actual critical temperature $T_c = 5.206$°K. and critical pressure $P_c = 2.26$ atm. recommended by Berman and Swenson (*10*) were used; the critical density $\rho_c = 0.0693$ g./cc. presented by Kobe and Lynn (*40*) was selected for the calculation of reduced densities. The saturation envelope was constructed from the vapor density data of Berman and Swenson (*10*) and the saturated liquid data of Kamerlingh Onnes and Boks (*34*) and Keesom and Keesom (*38*).

The experimental data of helium are available only for restricted regions. Their extension to cover the region to $P_R = 0.2$ was made possible through the use of the Nelson-Obert compressibility factor chart (*53*) and the relationship

$$\frac{\rho_R}{\rho_{R_1}} = \frac{z_1}{z} \frac{P_R}{P_{R_1}} \frac{T_{R_1}}{T_R} \tag{2}$$

For the case when $P_R = P_{R_1}$ Equation (2) enables the extension of an isobar from a single experimental density measurement. On the other hand, when experimental data are completely lacking in a region, isobars can be constructed by use of the density values of the nearest available isobar, and for conditions of constant temperature $T_R = T_{R_1}$. By using this dual approach and an extension of the isobars of the liquid region to properly join the corresponding isobars of the gaseous region, the reduced density correlation of helium presented in Figure 1 was developed. The isobars calculated in this manner are shown in Figure 1 as dashed lines. The availability of future experimental density data for these regions should prove valuable in definitely establishing the calculated portions of these constant pressure lines. The rather insignificant density change with temperature of helium in the saturated and supercompressed liquid region is unique to this substance, since values below $T_R = 1.0$ correspond to absolute temperatures of less than 5.2°K.

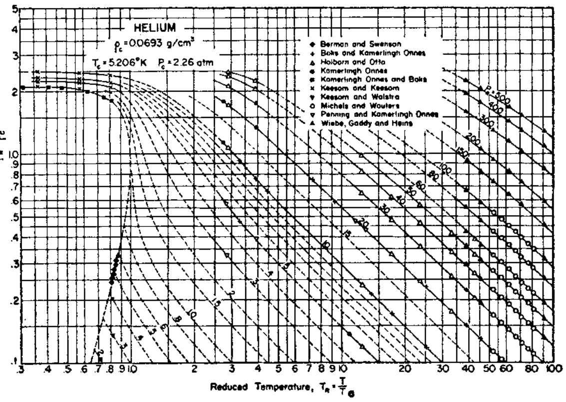

Fig. 1. Reduced density correlation for helium.

Neon ($z_c = 0.307$)

The experimental density data of Crommelin, Martinez, and Kamerlingh Onnes (*18*), Holborn and Otto (*27, 29*), and Michels and Gibson (*48*) for gaseous neon and those of Mathias, Crommelin, and Kamerlingh Onnes (*44*) for the saturated envelope were utilized to construct the reduced density correlation presented in Figure 2. By following the procedure used to extend the isobars for gaseous helium the Nelson-Obert compressibility factor chart (*53*) in conjunction with Equation (2) made possible the extension of the isobars for neon into regions where no data were available. As in the case for helium these regions are indicated by dashed lines. The effect of pressure on the available saturated liquid data for neon was accounted for through the use of ω and the density data of Benedict (*7, 8*) for liquid nitrogen. The density data of Benedict made possible the extension of the ω-factor plot of Watson (*65*) up to reduced pressures of $P_R = 40$. Consequent transformations to account for the effect of pressure were based on the relationship

$$\frac{\rho}{\rho_S} = \frac{\omega}{\omega_S} \tag{3}$$

By following this procedure isobars for pressures up to $P_R = 40$ were calculated for the liquid region and were extended to the corresponding isobar of neon in the gaseous state; these regions are also expressed with dashed lines. The resulting reduced-state correlation for neon presented in Figure 2 covers temperatures as high as $T_R = 20$ and pressures ranging from $P_R = 0.3$ to $P_R = 40$. For these conditions of temperature and pressure the reduced density varies from $\rho_R = 0.1$ to $\rho_R = 3.00$. Comparison of the reduced-state density correlation for helium and neon indicates that no direct correspondence exists between them despite the fact that their values of z_c are almost identical. This difference is anticipated owing to the unusual behavior of helium which can be associated in terms of excessive quantum deviations that can be quantitatively expressed in terms of the quantum mechanical parameter, Λ^*, proposed by de Boer and Bird (*19*).

Argon ($z_c = 0.291$)

The available density data for argon are presented in Figure 3. The experimental density data of Crommelin (*16*) and Herz (*22*) define quite adequately the saturated envelope. Furthermore the data of Kamerlingh Onnes and Crommelin (*35*) and the calculated values of the National Bureau of Standards (*23*) cover the region included below a pressure of $P_R = 2.0$. The high pressure data above $P_R = 15$ of Bridgman (*12*) and those of Michels, Wijker, and Wijker (*51*) are consistent and define the region extending up to $P_R = 300$ for temperatures ranging up to $T_R = 3.0$. The region between $P_R = 2.0$ and $P_R = 15$ is also established from the data of Michels, Wijker, and Wijker (*51*) over the limited temperature range of $1.8 \leq T_R \leq 2.8$. As a result the region immediately near the critical point between $P_R = 2.0$ and $P_R = 15$ cannot be accounted for directly from argon density data.

Krypton ($z_c = 0.292$)

Density data for krypton were reported only by Beattie, Brierley, and Barriault (*5*) and Mathias, Crommelin, and Meihuizen (*45*). The data of Mathias, Crommelin, and Meihuizen are restricted to conditions representing the saturated envelope, whereas those of Beattie et al. extend up to temperatures of $T_R = 2.75$ and pressures as high as $P_R = 8.0$. These data are also presented in their reduced state in Figure 3.

Xenon ($z_c = 0.290$)

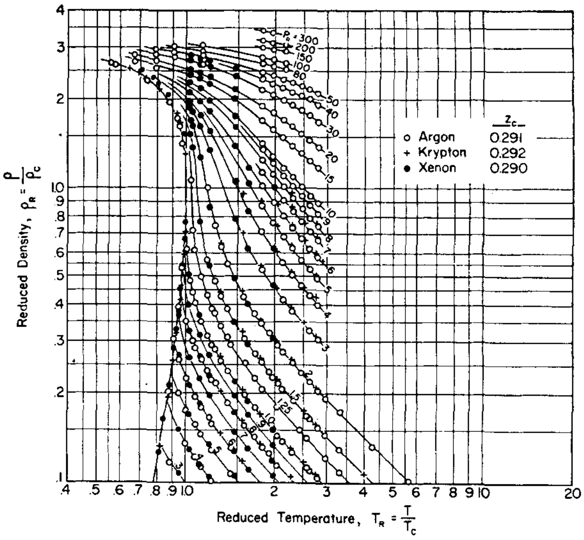

Fig. 3. Composite reduced density correlation for argon, krypton, and xenon.

Despite the fact that experimental values for xenon are available only from a few sources, these data are sufficient to define the saturated envelope and the region covering pressures up to $P_R = 40$ and temperatures up to $T_R = 2.0$. The data of Patterson, Cripps, and Gray (*55*) are restricted to conditions representing the saturated envelope, while those of Beattie, Barriault, and Brierley (*3*) and Michels, Wassenaar, and Louwerse (*50*) cover the gaseous region. The experimental data of Habgood and Schneider (*21*) are limited to the critical region and vary from 15.590 to 16.620°C. Consequently these data were used only to define the critical temperature, pressure, and density for xenon. The density values from these sources are presented in their reduced state in Figure 3 along with those of argon and krypton. In particular the data of Michels et al. have proved helpful in establishing the shape of isobars in the critical region.

GENERALIZED REDUCED DENSITY CORRELATION

The consolidated reduced-density values for argon, krypton, and xenon are presented in Figure 3. For these inert gases the critical compressibility factors are 0.291, 0.292, and 0.290, respectively. In Figure 3 it will be noted that the saturated enveloped of these inert gases almost superimpose each other. A slight inconsistency is noted for the saturated liquid line of xenon. Aside from this small discrepancy the remaining data follow a corresponding states' behavior and thus permit the establishment of isobars based on experimental data up to pressures of $P_R = 300$ and temperatures up to $T_R = 3$. The isobars of Figure 3 were extended up to temperatures of $T_R = 30$ by using the same technique adopted for helium and neon. The final correlation presented in Figure 4 represents the density behavior for nonpolar substances having a critical compressibility factor $z_c = 0.291$. From the results of these studies it is apparent that the proposals of Meissner and Seferian (*47*) are valid, since the density data of argon, krypton, and xenon are found to follow a corresponding states' behavior. The reduced-state correlation presented in Figure 2 is based on data for neon but should be applicable to substances having a critical compressibility factor of $z_c = 0.307$. On the other hand the reduced-state correlation of Figure 1 is specific to helium ($z_c = 0.306$); its use should be restricted to this substance, since it differs so markedly from the corresponding correlation for neon ($z_c = 0.307$). This different behavior can be explained from statistical quantum considerations for these two substances. Excessive quantum deviations found to exist for helium are responsible for the unusual behavior of this substance. A measure of these quantum deviations is accounted for by de Boer and Bird (*19*) in their dimensionless quantum mechanical parameter

$$\Lambda^* = \frac{h}{\sigma\sqrt{m\epsilon}} \qquad (4)$$

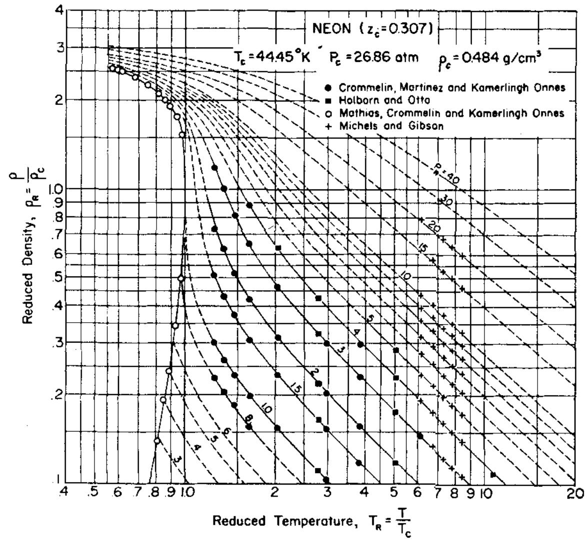

Fig. 2. Reduced density correlation for gases and liquids ($z_c = 0.307$).

Table 3. Comparison of Experimental Reduced Densities for Argon With Values Calculated From Several Reduced-State Correlations

		ρ_R Reduced Density Values				
T_R	P_R	From Experimental Values	Meissner and Seferian (*47*)	Maslan and Littman (*43*)*	Nelson and Obert (*53*)	This Investigation (Figure 4)
1.054	1.0	0.441	0.445	0.394	0.445	0.443
1.136	40.0	2.64	—	—	2.73	2.66
1.972	5.0	0.760	0.754	0.802	0.754	0.760
1.972	90.0	2.64	—	3.05	—	2.65
2.47	40.0	2.00	1.96	2.28	2.02	2.04

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*For these reduced densities the pseudocritical values recommended by Maslan and Littman (*43*) T_c = 143.7°K. and P_c = 50.5 atm. have been used.

To present orders of magnitude the quantum mechanical parameter has been calculated for the inert gases from the Lennard-Jones force constants ϵ and σ and the corresponding atomic weight. The values used for these calculations were obtained from Hirschfelder, Curtiss, and Bird (*24*) and are presented below:

	ϵ, erg	σ, cm.	Λ^*
Helium	14.11×10^{-16}	2.576×10^{-8}	2.74
Neon	49.28	2.789	0.58
Argon	117.18	3.418	0.182
Krypton	262.29	3.61	0.096
Xenon	316.13	4.055	0.062

The calculated value for helium $\Lambda^* =$ 2.74 represents the most excessive quantum deviation possible for the elements. Next in line is that of hydrogen which has a value of $\Lambda^* = 1.80$ followed by a value of $\Lambda^* = 0.58$ for neon. For argon, krypton, and xenon the calculated Λ^* values are 0.182, 0.096, and 0.062 and approach the limiting condition of zero for the idealized case. In view of these comparisons it is reasonable to expect helium to follow a pattern of behavior that is specific to it, since this is the only substance having a quantum mechanical parameter of the highest order of magnitude. Extending this line of reasoning it is expected that the reduced-state correlation of neon may be somewhat limited to this substance, since its quantum mechanical parameter cannot be completely neglected.

COMPARISON OF RESULTS

The reduced-state correlations of Figures 1 and 2 were based on the available experimental data for helium and neon; therefore for these substances the ability to read these charts establishes their accuracy. The validity of the regions where generalized approaches were utilized to complete these charts can only be established for accuracy with the introduction of new data specific to these regions.

Figure 1 cannot be used for any substance other than helium, despite the fact that the z_c values for helium (0.306), neon (0.307), and hydrogen (0.305) are essentially the same. The reasons underlying this pattern of behavior have already been explained by the quantum mechanical parameter.

An attempt was made to utilize Figure 2 for the prediction of hydrogen densities. Twenty-three experimental density values for hydrogen were checked in the temperature range of $T_R = 2.0$ to $T_R = 15.0$ and the pressure range of $P_R = 0.8$ to $P_R = 40$. Figure 2 was found to agree with these values within 1.8% for pressures below $P_R = 10$. For higher pressures the average deviation increased to 4.2%. This behavior is not unexpected in view of the fact that the quantum mechanical parameters of neon and hydrogen are significant and different from each other. Because of the unusual nature of hydrogen, as characterized by its value $z_c = 0.305$ and $\Lambda^* = 1.80$, it is essential that a density correlation specific to this substance be treated separately (*60*).

Figure 4 is applicable to nonpolar substances having values of z_c about 0.290. Since the greatest quantum deviations are exhibited by helium, hydrogen, and neon, the quantum mechanical parameter of other substances becomes unimportant. Therefore only the z_c values need be considered in the application of reduced-state correlations for substances other than helium, hydrogen, and neon. Experimental densities for the gaseous and liquid states of oxygen ($z_c = 0.290$), nitrogen ($z_c = 0.291$), carbon monoxide ($z_c = 0.294$), and methane ($z_c = 0.290$) were compared with those resulting from Figure 4 to produce the deviations presented in Table 2. The weighted average deviation of 1.5% for the gaseous and liquid regions of these substances suggests that the third parameter z_c is a valid criterion for the application of reduced-state correlations to nonpolar substances. No comparisons have been carried out with the original data for argon, krypton, and xenon to test the validity of Figure 4, since the densities of these substances superimpose each other satisfactorily (Figure 3).

Five arbitrarily selected values for argon were used to produce reduced densities for the experimental conditions presented in Table 3. For these conditions of temperature and pressure, reduced densities obtained directly from Figure 4 were compared with the corresponding values resulting from the experimental data. Additional reduced densities were calculated from several compressibility factor charts available in the literature (*43*, *47*, *53*). These results are presented in Table 3; they indicate, for the limited conditions investigated, that next to Figure 4 the Nelson-Obert compressibility chart offers a correlation capable of predicting adequately densities in the gaseous state.

Values from the Lydersen, Greenkorn, and Hougen (*41*) studies and also those of Pitzer (*57*) were not included in Table 3, since the ranges of temperature and pressure reported by them are limited and do not cover the majority of conditions presented in Table 3.

The results of these studies indicate the justification of using z_c in reduced-state correlations as a third correlating parameter for nonpolar substances as long as the quantum deviations of these substances can be ignored.

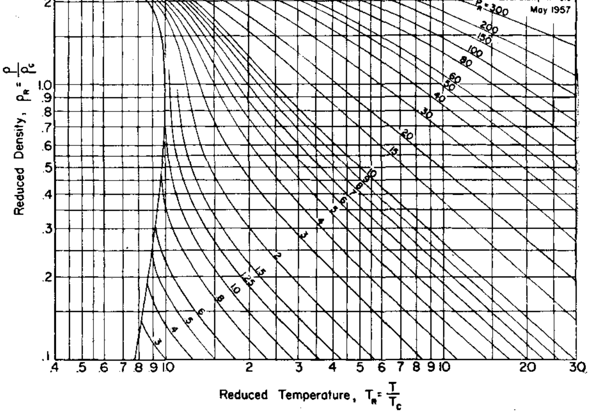

Fig. 4. Reduced density correlation for gases and liquids (z_c = 0.291).

NOTATION

A.U. = amagat unit, PV/P_0V_0
d_A = amagat density, ρ/ρ_0
h = Planck's constant, 6.624×10^{-27} erg. sec.
m = mass of molecule, g.
M = molecular weight, g./g. mole
P = pressure, atm.
P_c = critical pressure, atm.
P_0 = reference pressure, 1 atm. or 1 m. Hg
P_R = reduced pressure, P/P_c
P_{R_1} = reduced pressure for experimental density value
R = gas constant, 82.055 (cc.)(atm.)/(g. mole)(°K.)
T = absolute temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
T_{R_1} = reduced temperature for experimental density value
V = molar volume, cc./g. mole
V_c = critical molar volume, cc./g. mole
V_0 = reference molar volume at 0°C. and reference pressure, cc./g. mole
z = compressibility factor, PV/RT
z_1 = compressibility factor at P_{R_1} and T_{R_1}
z_c = critical compressibility factor, P_cV_c/RT_c

Greek Letters

α = residual volume, cc./g. mole
ϵ = maximum energy of attraction for Lennard-Jones potential, erg.
Λ^* = quantum mechanical parameter, dimensionless
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_0 = density at 0°C. and 1 atm.
ρ_R = reduced density, ρ/ρ_c
ρ_{R_1} = experimental reduced density at conditions T_{R_1} and P_{R_1}
ρ_S = saturated liquid density, g./cc.
σ = collision diameter for Lennard-Jones potential, cm.
ω = Watson expansion factor for liquids
ω_S = Watson expansion factor for saturated liquids

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Manuscript received March 14, 1958; revision received May 19, 1958; paper accepted May 20, 1958.