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Specific Conductance of Ammonium Nitrate Solutions

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Specific conductances at about 10° intervals between 30° and 100° C. are reported for ammonium nitrate solutions ranging in concentration from 30 to 80 weight %. Measurements were made with alternating current at a frequency of 2000 c.p.s. using a modified version of the method previously used.

THE SPECIFIC conductance data of concentrated ammonium nitrate solution have been reported by only Campbell (*1-6*) and a few others (*10, 11, 12*). Ammonium nitrate is an explosive that is not easily detonated. Occasionally it may explode for unknown reasons; hence, it should be handled with this fact in mind. Many data have been obtained at pressures above 1 atm., but, in general, there is a lack of values at temperatures between 35° and 95° C. at atmospheric pressure and at concentrations between 40 and 65 weight % ammonium nitrate. In this investigation specific conductance was measured for aqueous solutions containing from 30 to 82 weight % ammonium nitrate at temperatures varying from 28° to 99° C.

EXPERIMENTAL

The determination of the electric conductivity of concentrated salt solutions at high temperature presents difficulties which often lead to results of limited accuracy. These difficulties pertain generally to the temperature-controlling and the conductivity-measuring systems.

Even with the most elaborate temperature-controlling systems, cyclic variations of bath temperature are observed which lead to corresponding variations in the resistance of the conductivity cell. However, by recording such variations of temperature and resistance balance on a graph and then applying statistical analysis to the data so obtained, specific conductance values of high accuracy can be obtained.

Temperature Control. Since the specific conductance is influenced by slight variations in temperature, particular care was given to the temperature control of the cell. The related system used is schematized in Figure 1.

It consists essentially of three paraffin oil (*7, 8*) baths, B_1, B_2, and B_3. The temperature of bath B_2, in which the cell is immersed, is controlled by paraffin oil pumped by P_3 from bath B_3 through copper coils S_2. The temperature of B_3 is held at 10° C. above that of B_2. Stirring is effected by pump P_2 connected in series with heat exchanger E to compensate for mechanical heat transfer. In turn, the temperature of the cooling liquid flowing through E is thermostatically controlled in B_1, which is at 2° to 5° C. lower than liquid in B_2. Also, the temperature of B_1 is fixed by balancing cooling unit M with heater C_1.

A thermal balance is obtained by opposing heat input and heat removal by a proper coordination of heaters C_1, C_2, and C_3 with thermoregulators T_1, T_2, and T_3. This arrangement permits a stabilization of the temperature in B_2 within such narrow limits that the variation in the temperature of cell CE can be reduced to ±0.004° C. if necessary.

Cell. After having tested several commercial cells, authors believe that none of these had characteristics permitting a valuable determination of the conductivity of ammonium nitrate solutions at high temperatures. The authors therefore designed and built several cells, the last being shown in Figure 2. It has two arms, A, filled with mercury to provide electrical contact with the circular platinized platinum electrodes. The three 3-pronged branches have other functions. Prongs B are closed with mercury safety valves to maintain the pressure relatively constant during heating. Prongs C serve as thermocouple wells filled with paraffin oil. The bottom parts of the wells dip into the cell solution and, because of their positions and number (fore, aft, and center), permit a close evaluation of the average solution temperature. Prongs D serve only to fill the cell with the solution.

The body of the cell is cylindrical, with a concave shape between the branches to eliminate all gas bubbles that would form during heating and would render the resistance measurements imprecise.

Temperature. Nine iron-constantan thermocouples

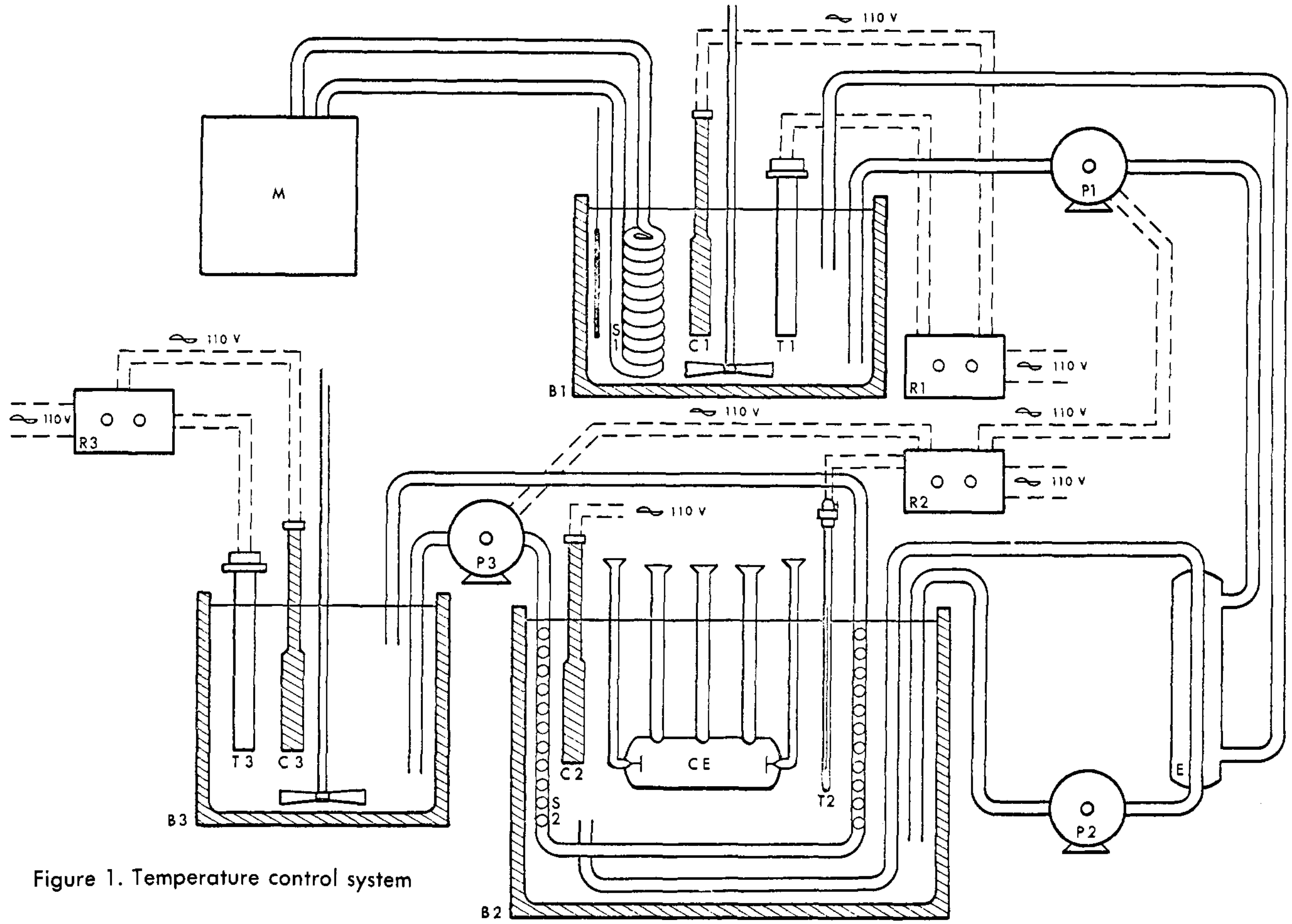

Figure 1. Temperature control system

B_1, B_2, B_3. Borosilicate glass baths
C_1, C_2, C_3. Heaters, 500 watts
CE. Conductivity cell
E. Heat exchanger
M. PCC-24SSA-2 cooling unit (Blue M Electric Co.)
P_1, P_2, P_3. Circulating pumps
R_1, R_2, R_3. Transistor relays
S_1, S_2. Copper coils
T_1, T_2, T_3. Thermoregulatars

Table I. Specific Conductance of NH_4NO_3 Solutions at High Concentrations

Concn., Wt. %	Temp., °C.	Specific Conductance, (Ohm – Cm.)$^{-1}$
30	29.88	0.323_9
	39.95	0.367_8
	49.92	0.411_7
	58.28	0.445_3
	67.25	0.487_{10}
	76.25	0.527_0
35	29.35	0.354_0
	38.99	0.401_7
	48.81	0.446_5
	58.41	0.489_8
	68.01	0.529_2
	76.76	0.566_{10}
	87.32	0.606_3
	97.00	0.639_6
37.863	48.86	0.458_4
	58.88	0.505_5
	67.97	0.545_6
	78.99	0.592_6
38.221	49.54	0.463_8
	57.65	0.499_6
	68.24	0.544_2
42.5	30.26	0.387_8
	39.04	0.429_9
	48.30	0.474_4
	57.94	0.519_4
	66.40	0.559_9
	77.25	0.606_4
	86.33	0.642_1
	95.08	0.681_8
50	29.17	0.396_7
	39.09	0.446_0
	48.68	0.492_5
	58.01	0.535_3
	67.48	0.577_4
	78.16	0.623_3
	87.72	0.664_3
	98.36	0.706_1
55.482	28.11	0.391_9
	38.09	0.441_5
	47.66	0.486_0
	57.89	0.533_1
	67.12	0.574_1
	77.88	0.618_4
	88.28	0.660_1
	98.23	0.701_2
59.976	29.82	0.390_{10}
	39.74	0.439_2
	49.55	0.486_3
	59.84	0.534_3
64	29.14	0.370_6
	38.05	0.413_1
	54.20	0.488_1
	72.49	0.567_6
	88.29	0.628_6
72	39.15	0.364_9
	54.39	0.431_2
	72.03	0.505_0
	88.48	0.556_4
82	68.50	0.370_2
	78.04	0.404_0
	88.17	0.440_6
	98.39	0.475_4

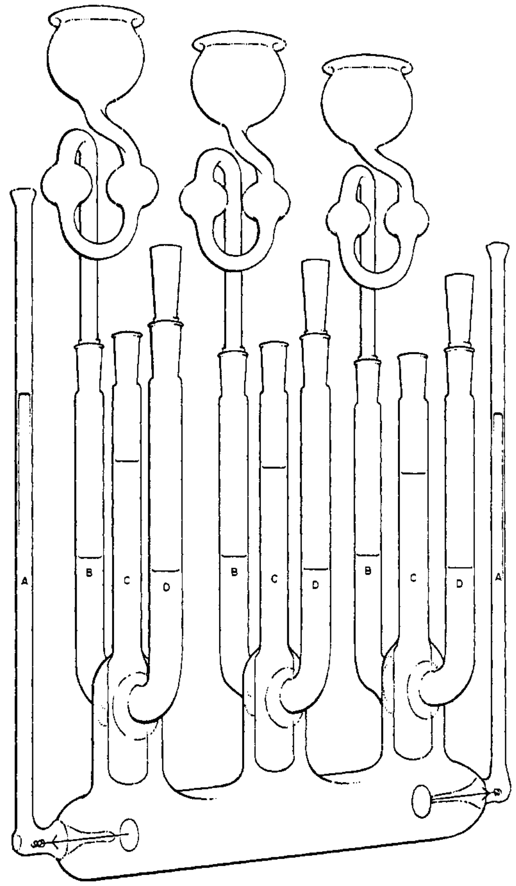

Figure 2. Conductivity cell

A.	Mercury lead connectors
B.	Pressure-control valves
C.	Paraffin-oil-filled wells
D.	Filling inlets

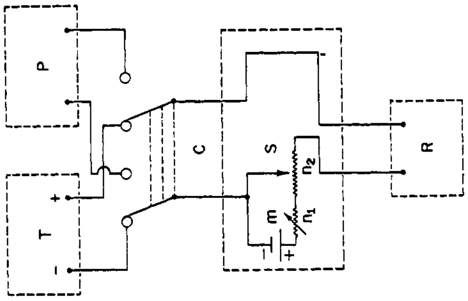

Figure 3. Temperature measurement system

C.	Double switch
T.	Iron-constantan thermocouples
P.	Leeds & Northrup K-3 Universal potentiometer
S.	Suppressor circuit
m.	1.35-volt mercury battery
n_1.	10,000-ohm variable resistance
n_2.	500 ohms ± 0.2% potentiometer
R.	Double-channel Moseley recorder

immersed in paraffin oil inside the three wells, *C*, are arranged so that the average temperature of the solution can be determined. To obtain with accuracy 0.01° C., a potentiometric circuit, able to detect a 0.005-mv. variation in the potential, was designed (Figure 3). The thermocouples are connected to the suppressor, *S*, and their potential

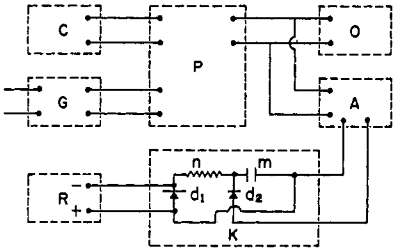

Figure 4. Resistance measurement system

A.	G.R.C. 0232-A tuned amplifier and null detector (General Radio Co.)
C.	Conductivity cell
d_1.	125-volt, 150-ma. diode
d_2.	200-volt, 200-ma. diode
G.	Oscillator
P.	LKB 3216B conductivity bridge (LKB-Producer-Sweden)
O.	Oscilloscope
K.	Rectifier and compressor
m.	1-μf. capacitance
n.	100-ohm resistance
R.	Double-channel Moseley recorder (Hewlett Packard Co.)

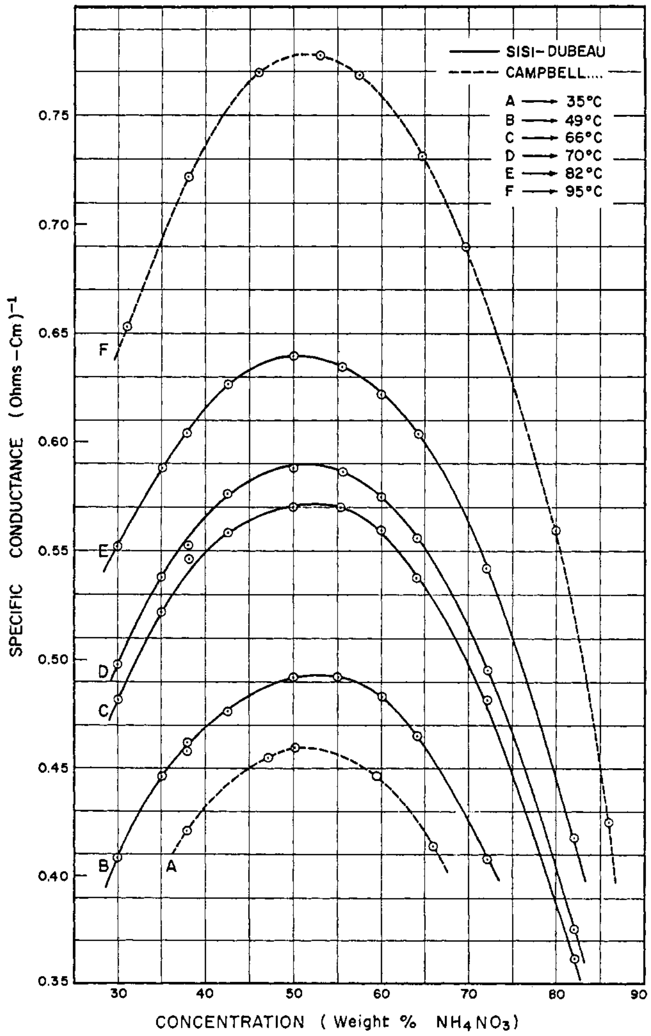

Figure 5. Variation of specific conductance with concentration

is counterbalanced through a potentiometric circuit made up of the variable resistance, n_1, and the potentiometer, n_2. Thereafter, only the potential resulting from the unbalancing of the system feeds a recorder, *R*. A standard source, *P*, of potential is used to determine with accuracy the absolute value of the balance point on the recorder.

Resistance. All resistance measurements of the solution were made with a conductivity bridge of Type LKB 3216B modified as follows: A set of decade-resistance units from 0.001 to 1000 ohms increased the precision of the bridge; a series of decade-capacitor units from 0.01 to 1 μf. was added to expand the Wagner earth circuit; finally an oscilloscope was substituted for the magic eye. Figure 4 shows how the signal coming from the bridge is filtered and amplified at *A*, rectified and compressed at *K*, and finally recorded at *R*.

Measurement. The cell is filled with ammonium nitrate solution at a temperature very close to that of the bath in which it will be immersed. At thermal equilibrium a balance point is preselected on the chart of the recorder and tied into the potentiometric circuit (Figure 3). Thereafter, the variations of resistance and temperature of the solution in the cell are simultaneously registered on one graph by a two-channel recorder.

The specific conductances for a 0.1*D* KCl solution reported by Gorbachev (*9*) were utilized to determine the cell constant which, in the temperature range 25° to 95° C., was found to be unchanged.

RESULTS AND DISCUSSION

Based on the precision of the instruments utilized, the accuracy obtained in the determination of the specific conductance of ammonium nitrate solutions is ±0.01% of the values shown in Table I. The absolute values are affected by an error of 0.1%, resulting mainly from the quality of standards used for thermocouple calibration.

The behavior of the specific conductance as a function of concentration is similar for all temperatures. The curves show a maximum in the vicinity of 52 weight % NH_4NO_3. Campbell's results (*3, 4*) have been plotted in a similar manner (broken lines). The maxima found are in very good agreement with the present data (Figure 5).

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Electrolytic Conductance and Ionic Association of Several Salts in Ethanol-Water Mixtures

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The electrolytic conductance of lithium chloride, potassium picrate (KPi), potassium tetraphenylborate ($KBPh_4$), triisoamyl-*n*-butylammonium picrate (TABPi), and triisoamyl-*n*-butylammonium tetraphenylborate (TAB BPh_4) was measured at 25° C. over the range of ethanol-water mixtures where ion-pair association was expected. Limiting equivalent conductances and ion-pair association constants for the electrolytes were derived using either the Fuoss-Onsager theory or the Shedlovsky function. Limiting equivalent conductances for the single ions were calculated on the basis of the Coplan-Fuoss assumption. Ion-size parameters are reported for the solutions analyzed by the Fuoss-Onsager theory.

THE PROPERTIES of triisoamyl-*n*-butylammonium (TAB) and of tetraphenylborate (BPh_4) salts in different solvents are of special interest. According to Coplan and Fuoss (*3*), the limiting equivalent conductances of TAB^+ and BPh_4^- ions in any given solvent can be equated, making it possible to calculate the conductances of other single ions. Popovych (*14*) assumed that the above two ions experience equal changes in their standard free energy of solvation upon transfer from water to nonaqueous solvents and proposed that they be used as reference ions for the establishment of a scale of single-ion medium effects. Lithium chloride was studied here because of its potential use for varying the ionic strength of ethanol-water solutions in the determination of activity coefficients. Its conductance was reported previously for 100% ethanol (*12*). The main objective of the present study was to determine the degree of ionic association for electrolytes in those ethanol-water mixtures where it was appreciable. No attempt was made

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