Gaseous $p−v−T$ Property Measurements for Titanium Tetrachloride from 873.0 to 1173.0 K and Low Pressure of 34.05 kPa

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ABSTRACT: For exploring the chemical reaction mechanism and the heat and mass transfer of the TiCl$_4$–Mg system in the Kroll process, it is of fundamental and practical importance to determine the gaseous $p−v−T$ property for titanium tetrachloride at supercritical temperature and low pressure. The $p−T−x$ data for the $x$TiCl$_4$ + $(1−x)$ Ar binary gas system are measured and presented in this study. Based on the Peng–Robinson (P–R) equation of state (EoS) of argon at temperatures from 873.0 to 1173.0 K, the gaseous $p−v−T$ property of titanium tetrachloride has been estimated, and a new three-term truncated virial EoS for titanium tetrachloride is developed along 10 isotherms and 8 isodensities.

INTRODUCTION

Although it has a high cost and is energy-intensive,¹ the Kroll process has the advantages that make it the most widely preferred primary industrial choice in titanium chain;² however, the reaction mechanisms of the TiCl$_4$–Mg system in the Kroll reactor are not fully understood. Also, the most important reason may be the insufficient theoretical understanding of the titanium system.³

Titanium tetrachloride or TiCl$_4$, acting as the main raw material in the production of sponge titanium, is introduced into a closed reactor and multistep reduced by molten magnesium⁴–⁶ in the Kroll process. Furthermore, the gas phase temperature of the TiCl$_4$–Mg system is about 873.0–973.0 K in the reduction reactor,⁷ which is the supercritical temperature for titanium tetrachloride. Thus, the liquid titanium tetrachloride is heated to its boiling point and vaporized completely and then reacted with magnesium near the gas–melt interfaces.⁸ During these processes, not only the titanium tetrachloride could exist as a gas, but also it cannot be considered as the ideal gas. To avoid the unreliability of the interaction mechanisms, it is essential to determine the corresponding gaseous $p−v−T$ relationship or equation of state (EoS), which must be accurately obtained to explore the chemical reaction mechanism and the heat and mass transfer of the TiCl$_4$–Mg system in the Kroll process.⁹ However, the complete set of experiments used for establishing the EoS of titanium tetrachloride are scarce in the literature,¹⁰ and there is a lack of available experimental data on the EoS. Therefore, it is of fundamental and practical importance to determine the gaseous $p−v−T$ property for titanium tetrachloride at supercritical temperature and low pressure.

The current work reports a new gaseous $p−T−x$ data measurements for the $x$TiCl$_4$ + $(1−x)$ Ar binary gas system at temperatures from 873.0 to 1173.0 K and pressures from 261.24 to 357.92 kPa, while the molar fractions of titanium tetrachloride $x$ are from 0.1320 to 0.2901, respectively. Based on the Peng–Robinson EoS (P–R EoS) of argon, the gaseous $p−v−T$ property of titanium tetrachloride has been estimated, and a new three-term truncated virial EoS for titanium tetrachloride is developed for the present gaseous $p−v−T$ data.

TECHNOLOGICAL BACKGROUND

As a binary mixing gas system consisting of nonpolar molecules at temperatures from 873.0 to 1173.0 K, the gas phase pressure of the $x$TiCl$_4$ + $(1−x)$ Ar binary gas system is contributed by gaseous titanium tetrachloride and argon, and the gas phase temperature of that system is uniform. Also, there was no noticeable change in both the physical state and the chemical state as observed at temperatures higher than 873.0 K in the binary system. Thus

$$p_{total} = p_1 + p_2 = p + p_0$$  (1)

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\[ T = T_1 = T_2 \] (2)

However, the amount or the molar fraction of titanium tetrachloride or argon does not change in the closed experimental system. In the present study, the molar fraction of the titanium tetrachloride, \( x \), in the gas phase could be calculated as follows

\[ x = \frac{N_i}{N_1 + N_2} = \frac{v_iM_i}{v_1M_1 + v_2M_2} \] (3)

Here, \( p_{\text{total}} \) is the overall standard pressure of the binary system; \( p_i, T_i, N_i, v_i \) and \( M_i \) are the partial pressure, the temperature, the amount, the specific volume, and the molar mass of component \( i \), respectively; and the subscripts 1 and 2 are the gaseous titanium tetrachloride and argon, respectively.

## RESULTS AND DISCUSSIONS

### \( p-T \) Data for the Binary System

In the present experiment, all pressure measurements were carried out in the gaseous state at all investigated temperatures except for \( T = 350.0 \) K. The estimated gaseous \( p-T-x \) data for the \( x \text{TiCl}_4 + (1-x) \) Ar binary system are listed in Table 1. The experimental temperature, the overall standard pressure, and the molar fraction of titanium tetrachloride in the gas phase for the mixture system are 873.0–1173.0 K, 261.24–357.92 kPa, and 0.1320–0.2901, respectively. By observing the \( p-T-x \) behavior of the binary system, the overall pressure trends and the temperature are similar at the same molar fraction and the overall pressures are close at the same temperature.

**Gaseous \( p-v-T \) Property for Titanium Tetrachloride.**

The titanium tetrachloride gaseous \( p-v-T \) data were obtained along 10 isotherms and 8 isodensities at temperatures from 873.0 to 1173.0 K and pressures from 34.05 to 101.81 kPa, as indicated in Table 2. Besides, the molar fraction and the ratio of the partial pressure for the gaseous titanium tetrachloride in the binary system according to the data in Tables 1 and 2 are plotted in Figure 1. The calculated values of the molar fraction for the gaseous titanium tetrachloride are approximately equal to its ratio values of the partial pressure with a maximum relative error of \( \pm 3.18\% \) in this binary system. Therefore, Dalton’s Law is applicable in mathematically describing the partial pressure for the gaseous titanium tetrachloride or argon in the binary system in this experiment.

### Virial Coefficients for Titanium Tetrachloride

The calculated compressibility factors \( Z \) for the gaseous titanium tetrachloride in the experimental measurements are shown in Figure 2, wherein the critical compressibility factor \( Z_{\text{crit}} \) is 0.292. A three-term truncated virial EoS could be expressed as follows

\[ Z = \frac{P_i}{R_i T} = 1 + \frac{B}{v_i} + \frac{C}{v^2_i} \] (4)

where \( B \) and \( C \) are the second and the third virial coefficients, respectively. The virial coefficients for titanium tetrachloride derived from the gaseous data for each isotherm are fitted and listed in Table 3.
The second and the third virial coefficients are fitted to the following forms, with a maximum relative error of ±0.24% for the compressibility factor.

\[ B = -58.53 \times 10^4 \exp \left( -\frac{T}{46.06} \right) - 1.52 \times 10^{-2} \]  
\[ C = 72.60 \times 10^4 \exp \left( -\frac{T}{44.02} \right) + 0.09 \times 10^{-2} \]

Table 3. Second and Third Virial Coefficients at the Desired Temperature of Titanium Tetrachloride

| T/K | \( B \times 10^4 \,(\text{m}^3/\text{kg}) \) | \( C \times 10^4 \,(\text{m}^3/\text{kg}) \) |
|-----|-----------------|-----------------|
| 873.0 | -18.58 | 0.81 |
| 893.0 | -17.59 | 0.95 |
| 933.0 | -16.46 | 1.17 |
| 953.0 | -15.32 | 1.46 |
| 993.0 | -15.64 | 1.40 |
| 1013.0 | -15.55 | 1.15 |
| 1053.0 | -14.84 | 1.29 |
| 1093.0 | -15.03 | 1.19 |
| 1153.0 | -15.75 | 0.75 |
| 1173.0 | -15.27 | 0.76 |

\( ^{\text{a}} \)Uncertainties of the virial coefficients are the expanded uncertainties with a confidence level of 0.95 (k = 2).

CONCLUSIONS

To determine the gaseous \( p-v-T \) property of the gaseous titanium tetrachloride, the temperature and pressure measurements for the \( \text{TiCl}_4 + (1 - x) \text{ Ar} \) binary gas system were carried out in this work. The overall standard pressures ranging from 261.24 to 357.92 kPa are obtained at temperatures ranging from 873.0 to 1173.0 K, and the molar fraction of titanium tetrachloride ranges from 0.1320 to 0.2901. The specific volume of argon is calculated by the \( p-T \) data at a temperature of \( T = 350.0 \text{ K} \) with \( \text{P} - \text{R EoS} \) and the gaseous \( p-v-T \) property for titanium tetrachloride in the gas phase is also obtained at temperatures from 873.0 to 1173.0 K, pressures from 34.05 to 101.81 kPa, and specific volumes from 0.4914 to 1.1079 m\(^3\)/kg. The second and third virial coefficients along 10 isotherms are also fitted in this work, and a three-term truncated virial EoS is established with a maximum relative error of ±0.24%.

EXPERIMENTAL APPARATUS AND PROCEDURE

Chemicals. The typical industrial titanium tetrachloride sample (liquid phase) in this work was sampled from the same sponge titanium plant (Zunyi, China) as in a previous work and was from the same batch with a declared mass fraction purity of better than 99.70%, and the argon sample with the minimum mass fraction purity of 99.90% was purchased from Shennian Gas (Guiyang, China). The chemicals are summarized in Table 4.

Table 4. Chemicals Used This Study

| name | CAS RN | purity (wt %) | source | purification |
|------|-------|--------------|--------|-------------|
| titanium tetrachloride | 7550-45-0 | ≥0.997 | Zunyi Titanium Co., Ltd. | none |
| argon | 7440-37-1 | ≥0.999 | Guiyang Shennian Gas Co. | none |

\( ^{\text{a}} \)CAS registry number.

Experimental Apparatus. The experimental apparatus with present measurements is illustrated in Figure 3. The cylindrical vessel with a removable cover for the \( \text{TiCl}_4 + (1 - x) \text{ Ar} \) binary gas system is made of a 06Cr25Ni20 duplex stainless steel in Chinese Standard (or numbered 310S in ASTM) with an inner volume of about 150.00 ± 4.56 cm\(^3\) and sealed with a common tenon/mortise structure.
vessel is embedded in a set of resistance heaters with a total maximum power of 6.00 kW, and the input power of the heaters is controlled by two voltage regulators, such that the experimental apparatus could be immersed in thermostatic surroundings to establish temperature uniformity with the fluctuation of less than 0.5 K per 10 min. The heat loss on the wall of the whole apparatus is prevented by annular firebricks with insulation materials, and the total thickness of the firebricks and the insulation is about 5.0 cm. The whole experimental apparatus provides excellent sealing performance along with the whole experimental work.

The temperature measuring system includes a thermocouple (type K, class II) installed near the axis of the vessel and a digital temperature indicator (−50.0 to 1200.0 °C, ZJ-1008). The accuracy of the temperature indicator is better than 0.10% full scale. The type K thermocouple is cross-calibrated with a standard thermocouple (type S, class II) at temperatures from 873.0 to 1173.0 K and the total thickness of the firebricks and the insulation is about 5.0 cm. The whole experimental apparatus provides excellent sealing performance along with the whole experimental work.

The temperature measuring system includes a thermocouple (type K, class II) installed near the axis of the vessel and a digital temperature indicator (−50.0 to 1200.0 °C, ZJ-1008). The accuracy of the temperature indicator is better than 0.10% full scale. The type K thermocouple is cross-calibrated with a standard thermocouple (type S, class II) at temperatures from 25.0 to 1000.0 °C. The gage pressure of the mixture system is measured by a digital pressure gauge (−400.00 to 400.00 kPa, ConST-211) with an accuracy of 0.02% full scale stated by the manufacturer. A handle pump is used to adjust the gage pressure. A buffer tube is placed between the pressure gauge and the vessel to avoid the instantaneous impact and high-temperature damage of the mixture on the pressure gauge. The ambient pressure is measured by a digital atmospheric pressure gauge (80.00−110.00 kPa, DPH-101) with an accuracy of 0.30% full scale. The pressure gauges are calibrated against a DHI piston gauge. The bleeding of the exhaust gas sample or the charging of the argon sample is controlled by a bidirectional valve, and the safety relief valve plays a protective role in the experimental system.

Experimental Procedure. Before an experiment, a suitable amount of the liquid titanium tetrachloride sample is supplied into the vessel with oxygen-free surroundings. And then, the vessel system is thoroughly purged with the measured argon sample for at least 5 min.

For $p−T$ properties of the binary gas system, the experimental apparatus is heated and maintained at the desired sample temperature of about 1180.0 K. To avoid a sharp increase in pressure, a reasonable openness of the bidirectional valve is needed, and the value is turned to the exhaust gas treatment unit during the heating. After the desired temperature is reached, the bidirectional valve is closed. The temperature and pressure measurements are carried out in the decreasing direction order of temperature to avoid the hysteresis. The temperature at each desired state is recorded for at least 10 min to reduce the experimental error of the pressure and to ensure adequate mixing for the gaseous titanium tetrachloride and argon in the gaseous $p−v−T$ property measurements.

The specific volume of argon can be calculated from the $p−T$ data measured at 350.0 K by $p−R$ EoS,13 in which case only argon exists in the gas phase in the vessel. Then heating is stopped, the experimental measurements are ended, and the bidirectional valve is turned in the direction of the argon tank. The specific volume of the titanium tetrachloride is calculated by its remaining mass in the vessel and the volume of the vessel.

### APPENDIX. UNCERTAINTY ANALYSIS METHOD

Since there is no $p−v−T$ experimental data for gaseous titanium tetrachloride in the literature, the measurement uncertainty analysis is essential for determining the viability of this new experiment. The standard uncertainties ($k = 1$) of the directly measured quantities are considered, and then the overall uncertainties of the indirectly measured quantities are combined at a confidence level of 0.95 ($k = 2$).

### Uncertainty in Temperature Measurement

The uncertainty of temperature is dominated by uncertainties in the thermocouple, in the indicator and its resolution. The individual and combined uncertainties in temperature are listed in Table 5. Relative standard temperature uncertainty is $u_r(T)$, and $u_r(T) = 0.0004$ at temperatures from 873.0 to 1173.0 K and $u_r(T) = 0.0004$ at $T = 350.0$ K.

### Uncertainty in Pressure Measurement

The uncertainties of the gauge pressure and the ambient pressure both arise from three sources. First, five experimental tests are made for both the gauge pressure and ambient pressure measurements.

### Table 5. Uncertainty in Temperature Measurement

| $T/K$ | $u_r(T)$ | standard uncertainty, $u(T)$ |
|-------|---------|-----------------------------|
| 350.0 | 0.1111  | 0.0148 0.0577 0.1261 0.0004 |
| 873.0 | 0.8660  | 0.1155 0.0577 0.8756 0.0011 |
| 893.0 | 0.8949  | 0.1193 0.0577 0.9047 0.0011 |
| 933.0 | 0.9526  | 0.1270 0.0577 0.9628 0.0011 |
| 953.0 | 0.9815  | 0.1309 0.0577 0.9919 0.0011 |
| 993.0 | 1.0392  | 0.1386 0.0577 1.0500 0.0011 |
| 1013.0| 1.0681  | 0.1424 0.0577 1.0791 0.0011 |
| 1053.0| 1.1258  | 0.1501 0.0577 1.1373 0.0011 |
| 1093.0| 1.1836  | 0.1578 0.0577 1.1954 0.0011 |
| 1153.0| 1.2702  | 0.1694 0.0577 1.2827 0.0011 |
| 1173.0| 1.2990  | 0.1732 0.0577 1.3118 0.0011 |

$^a$Square root of the sum of the squares. $^b$Relative standard uncertainty ($k = 1$).
The individual uncertainties caused by repeated measurements could be calculated from

\[ u_i(p) = \frac{s(p)}{\sqrt{S}} = \sqrt{\frac{1}{20} \sum_{i=1}^{5} (p_i - \bar{p})^2} \]  
(A1a)

\[ u_i(p_0) = \frac{s(p_0)}{\sqrt{S}} = \sqrt{\frac{1}{20} \sum_{i=1}^{5} (p_{0i} - \bar{p_0})^2} \]  
(A1b)

\[ \bar{p}_0 = \frac{1}{S} \sum_{i=1}^{5} p_{0i} \]

Next, the individual uncertainties caused by the digital pressure gauge and the digital atmospheric pressure gauge are shown as

\[ u_2(p) = \frac{0.02\% \times p}{\sqrt{3}} = 0.000122p \]  
(A2a)

\[ u_2(p_0) = \frac{0.30\% \times p_0}{\sqrt{3}} = 0.0018p_0 \]  
(A2b)

A third contribution arises from the resolution of the pressure gauge, which is estimated to be \( u_3(p) = u_3(p_0) = 0.0058 \) kPa. The relative standard uncertainty \( (k = 1) \) results in pressure measurement are given by

\[ u_i(p) = \frac{u(p)}{p} = \frac{1}{p} \sqrt{u_1^2(p) + u_2^2(p) + u_3^2(p)} \]  
(A3a)

\[ u_i(p_0) = \frac{u(p_0)}{p_0} = \frac{1}{p_0} \sqrt{u_1^2(p_0) + u_2^2(p_0) + u_3^2(p_0)} \]  
(A3b)

**Expanded, Combined Uncertainty.** According to the error propagation methods,\(^6,^{14}\) the combined, expanded uncertainty of the overall pressure with a confidence level of 0.95 is

\[ u_i(p_{\text{total}}) = 2 \sqrt{\left(\frac{u_i(p)}{p_0}\right)^2 + \frac{u(p)}{p}^2} \]  
(A4)

\[ = 2 \sqrt{\left(u_i(p_0)\right)^2 + \left(u_i(p)\right)^2} \]

The specific volume of argon is calculated by the \( p-T \) data measured at 350.0 K. In this case

\[ p_2 = p_{\text{total}} \]  
(A5)

\[ u_{i}(v_2) = 2 \sqrt{\left(\frac{\partial \ln v_2}{\partial p_2} u(p_2)\right)^2 + \left(\frac{\partial \ln v_2}{\partial T} u(T)\right)^2} \]  
(A6)

However, the binary system at the temperature from 873.0 to 1173.0 K is

\[ u_i(p_2) = 2 \sqrt{\left(\frac{\partial \ln p_2}{\partial v_2} u(v_2)\right)^2 + \left(\frac{\partial \ln p_2}{\partial T} u(T)\right)^2} \]  
(A7)

\[ u_i(p_1) = 2 \sqrt{\left(u_i(p_{\text{total}})\right)^2 + \left(u_i(p_2)\right)^2} \]  
(A8)

\[ u_i(x) = 2 \sqrt{\left(\frac{\partial \ln x}{\partial v_1} u(v_1)\right)^2 + \left(\frac{\partial \ln x}{\partial v_2} u(v_2)\right)^2} \]  
(A9)

\[ u_i(Z) = 2 \sqrt{\left[u_i(p_2)\right]^2 + \left[u_i(v_1)\right]^2 + \left[u_i(T)\right]^2} \]  
(A10)

Also, the expanded uncertainty of specific volume for the gaseous titanium tetrachloride, \( u_i(v_1) \), is shown as

\[ u_i(v_1) = 2 \sqrt{\left[u_i(V)\right]^2 + \left[u_i(m)\right]^2} \]  
(A11)

\[ = 2 \sqrt{\left[u_i(V)\right]^2 + \left(\frac{u(m)}{m}\right)^2} \]

where \( m \) is the mass for titanium tetrachloride in the vessel. The standard uncertainty of the mass is \( u(m) = 0.03 \times 10^{-3} \) kg.

The expanded uncertainty of the volume for the experimental vessel, \( u_i(V) \), is shown as

\[ u_i(V) = 2 \left(\frac{\partial \ln V}{\partial r} u(r)\right)^2 + \left(\frac{\partial \ln V}{\partial h} u(h)\right)^2 \]

\[ = 2 \left[\frac{\partial}{\partial r} u(r)\right]^2 + \left[\frac{1}{h} u(h)\right]^2 = 0.0274 \]

(A12)

where \( r \) and \( h \) are the internal radius and depth of the steel vessel, respectively. The standard uncertainty of the internal radius of the steel vessel is the same as that of the depth of the vessel and \( u(r) = u(h) = 0.10 \times 10^{-2} \) m.

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**Notes**

The authors declare no competing financial interest.

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