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**Citation for published version:**

Di Nicola, G, Moglie, M, Santori, G, Stryjek, R & Polonara, F 2010, 'Carbon Dioxide + Fluoromethane and Nitrous Oxide + Fluoromethane: SolidLiquid Equilibria Measurements' Journal of Chemical and Engineering Data, vol 55, no. 11, pp. 5018-5022., 10.1021/je100606z

**Digital Object Identifier (DOI):**

[10.1021/je100606z](https://doi.org/10.1021/je100606z)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Preprint (usually an early version)

**Published In:**

Journal of Chemical and Engineering Data

**Publisher Rights Statement:**

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# **Carbon Dioxide + Fluoromethane and Nitrous Oxide + Fluoromethane: Solid-Liquid Equilibria Measurements**

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## **Abstract**

A recently built experimental set-up was employed for the estimation of the solid-liquid equilibria of alternative refrigerants systems. The behavior of two binaries, i.e. carbon dioxide + fluoromethane ( $\text{CO}_2 + \text{R41}$ ) and nitrous oxide + fluoromethane ( $\text{N}_2\text{O} + \text{R41}$ ), was measured down to temperatures of 126.5 K.

To confirm the reliability of the apparatus, the triple points of the pure fluids constituent the binary systems were measured. All triple point data measured revealed a generally good consistency with the literature.

The results obtained for the mixtures were corrected by the Rossini method and interpreted by means of the Schröder equation.

## Introduction

In industrial applications, the cascade refrigeration cycle is useful when low temperatures are required (i.e. below 233.15 K). The conventional cascade system often relies on R13 (chlorotrifluoromethane,  $\text{CClF}_3$ ) and R23 (trifluoromethane,  $\text{CHF}_3$ ) as refrigerants. Due to the heavy environmental impact of these two fluids, however, several natural refrigerants, i.e. carbon dioxide and nitrous oxide, have recently been considered for use in cascade refrigeration systems. In particular, several studies evaluated ammonia (R717) as the high-stage fluid and carbon dioxide (R744) as the low-stage fluid. The lowest evaporator temperature achievable was limited by the melting temperature of carbon dioxide ( $T_m/\text{K} = 216.58$ ). The lower temperatures needed in some applications can be achieved by using blends. That is why we recently turned our attention to (carbon dioxide and nitrous oxide) + hydrofluorocarbons (HFCs) mixtures<sup>1-8</sup> as potentially suitable working fluids in low-temperature refrigeration applications.

Data on solid-liquid equilibria (SLE) are important in refrigerating industry defining the lowest temperature limit at which the refrigerant may circulates in fluid state. In addition, SLE provide theoretical information on the behavior of studied systems at low temperatures in terms of activity coefficients. But, in a fact, the SLE for mixtures containing HFCs refrigerants are extremely scarce in literature.

Due to expected temperatures of the SLE of the systems formed with  $\text{CO}_2$  and/or  $\text{N}_2\text{O}$  + HCF refrigerants that usually spans from about 100 up to 217 K (in case of  $\text{CO}_2$  as the mixtures component), SLE measurements generally creates difficulties in the visual observation of the disappearance of the last amount of solid phase. Hence a set-up was specifically built<sup>1</sup> avoiding the need of the visual observation of phase behavior.

Recently, our lab measured the SLE of several ( $\text{CO}_2$  and  $\text{N}_2\text{O}$ ) + HFCs binary systems.<sup>1-5</sup> In order to study the behavior of the binary systems in terms of the Raoult's and Dalton's laws, the  $PVT_x$  of the  $\text{CO}_2$  + R41 and  $\text{N}_2\text{O}$  + R41 were recently studied by the same lab with isochoric and Burnett

apparatus,<sup>6-8</sup> but no information on the SLE of both title systems are available in the literature. The present study was also undertaken to fill this gap.

In this work, the SLE was measured down to temperatures of 126.5 K for CO<sub>2</sub> + R41 and N<sub>2</sub>O + R41 binary systems.

### **Experimental Set-up and Procedure**

The apparatus comprises a measuring cell and a system for drawing the liquid nitrogen directly from its insulated tank with the aid of compressed air: the carrier fluid circulating in the circuit is thus the refrigerant fluid itself.

The experimental setup is shown in Figure 1. The measuring cell (1) was made out of a stainless steel cylinder with a cover welded to the body. The volume was of approximately 47 cm<sup>3</sup>. A stirrer (2) was placed in the cell. Two holes were drilled in the cover, and a stainless steel tube with a diameter of 4 mm was inserted through and welded to the hole on the left for charging the cell with gas, while the hole on the right was used to house the thermometer with a diameter of 3 mm (3). The purpose of the stirrer was to prevent any premature stratification of the fluids comprising the various mixtures, while also assuring greater homogeneity during the liquefaction and crystallization of the mixture. The stirrer inside the cell was turned by a magnet, which drives the plate welded onto the lower end of the rod. An absolute pressure transducer (HBM, Mod. P8A) (4) was installed in the charging tube. A mass flow control (5) was installed upstream from the dehumidifier: a needle valve with a shutter was used to adjust the flow rate coming from the dry air supplier (6), as measured by means of the pressure difference read on a pressure gauge alongside it. The airflow was also measured by a rotameter (7).

The operation of the system as a whole can be divided into two separate circuits and consequently two operating modes: a cooling and an heating mode.

*Cooling mode.* The cooling system as a whole is composed by four functional parts: the compressed air circuit that creates a positive pressure in the liquid nitrogen tank, the thermally-insulated liquid

nitrogen tank (8), the hose connecting the tank to the circuit, complete with a faucet, and the copper coil that surrounds and exchanges heat with the cell.

The core element in the whole cooling system is the copper coil surrounding the measuring cell; through its contact surface, the coil removes heat by means of the refrigerant fluid flowing inside it. The copper coil and cell are placed together inside a Dewar flask (9) so as to further isolate them from the outside environment. The system as a whole is suitably covered with neoprene foam for thermal insulation.

When the system is used in the cooling mode, the compressed air (after passing through suitable dehumidifier filters) is delivered to the liquid nitrogen tank, which is thus placed under a positive pressure. Inside the tank, a PVC hose draws the refrigerant fluid from the bottom, which begins to flow through the circuit as soon as the pressure in the tank, controlled by a manometer (10), is sufficient to overcome the load losses produced by the circuit. When a steady state is reached, the liquid nitrogen flows through the circuit, rapidly cooling all of its surfaces to a very low temperature. The refrigerant fluid passes first through the silicone capillary, then through the copper piping, exchanging heat with the measuring cell by evaporation as it moves through the coil, and finally flows out from the nitrogen outlet (11). In this cooling configuration, the nitrogen valve remains open and the heating circuit valve remains closed.

*Heating mode.* When the system is operated in the heating mode, the dehumidified compressed air circuit is connected directly to the measuring cell's circuit and, in this case, the air acts as a carrier fluid and warms the cell, which is at a very low temperature by the end of a measuring procedure. In this configuration, the nitrogen inlet valve remains closed. An external copper coil (12) has also been provided: this can be heated by the operator to speed up the warming of the measuring cell.

*Temperature Measuring System.* To monitor the temperatures, the apparatus was equipped with one thermoresistance put in the measuring cell. The system parameters and the efficiency of the coil immersed in the liquid nitrogen were assessed using thermocouples at specific points on the copper tube. The platinum resistance thermometer used in the apparatus (Model: S7929, 100  $\Omega$ , Minco)

was calibrated by comparison with a 25  $\Omega$  platinum resistance thermometer (Model: 5680, SN1083, Hart Scientific).

*Experimental Procedure.* The charging procedure consisted of the following steps: the bottle containing the refrigerant gas (13) was weighed on the electronic balance (the uncertainty of which is 0.5 mg); then the bottle was connected to the apparatus and to the vacuum pump (14) (Vacuubrand, Mod. RZ2), a vacuum was created inside the measuring cell and the charging tube as recorded on the vacuum pump gauge (Galileo, Mod. OG510); then the fluid was charged by opening the valve on the gas bottle; the temperature of the cell was brought down by a flow of liquid nitrogen so as to insert the whole mass in the cell, leaving as little as possible in the charging tube; a suitable time interval was allowed so that the pressure, being lowered by the temperature reduction, could drop to below atmospheric pressure, then the on/off valve was closed; and the gas bottle was disconnected and weighed again to establish the actual mass charged in the cell.

The coil with liquid nitrogen was wrapped around the measuring cell. Monitoring the time dependence of temperature, a cooling curve was obtained for each sample concentration. While the change of phase occurs, the heat removed by cooling is compensated for by the latent heat of the phase change, showing a change of slope in the temperature trend. The arrest in cooling during solidification allows the melting point of the material to be identified on the time-temperature curve. The melting points can then be plotted versus the composition to give a phase diagram.

### **Experimental Uncertainties**

All the uncertainties were calculated using the law of error propagation, as reported elsewhere.<sup>1</sup>

Here, the previously reported results will be briefly summarized.

The total uncertainty of the mass of sample mixture was less than 0.01 g. The uncertainty in composition measurements was estimated to be always lower than 0.005 in mole fraction.

The global uncertainty of the temperature, considering also the contribution of the Rossini method correction, was estimated to be less than  $\pm 1$  K.

Since the measured vapor-pressure data were not accurately measured at very low temperatures within the declared precision of the used instrument (the pressure values were acquired by an absolute pressure transducer HBM, Model: P8A, and the global uncertainty of the pressure measurements was estimated to be less than 3 kPa), the vapor-pressure data were not reported in the present paper.

## **Experimental results**

*Chemicals.* Carbon dioxide and nitrous oxide were supplied by Sol SpA. Their mole purity was checked by gas chromatography, using a thermal conductivity detector. In the estimation, it was considered that for small contents of impurity, the mole ratio was proportional to the area ratio. The mole purity was found to be 99.99 % for both fluids, basing all estimations on an area response. R41 was supplied by Lancaster Inc.; its mole purity was found to be 99.9 % on an area response.

*Pure fluids.* The triple point temperatures for the mixture constituent fluids were obtained in different experiments, and different runs were repeated for each pure fluid. These data relate to the tests conducted with the stirrer switched on.

For carbon dioxide and nitrous oxide, the measurements were reported elsewhere.<sup>1,2</sup> For both pure fluids, a metastable phase was appearing during the measurements. In addition, a faster cooling rate coincided with a greater supercooling effect. The cooling rate that seemed to guarantee the greatest repeatability of the results was approximately  $-0.01 \text{ K}\cdot\text{s}^{-1}$ , corresponding to an air flow rate of approximately  $0.17 \text{ dm}^3\cdot\text{s}^{-1}$ . Triple-point measurements for the two fluids showed good agreement with literature sources, both in terms of temperature and pressure.<sup>1,2</sup>

For R41, the metastable phase was not observed during the measurements, and better results were achieved with the system operating in the heating mode. In this way, a change of slope was evident in the temperature-time diagram during the heating, as witnessed by Figure 2. The triple point measurement ( $T_{tp}/ \text{K} = 129.77$ ) revealed a very good consistency with the literature value ( $T_{tp}/ \text{K} = 129.82$ ).<sup>10</sup>

*Results for mixtures.* Regarding the studied mixtures, no literature data on the SLE of the analyzed binary systems are available in the open literature. Measurements were taken using different concentrations of the two components, obtaining a satisfactory number of points, which were then recorded on a concentration/temperature graph ( $T$ - $x$ ).

Conducting several tests on the same sample, we noted that we obtained better, more reliable results by switching off the stirrer at least about 20 to 40 K (values suggested by experience) before reaching the triple point temperature. This was probably due to the turning of the stirrer, that helps to keep the mixture's components well mixed and the homogeneity of temperature inside the cell, but once near-freezing temperatures have been reached, it probably interferes with the solidification of the mixture, fragmenting the solid crystals when they began to form.

In addition, conducting several tests on different sample compositions, better results were generally achieved when the apparatus was used in the cooling mode; at very high R41 concentrations, results obtained with the apparatus in the heating mode were found to be more reliable. When possible, however, data were collected with both configurations for the same concentrations and results were mutually consistent, with deviations always well within 1 K. This value could be considered the reproducibility limit of our experimental measurements. This is confirmed by figures 4 and 5, where the  $T$ - $x$  measurements for the two systems considered ( $\text{CO}_2 + \text{R41}$  and  $\text{N}_2\text{O} + \text{R41}$ , respectively) are reported. The results were also summarized in Table 1. From the  $T$ - $x$  data it is evident that both systems form eutectics ( $x_1 = 0.04$  at  $T/\text{K} = 126.5$  for  $\text{CO}_2 + \text{R41}$  and  $x_1 = 0.16$  at  $T/\text{K} = 127$  for  $\text{N}_2\text{O} + \text{R41}$ ).

*Rossini method corrections.* The results of the temperature data acquisitions were corrected using the Rossini method<sup>11</sup> because a constant cooling rate is not indispensable and was not guaranteed by our experimental method. The entity of the corrections takes into account the fact that the fluid is still in a liquid state during the metastable state (supercooling) that precedes proper solidification. In this phase, the temperature is distinctly lower than the one characterizing the instant when crystallization begins, its amplitude depending mainly on the rate at which the temperature is



lowered. The resulting corrections were nonetheless always very limited, of the order of a few tenths of a Kelvin in the majority of cases, and always well below 1 K.

### Interpretation of the results

When an organic system forms eutectic, the course of the *liquidus* is well described by the Schröder equation.<sup>12</sup> The SLE depend both on the crystals formed in solution and on the properties of the liquid phase. VLE derived from our previous isochoric measurements for the binaries under study witnessed that the two systems showed an almost ideal behavior in terms of the Raoult's law.<sup>8,9</sup> The exact course of the *liquidus* for mixtures showing a small deviation from Raoult's law depends mainly on the enthalpy of fusion of the solute (CO<sub>2</sub> and N<sub>2</sub>O in our case).

As both systems formed eutectics, the solubility of the solid solute in the solvent (here, R41) can be described by the Schröder equation; which disregarding any difference between the heat capacity of the subcooled liquid solute and solid solute takes the following form:

$$\ln \gamma_2 x_2 = -\frac{\Delta h_m}{RT} \left( 1 - \frac{T}{T_m} \right) \quad (1)$$

where the subscript 2 denotes the solute and the subscript m denotes property at melting point.

Assuming as a first approximation that the solute's activity coefficient,  $\gamma_2=1$ , we can write:

$$\ln x_2 = -\frac{\Delta h_m}{RT} \left( 1 - \frac{T}{T_m} \right) \quad (2)$$

This simplification leads to the consideration that the solubility of the solid solute is independent of the solvent as far as the assumptions hold. The enthalpies at melting point ( $\Delta h_m$ ) were assumed to be 9020 J·mol<sup>-1</sup>,<sup>13</sup> 6540 J·mol<sup>-1</sup>,<sup>13</sup> and 4590 J·mol<sup>-1</sup>,<sup>14</sup> for CO<sub>2</sub>, N<sub>2</sub>O and R41, respectively.

The course of the liquidus calculated with the Schröder equation is included in Figures 3 and 4. Both systems well followed the Schröder equation. For the CO<sub>2</sub> + R41 system, a very good agreement (generally within 1 K and never exceeding 2 K) with the equation prediction was evident at low CO<sub>2</sub> concentrations, while a discrepancy of few degrees with the Schröder equation

prediction at higher CO<sub>2</sub> concentration ( $0.55 < x_1 < 0.85$ ) was evident. For the N<sub>2</sub>O + R41 system, a general agreement with the Schröder equation was evident.

## **Conclusion**

In this paper, the solid-liquid equilibria of two binaries, i.e. carbon dioxide + fluoromethane (CO<sub>2</sub> + R41) and nitrous oxide + fluoromethane (N<sub>2</sub>O + R41), was measured down to temperatures of 126.5 K. The two binary systems are potentially suitable working fluids in low-temperature refrigeration applications, as cascade cycles. The triple points of the pure fluids contained in the mixture were measured to check the reliability of the new apparatus, revealing a good consistency with the literature. The measurements were performed both in the cooling and in the heating mode. The two configurations showed mutually consistent results.

The CO<sub>2</sub> + R41 and N<sub>2</sub>O + R41 systems showed the presence of an eutectic for both systems at temperatures very close to R41 triple point temperature ( $x_1 = 0.04$  at  $T/ K = 126.5$  for CO<sub>2</sub> + R41 and about  $x_1 = 0.16$  at  $T/ K = 127$  for N<sub>2</sub>O + R41).

For the CO<sub>2</sub> + R41 system, a very good agreement with the equation prediction was evident at low CO<sub>2</sub> concentrations, while a discrepancy of few degrees with the Schröder equation prediction at higher CO<sub>2</sub> concentration ( $0.55 < x_1 < 0.85$ ) was evident. For the N<sub>2</sub>O + R41 system, a general agreement with the Schröder equation was evident.

## Literature cited

- (1) Di Nicola, G.; Giuliani, G.; Polonara, F.; and Stryjek, R. Solid-liquid equilibria for the CO<sub>2</sub> + R125, and N<sub>2</sub>O + R125 systems: a new apparatus. *J. Chem. Eng. Data* **2006**, *51*, 2209-2214.
- (2) Di Nicola, G.; Giuliani, G.; Polonara, F.; and Stryjek, R. Solid-liquid equilibria in the CO<sub>2</sub> + N<sub>2</sub>O, CO<sub>2</sub> + R32, and N<sub>2</sub>O + R32 systems. *Fluid Phase Equilib.* **2007**, *256*, 86-92.
- (3) Di Nicola, G.; Santori, G.; and Stryjek, R. Solid-Liquid Equilibria for the Carbon Dioxide + 1,1-Tetrafluoroethane and Nitrous Oxide + 1,1-Tetrafluoroethane Systems. *J. Chem. Eng. Data* **2008**, *53*, 1980-1983.
- (4) Di Nicola, G.; Moglie, M.; Santori, G.; and Stryjek, R. Solid-Liquid Equilibria for the CO<sub>2</sub> + R143a, and N<sub>2</sub>O + R143a Systems. *Int. J. Thermophys.* **2009**, *30*, 1155-1164.
- (5) Di Nicola, G.; Giuliani, G.; Polonara, F.; Santori, G.; and Stryjek, R. Solid-Liquid Equilibria for the CO<sub>2</sub> + R23, and N<sub>2</sub>O + R23 Systems. *Int. J. Thermophys.* DOI 10.1007/s10765-008-0511-0.
- (6) Di Nicola, G.; Giuliani, G.; Polonara, F.; and Stryjek, R. Second and Third Virial Coefficients for the R41+N<sub>2</sub>O System. *Fluid Phase Equilib.* **2004**, *225*, 69-75.
- (7) D'Amore, A.; Di Nicola, G.; Polonara, F.; and Stryjek, R. Virial Coefficients from Burnett Measurements for the Carbon Dioxide+ Fluoromethane System. *J. Chem. Eng. Data* **2003**, *48*, 440-444.
- (8) Di Nicola, G.; Polonara, F.; Ricci, R.; and Stryjek, R. PVT<sub>x</sub> Measurements for the R116 + CO<sub>2</sub> and R41 + CO<sub>2</sub> Systems. New Isochoric Apparatus. *J. Chem. Eng. Data* **2005**, *50*, 312-318.
- (9) Di Nicola, G.; Giuliani, G.; Polonara, F.; and Stryjek, R. PVT<sub>x</sub> Measurements for N<sub>2</sub>O + CH<sub>3</sub>F, + CH<sub>2</sub>F<sub>2</sub>, and + CHF<sub>3</sub> Binary Systems. *Fluid Phase Equilib.* **2005**, *230*, 81-89.
- (10) Magee, J. W. in *NIST Technical Note 1397*, Holcomb, C. D.; Magee, J. W.; Scott, J. L.; Outcalt, S. L.; and Haynes, W. M. eds. 1997, 14.
- (11) Mair, B. J.; Glasgow, J. A. R.; and Rossini, F. D. Determination of the freezing points and amounts of impurity in hydrocarbons from freezing and melting curves. *J. Res. Nat. Bur. Standards* **1941**, *26*, 591-620.

- (12) Schröder, I. Über die Abhängigkeit der Löslichkeit eines festen Körpers von seiner Schmelztemperatur. *Z. Phys. Chem.* **1893**, *11*, 449-465.
- (13) Lide, D. R.; and Kehiaian, H. V. CRC Handbook of Thermophysical and Thermochemical Data. CRC press, Inc. 1994.
- (14) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Yang, Y.; and Giles, N. F. DIPPR® Data Compilation of Pure Chemical Properties, Design Institute for Physical Properties, AIChE, New York, 2010.

**Table 1.** *T-x* Measurements for the CO<sub>2</sub> + R41 and N<sub>2</sub>O + R41 Binary Systems.

CO <sub>2</sub> (1) + R41 (2)		N <sub>2</sub> O(1) + R41 (2)	
<i>x</i> <sub>1</sub>	<i>T</i> / K	<i>x</i> <sub>1</sub>	<i>T</i> / K
0.000	129.77*	0.000	129.77*
0.040	126.45*	0.035	131.05*
0.040	124.65	0.036	129.15*
0.057	137.9*	0.052	130.02*
0.068	142.35*	0.090	128.55*
0.101	146.25*	0.099	128.35*
0.101	146.65	0.157	128.65*
0.129	153.82*	0.249	137.64*
0.129	153.93	0.249	137.62
0.131	154.35	0.298	142.05*
0.196	164.05*	0.298	141.85
0.196	163.81	0.345	145.04*
0.282	173.35*	0.397	150.95*
0.282	173.15	0.397	151.55
0.321	177.25*	0.452	154.35*
0.321	177.65	0.498	156.84*
0.348	179.65*	0.633	164.75
0.348	178.45	0.662	166.85
0.400	183.00	0.696	167.16
0.459	190.25	0.790	174.15
0.475	190.35*	0.831	174.18*
0.509	191.25*	0.831	174.15
0.509	190.79	0.866	176.15
0.534	199.45	0.889	175.35
0.608	199.45	0.923	178.92*
0.663	203.81	0.923	179.00
0.687	206.95	0.938	178.05
0.758	209.05	1.000	181.99
0.765	210.55		
0.817	212.38		
0.855	213.45		
0.908	212.05		
0.922	212.75		
0.941	213.80		
0.963	215.03		
1.000	216.05		

\*results obtained with the heating mode

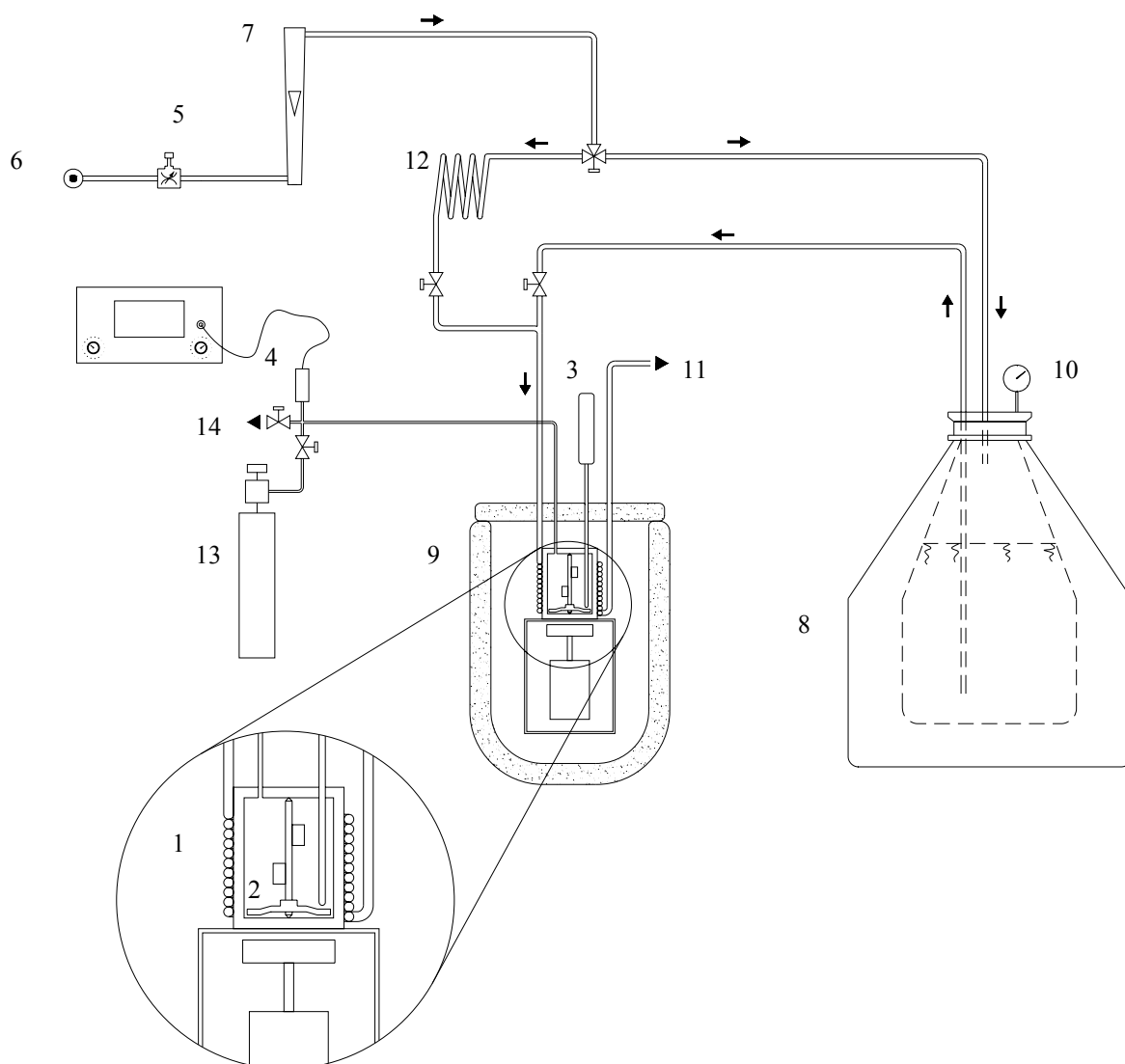


Figure 1. Schematic illustration of the apparatus.

Notation:

- 1 Measurement cell
- 2 Stirrer
- 3 Platinum resistance thermometer
- 4 Pressure transducer
- 5 Mass flow controller
- 6 Dry air supplier
- 7 Rotameter
- 8 Liquid nitrogen tank
- 9 Dewar containing the measurement cell
- 10 Liquid nitrogen dewar manometer
- 11 Nitrogen outlet
- 12 External heating coil
- 13 Charging bottle
- 14 Vacuum pump system

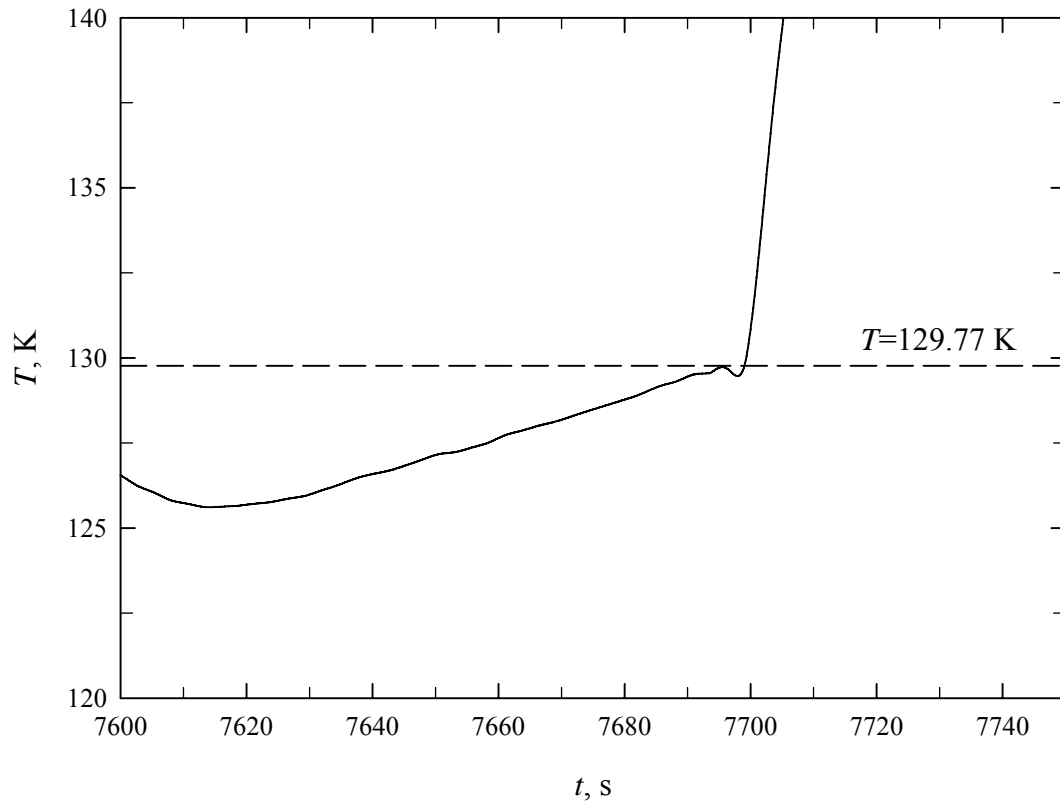


Figure 2. Acquisition of the R41 triple point temperature measurements.

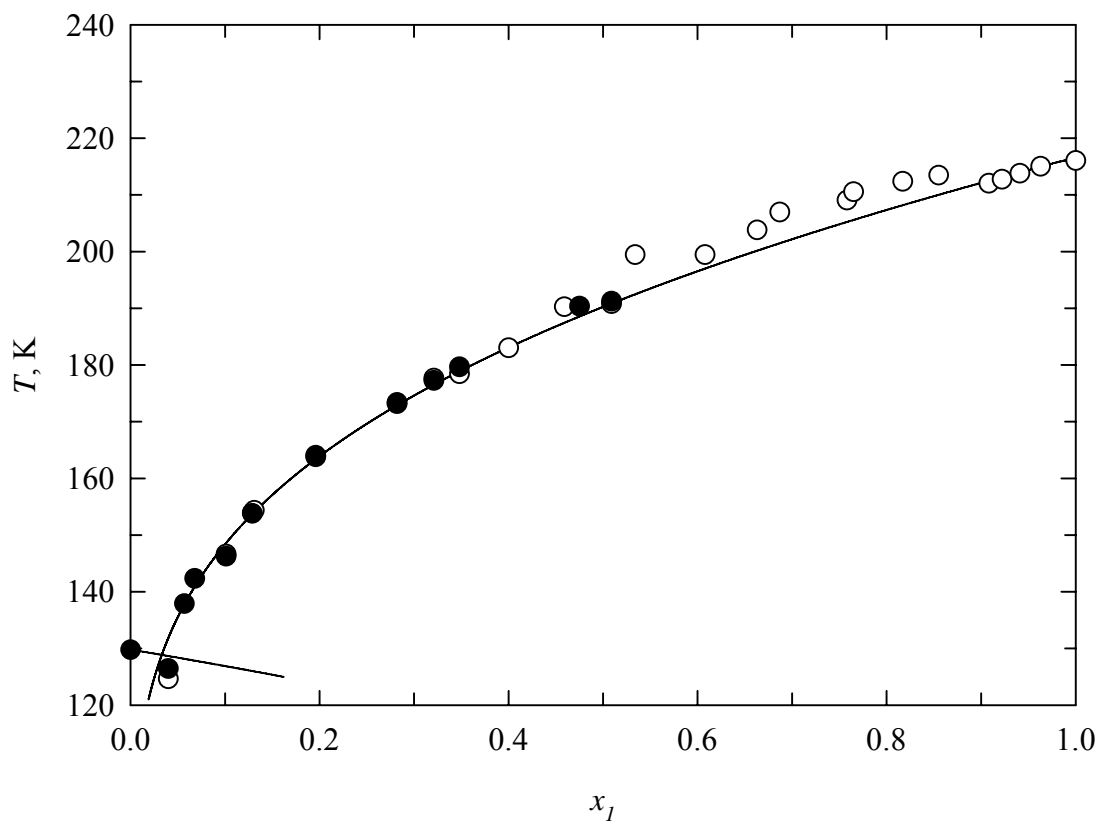


Figure 3. SLE for the CO<sub>2</sub> + R41 system. Black symbols denote the experimental points obtained by the heating mode, while open symbols denote the experimental points obtained by the cooling mode. The lines denote the Schröder eq.



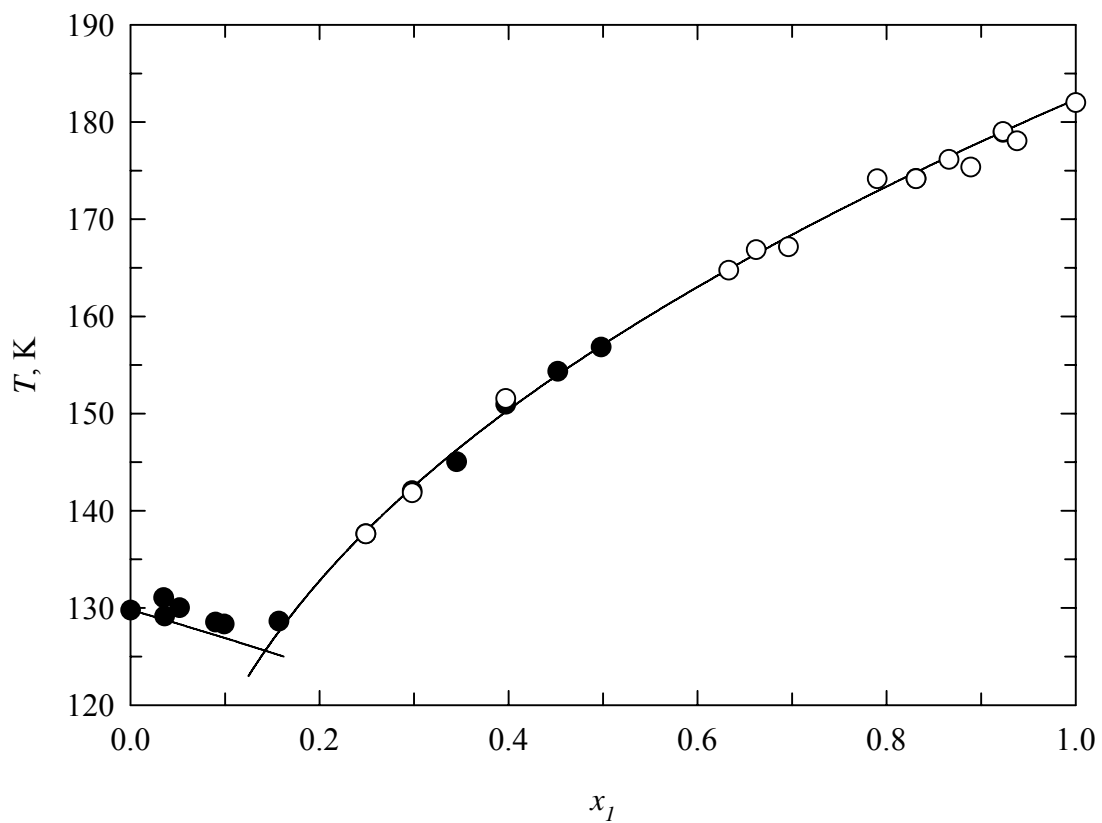


Figure 4. SLE for the  $N_2O + R41$  system. Black symbols denote the experimental points obtained by the heating mode, while open symbols denote the experimental points obtained by the cooling mode. The lines denote the Schröder eq.