

A NMR Spin-Echo Study of Diffusion in Molten Salts

Günter Palmer, Joachim Richter, and Manfred D. Zeidler

Institut für Physikalische Chemie, Rheinisch-Westfälische Technische Hochschule Aachen, Templergraben 59, 52056 Aachen, Germany.

Reprint requests to Prof. J. R.; Fax: 0049(0)2418092235; E-mail: Richter@RWTH-Aachen.de

Z. Naturforsch. **59a**, 51 – 58 (2004); received October 1, 2003

Pressure-dependent measurements of the cationic self-diffusion coefficients of molten (Na, Li)NO₃ were carried out at 613 K. The pressure range lies between ambient pressure and 200 MPa. A new high-pressure probe, operating with heating coils, was constructed from titanium alloy. The temperature difference across the probe could be confined to 2.5 K. By use of a switchable high-frequency coil the nuclei lithium and sodium could be measured in succession within the same sample. The activation volumes are composition-dependent and range from 5 to 9 cm³mol⁻¹.

Key words: Molten Salts, Self-diffusion, NMR Spin Echo.

1. Introduction

Self-diffusion coefficients of Li⁺ and Na⁺ are available for molten LiNO₃ and NaNO₃ [1–3], but there exist no data for the mixtures. Results for other mixtures with NaNO₃ can be found in the literature [4, 5]. All these data are confined, however, to ambient pressure.

Our previously developed high-pressure system [6] could only be operated up to 100 MPa and had problems with the electric throughputs at high pressures. Other problems were leaks at the fittings at high temperature, short circuits at the gradient coil, failures of the gradient current supply, vibrations during the monitoring of the heating current, and a too large temperature gradient of the heating system.

In the present paper we describe an improved version of a high-pressure probe which operates between ambient pressure and 300 MPa at room temperature and 200 MPa at 650 K. The new device was tested by performing self-diffusion measurements of the lithium and sodium ions in molten (Li, Na)NO₃ up to 613 K.

2. High-pressure Probe

The new probe had to fit the available Bruker CXP 300 NMR spectrometer with a magnet having a bore of 89 mm (without shim coils) and a field strength of 7.02 T. A higher temperature than 300 K in the bore had to be avoided to protect the magnet. Thus for the

desired highest sample temperature of 650 K a perfect thermal isolation of the probe was needed.

Figure 1 shows the probe, consisting of a cylinder made from the titanium alloy IMI 834. Its measures are shown in a technical drawing. Both ends of the cylinder are closed with a system consisting of screws having M29 × 1.5 winding, a ring, a Bridgman seal and a lid, as shown in Figure 2; technical drawings of these components are included in the figure. All these parts, except the Bridgman seal, are made of the same titanium alloy, the seal is made of soft copper. The copper seal is heated to red hot in order to soften it by a phase transformation. Soft copper seals deform easier and provide maximum closure, which keeps for several hours. A new seal must be used at each sample change. For safety reasons a hole is drilled through the cylinder at the position of the ring to avoid pressure build-up between the lid and the screw in case of a leakage. The pressure lead and thermocouple pass through the upper closure system, while the electric leads pass through the lower one.

For diffusion measurements any convection must be excluded. Therefore we need a homogenous temperature across the sample, which becomes a problem above 450 K. As Fig. 1 shows, a pair of heating coils was arranged symmetrically on the cylinder, each set of coils consisting of 8 windings of a wire with 5.5 Ω m⁻¹ resistance (Thermocoax Company, Hamburg, Germany, type 1NcAc15). The two sets were wound 10 mm apart from each other on

Fig. 1

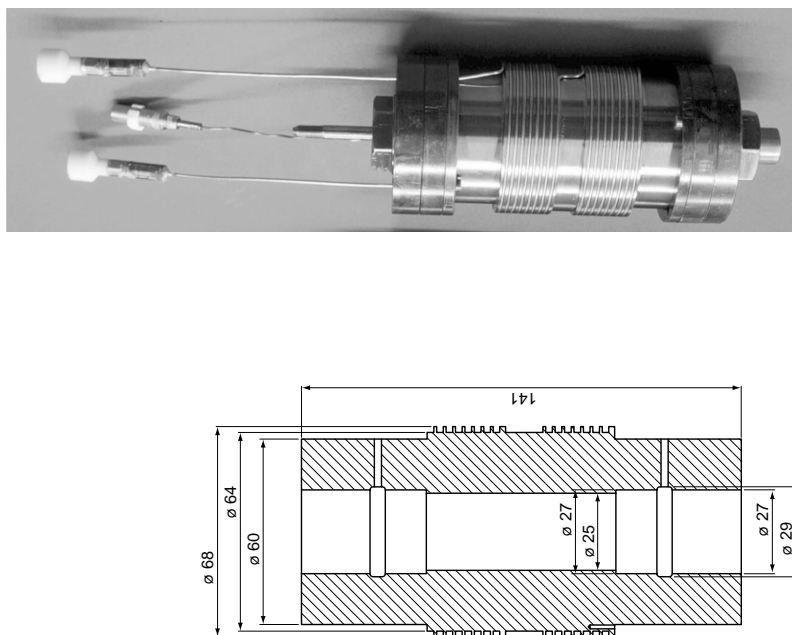


Fig. 1. Technical drawing and photo of the probe (lengths in mm).

Fig. 2

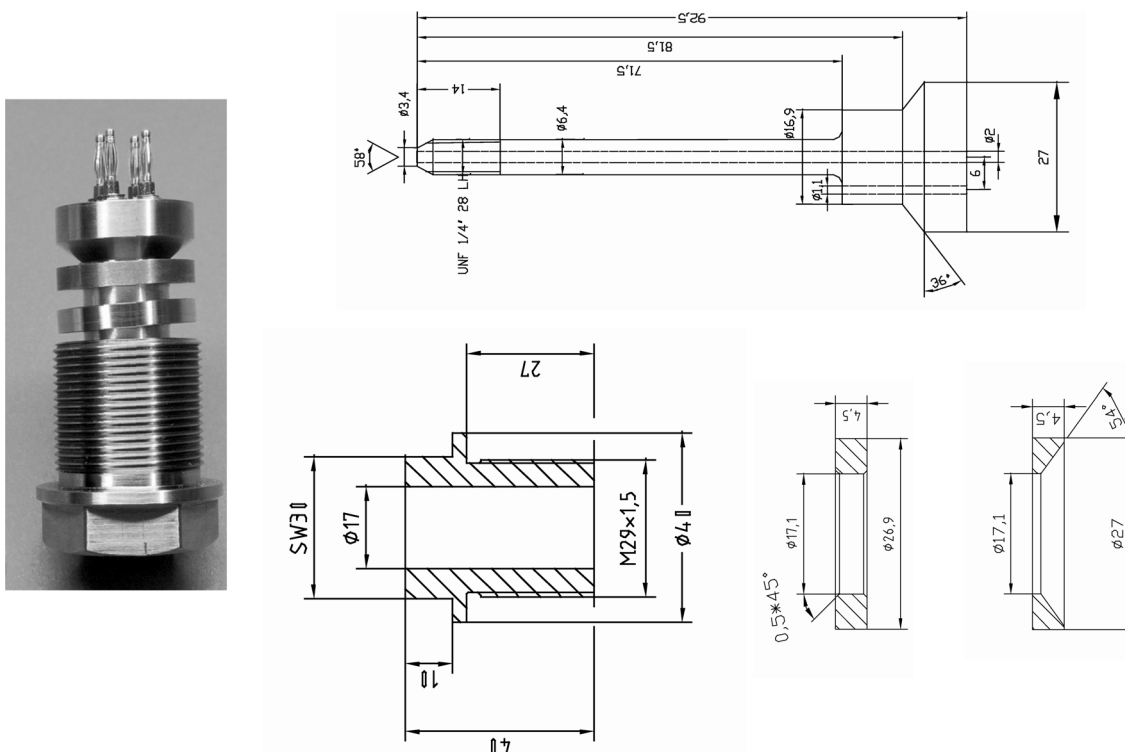


Fig. 2. Closure system of the high-pressure cylinder. Under the photo technical drawings of the screw, ring, Bridgman seal and lid (from top left to right) are shown.

the titanium cylinder into appropriate grooves with inverse direction in order to compensate the magnetic fields originating from the coils. Temperature regulation was done with a PID control unit (West Company, Wölferstheim, Germany, type 5010), the sensing thermocouple (Thermocoax Company, Hamburg, Germany, type E) was placed inside the cylinder wall because a position within the high-pressure compartment is disadvantageous due to disturbing pressure sensitivity. The PID control was modified (see Fig. 3) in such a way that instead of switching the heating current on and off, a current splitter varies the current by less than 30 mA. This procedure avoids any vibrations which were observed previously with the original PID control.

A cooling cylinder made from brass is pushed over the high-pressure cylinder; it has 71.8 mm inner and 88 mm outer diameter and a length of 210 mm, thus extending 69 mm beyond the titanium cylinder. The space between the cooling and high-pressure cylinders (11.8 mm) is fixed by copper rings 25 mm high at both ends of the cylinders which permit cooling. This is necessary for the electric throughputs made of vespel to avoid their aging. The height of the rings must be adjusted to the wanted temperature. The use of copper is therefore preferred to ceramic rings, although they would provide better heat isolation. The electrical throughputs are only at the lower end, but a symmetrical design must be kept and the same ring is applied at the top. With a water flow of 3 l/min from below the exterior temperature of the cooling cylinder did not exceed 300 K. Of course the temperature of the cooling water is of importance and must be observed together with the control parameters of the PID device. All these data must be optimized. This resulted in a temperature difference of 2.5 K at 623 K and of 1.5 K at 473 K. In addition, to the optimized regulation the PID control had an automatic switch-off if the temperature exceeded more than 15 K at the sensing thermocouple, if the cooling water got warmer than 303 K or its flow rate fell to less than 3 l/min.

The electrical throughputs consist of plugs as shown in Figure 4. They consist of three parts, as the upper photo and the technical drawings clearly show. The metallic part is made of copper-beryllium alloy, the isolations are of vespel. The left conical part is at the outside, the right part with the feather-like plug is at the inside of the high-pressure vessel. The ready mounted plug at the bottom of the photo is built into the lower closure lid.

Photos of the high-frequency coil and the circuit diagram are shown in Figure 5. The switch S1 allows the use of both NMR frequencies, 116.63 MHz and 79.39 MHz for the lithium-7 and sodium-23 nuclei, respectively. The saddle coil is made of 1 mm thick silver-coated copper wire. It is mounted on a macor support with a glass tube, into which the sample is shifted. The molten salt is placed into a 7 mm thick MAS zirconium dioxide container which is closed by a piston (Cerobear Company, Herzogenrath, Germany, type MASWP5017180). The sample volume is 0.4 ml. The tuning and matching capacitors in the circuit are very finely tunable, high-voltage resistant and of course nonmagnetic (Voltronics Corporation, Denville, New Jersey, USA, types NMNT70E and NMNT15E).

As pressurizing fluid we use an isomeric mixture of dibenzyl toluene (Dr. R. Wobser Company, Lauda, Germany, type Ultra-Therm 330SCB). The pressure is applied through a screw press and led to the probe by a capillary.

3. Pulsed-gradient Unit

The gradient coil is a Maxwell coil as in our previous setup [6], wound with a better insulated wire as before (EKS Isodraht Company, Mannheim, Germany). The lacquer insulation can withstand temperatures up to 700 K. The gradient and high-frequency coils are shielded against each other by a 1 mm thick copper tube placed between them, furthermore two low-pass filters are introduced into the circuit of the gradient unit (see Figure 6). A newly developed steering unit and current readout unit were published recently [7].

The gradient had a value of $0.044 \text{ Tm}^{-1} \text{A}^{-1}$. The sample temperature, heating current, pressure and gradient current are recorded and fed through an analog to digital (AD) converter (see Fig. 7) into a computer so that any failure can be traced.

4. Sample Preparation and Measurement

Lithium and sodium nitrate were filled into the sample container as solids, either pure or as a mixture with the desired composition, and are melted therein. Until the container is completely filled with the melt, solid material is added. Then the hot piston is positioned and the sample is cooled slowly in the oven. The cold sample container is then transferred to the coil and mounted into the high-pressure cylinder from

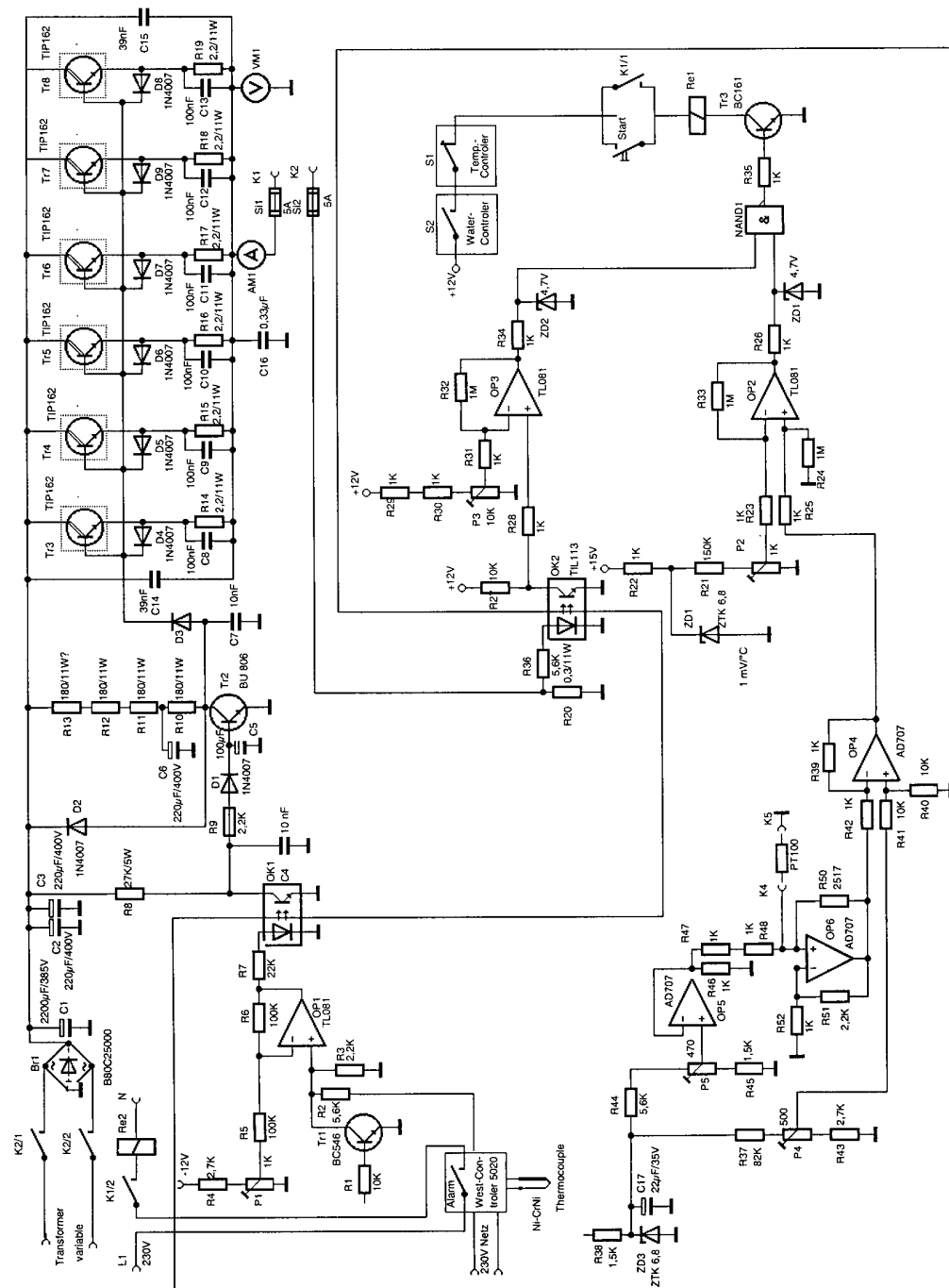


Fig. 3. Circuit of the heating control.

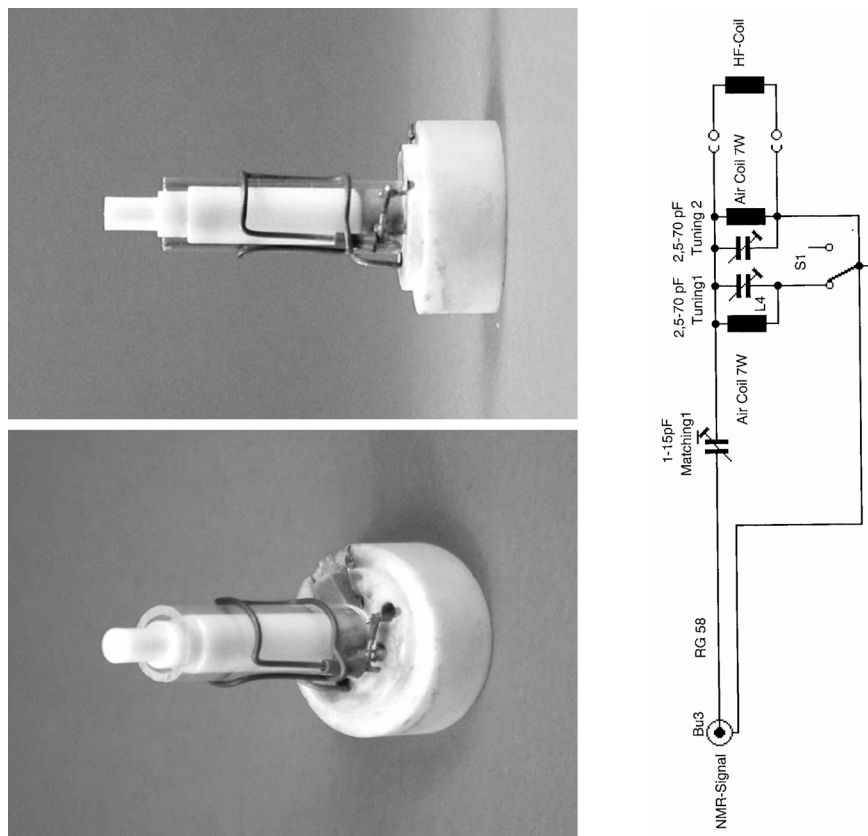


Fig. 5. Photo of the high-frequency coil with sample and sample circuit.

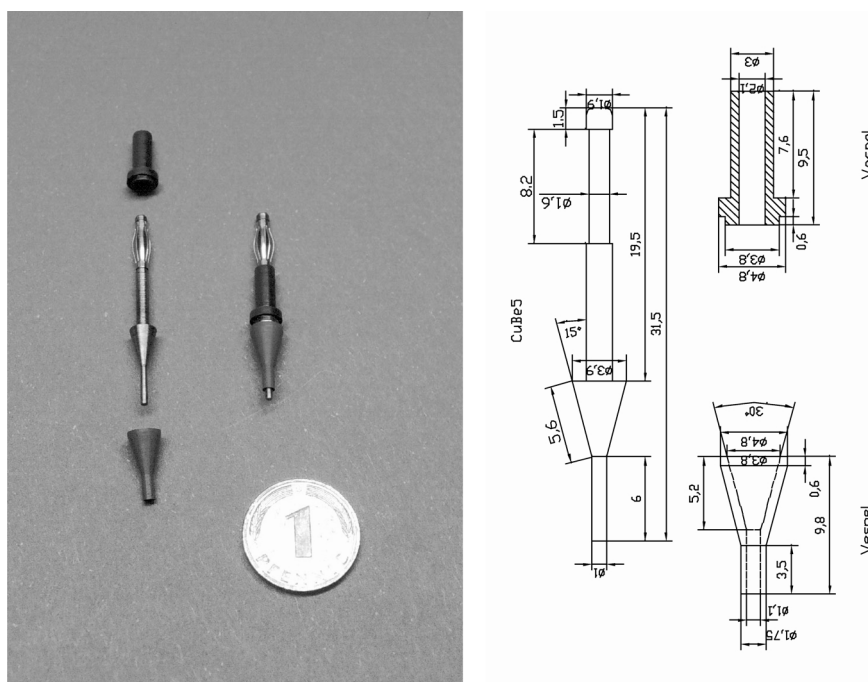


Fig. 4. Photo and technical drawings of the electrical throughputs.

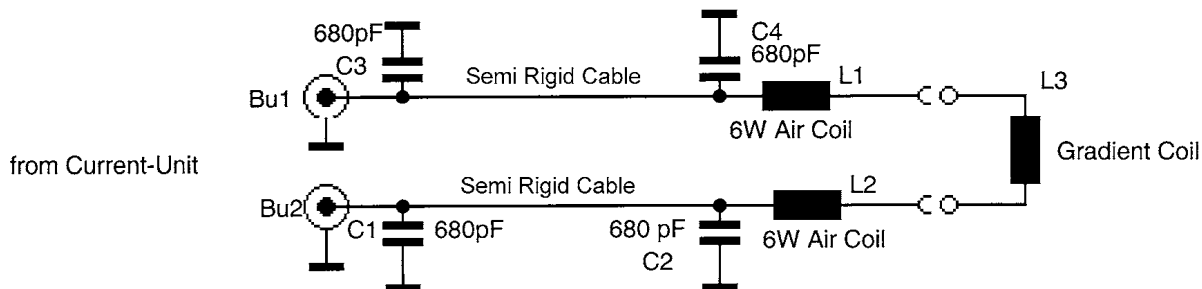


Fig. 6. Circuit of the gradient unit.

below. The pressurizing fluid is filled into the cylinder, and the upper closure system is fixed. The cooling system, the sample circuit, and all the connections, i. e. heating supply, cooling water, thermocouples, gradient current supply, high-frequency, pressure capillary are mounted. The resonance frequency is adjusted, then the probe head is shifted from below into the magnet and another fine adjustment of the frequency is performed. When the desired temperature of the sample is reached, the final adjustment of the frequency and the length of the 90° pulse (the 180° pulse is simply taken twice as long) are made.

The self-diffusion coefficient D is determined by the relation [8]

$$E \sim \exp \left(-\gamma^2 g^2 D \delta^2 \left[\tau - \frac{\delta}{3} \right] \right),$$

where E is the echo amplitude, τ the time in the sequence 90° pulse- τ - 180° pulse- τ -echo, g the gradient strength, and δ the length of the gradient pulse. The determination of D is done by using variable δ values, while g is kept constant.

5. Results and Discussion

Figures 8 and 9 (on page 58) give an overview of the resulting self-diffusion coefficients as functions of pressure at the fixed temperature of 613 K. For

Table 1. Activation volumes of self-diffusion for the lithium and sodium ions at different compositions of the mixture LiNO_3 with NaNO_3 at 613 K.

Mol fraction of lithium	0	0.1	0.3	0.5	0.7	0.9	1
$\Delta V/\text{cm}^3 \text{mol}^{-1}$ for lithium	–	8.1	8.5	8.3	8.5	7.3	6.5
$\Delta V/\text{cm}^3 \text{mol}^{-1}$ for sodium	5.1	6.3	6.3	7.4	8.2	–	–

the less sensitive sodium the data could not be obtained at the mol fraction of 0.9 for lithium. From the single errors of 1% for the gradient current and 0.5% for the gradient-pulse length a total error of the diffusion coefficient of 3% results.

The self-diffusion coefficients show as function of the composition a parabolic behaviour. At small mol fractions of lithium the self-diffusion coefficients of Li^+ and Na^+ are comparable, but then Li^+ diffuses faster. The maxima lie at lithium mol fractions 0.5 for lithium and 0.3 for sodium. At the lowest mole fractions of each respective component the diffusion data lie below those for the pure components with increasing pressures.

Table 1 contains the activation volumes which lie between 5.1 and $8.5 \text{ cm}^3 \text{mol}^{-1}$. All our data show good agreement with literature values if available [1–3].

Acknowledgement

Financial support from Fonds der Chemischen Industrie is gratefully acknowledged.

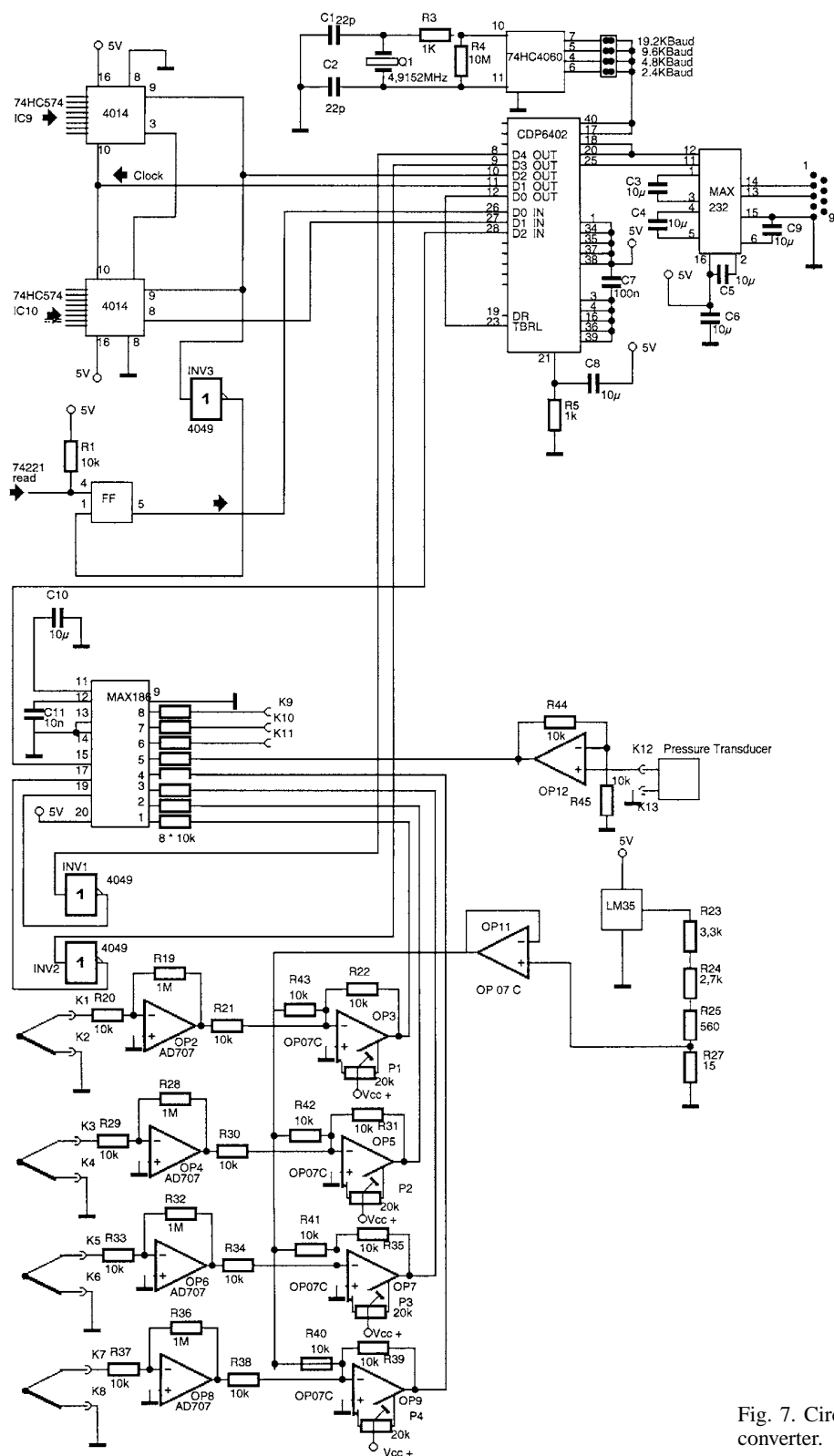


Fig. 7. Circuit of the AD converter.

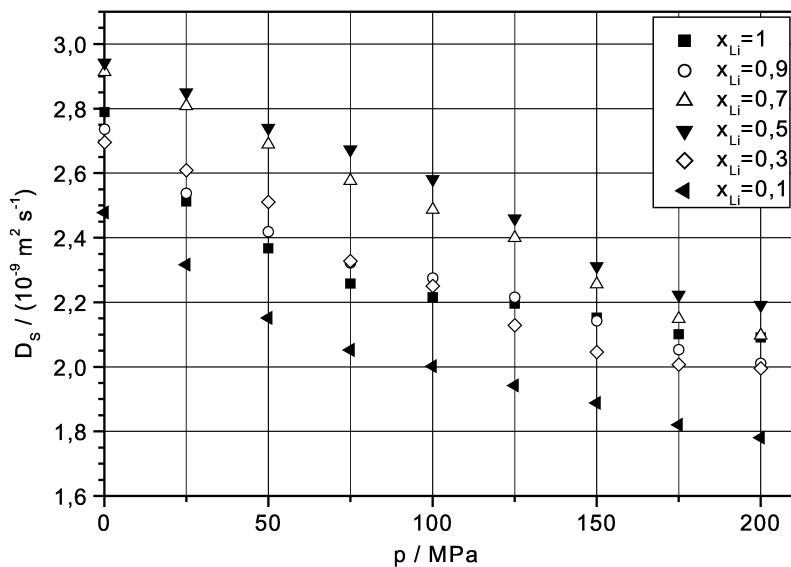


Fig. 8. Self-diffusion coefficients of Li^+ as function of pressure and composition in the mixture LiNO_3 with NaNO_3 at 613 K.

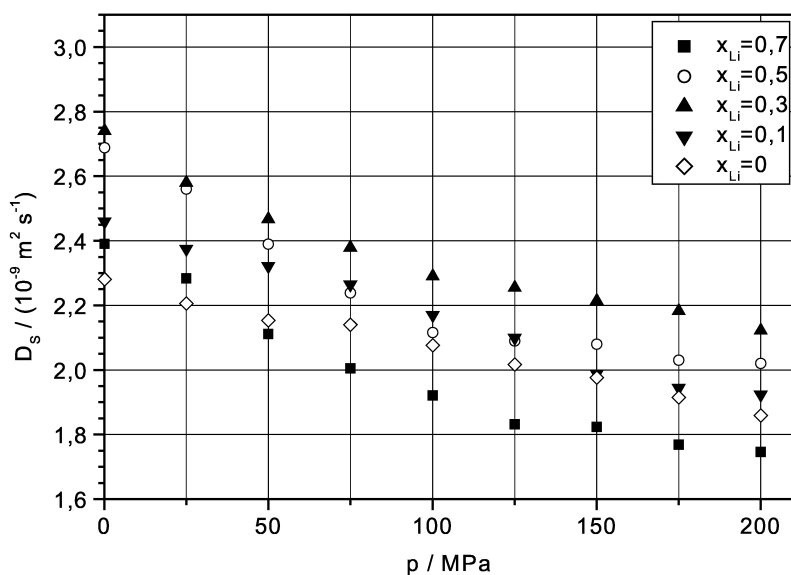


Fig. 9. Self-diffusion coefficients of Na^+ as function of pressure and composition in the mixture LiNO_3 with NaNO_3 at 613 K.

- [1] A. S. Dworkin, R. B. Escue, and E. R. van Artsdalen, *J. Phys. Chem.* **64**, 872 (1960).
- [2] C. Herdlicka, J. Richter, and M. D. Zeidler, *Z. Naturforsch.* **43a**, 1075 (1988).
- [3] C. Herdlicka, J. Richter, and M. D. Zeidler, *Z. Naturforsch.* **47a**, 1047 (1992).
- [4] H. Hoppe, G. Enge, and F. Winkler, *Z. Chem.* **16**, 164 (1976).
- [5] H.-H. Emons, G. Bräutigam, and A. Winzer, *Chem. zvesti* **32**, 776 (1978).
- [6] U. Matenaar, J. Richter, and M. D. Zeidler, *J. Magn. Reson.* **122**, 72 (1996).
- [7] A. C. Jacob and M. D. Zeidler, *Phys. Chem. Chem. Phys.* **5**, 538 (2003).
- [8] E. O. Stejskal and J. E. Tanner, *Chem. Phys.* **42**, 288 (1965).