decreasing the bond order for the carbonyl group and thus its frequency. As reference to Table III will show, this is indeed the case. The frequencies of the carbonyl group in both donors are lowered when the iodine complex is formed.

LITERATURE CITED

(1) Bright, J.H., Drago, R.S., Hart, D.M., Madan, S.K., *Inorg. Chem.* **4**, 18 (1965).
(2) Carlson, R.L., Drago, R.S., *J. Am. Chem. Soc.* **84**, 2320 (1962).
(3) Drago, R.S., Carlson, R.L., Rose, N.J., Wenz, D.A., *Ibid.*, **83**, 3572 (1961).
(4) Drago, R.S., Wenz, D.A., Carlson, R.L., *Ibid.*, **84**, 1106 (1962).
(5) Huisigen, R., Brade, H., Walz, H., Glogger, I., *Ber.* **90**, 1437 (1957).
(6) Katritzky, A.R., Jones, R.A., *Chem. & Ind. (London)* **1961**, 722.
(7) Rose, N.J., Drago, R.S., *J. Am. Chem. Soc.* **81**, 6138 (1959).
(8) Schmulbach, C.D., Drago, R.S., *Ibid.*, **82**, 4484 (1960).
(9) Schmulbach, C.D., Hart, D.M., *J. Org. Chem.* **29**, 3122 (1964).

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Solubility and Refractive Index of Ammonium Perchlorate in Water

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The solubility of ammonium perchlorate in water has been determined for the temperature range 10° to 80° C. The data are represented with an accuracy of 0.1% by

$$\log x = \frac{-1531}{T} - 0.006846\,T + 5.733$$

where x is the mole fraction of ammonium perchlorate at absolute temperature T. The presence of a small quantity of potassium perchlorate decreases the solubility of ammonium perchlorate. Two sets of data are presented on high grade commercial and recrystallized ammonium perchlorate and the results are compared with published work which shows inconsistency. Refractive index values for a solution in water at a known temperature and concentration are given by the equation

$$\text{R.I.} = 1.3325 + 0.00079c - 0.00016\,(t - 20)$$

where c = concentration in grams per 100 grams of solution
t = temperature, ° C.

The equation is valid over the range 20° to 50° C., and a significant feature is the linearity of the relation whether the solution is saturated, undersaturated, or supersaturated.

THREE ORIGINAL PUBLICATIONS (*1, 2, 3*) give solubility figures for ammonium perchlorate but there is an inconsistency between them, arising perhaps from impurities or analytical difficulties. Solubility and refractive index measurements have been made and the former are compared with existing data.

In this work the solutions were prepared either from high grade commercial Swedish ammonium perchlorate or from material from the same source recrystallized from distilled water to give a product with the analysis shown in Table I. The analysis shows a typical high potassium content which is reduced only by many recrystallizations or by special methods. Specially prepared material with low potassium content can be prepared by reacting ammonia and perchloric acid. The solubility was determined only at 25° C. on a special preparation of this kind as shown below. In all cases the crystals in contact with the liquor at or below saturation point were in the size range 200 to 400 microns.

EXPERIMENTAL PROCEDURE FOR SOLUBILITY

Gravimetric analysis was used for the determination of concentration by evaporation to dryness at 110° C. There is some decomposition of ammonium perchlorate at this temperature which introduces an error not exceeding 0.1%, as shown by preliminary experiments.

A stainless steel container, with a tightly fitting polytetrafluoroethylene bung equipped with a stirrer, was immersed in a constant temperature bath, the temperature

Table I. Analysis of Ammonium Perchlorate

Volatile matter, wt.%	0.015
Sulfated ash, wt.%	0.022
Ammonium chloride, wt.%	<0.0002
Chlorate as sodium chlorate, p.p.m.	144
Potassium ion, p.p.m.	700
Lead, sodium, iron, aluminum, p.p.m.	<10
Copper, chromium, p.p.m.	<1

of which was measured by a mercury-in-glass thermometer calibrated at the National Physical Laboratory, Teddington. The bath temperature was constant to ±0.05° C. over the test period.

In the determinations, equilibrium was approached from both the undersaturated and supersaturated regions. An excess of solid was stirred with an undersaturated, or a supersaturated, solution for 24 hours before the solution was drawn off and analyzed. A sample of solution was withdrawn from the test vessel with a modified 60-ml. pipet, fitted with a 2-cm. diameter sintered glass disk of porosity 1 (90 to 150 microns) in place of a jet end. The temperature of the pipet was raised to 5° C. above the solution temperature to prevent obstruction of the sintered glass disk by nucleation and crystal deposition during sampling. Precautions were taken during the transfer operations to prevent evaporation—for instance, little or no suction was applied to the pipet.

SOLUBILITY RESULTS

The solubility was calculated as the mean of the values obtained when the equilibrium was approached from the supersaturated and the undersaturated sides.

These figures are in good agreement with determinations on a commercial Swedish ammonium perchlorate of high chemical purity. The results for this are given in Table III, with some corresponding figures from Table II.

These values plotted in Figure 1 show consistency with the data of Mazzucchelli and Rosa (*3*) and deviations from Carlson (*1*) and Freeth (*2*).

ERRORS

The possible loss of solute during sampling the solution was 0.04 gram per 100 grams of solution at 25° C., increasing to 0.1 gram per 100 grams of solution at 70° C. The possible loss on evaporating the solution to dryness was 0.01 gram per 100 grams solution at 25° C., and 0.03 at 70° C. Both these errors are in the same direction and would tend to give a result which might be lower than the actual value by 0.05 gram per 100 grams solution at 25° C. and 0.13 at 70° C.

Table II. Solubility of Ammonium Perchlorate in Water[a]

Temperature, ° C.	Solubility, G./100 G. Solution: From supersaturated solution	From undersaturated solution	Mean
20.0	17.94	17.92	17.9
25.0	19.75	19.78	19.8
30.0	21.76	21.75	21.8
40.0	25.65	25.62	25.6
50.0	29.45	29.47	29.5
60.0	33.30	33.47	33.4
70.0	36.94	36.82	36.9
80.0	40.45	40.38	40.4

[a] High grade commercial material, recrystallized; analysis as in Table I.

Table III. Solubility of High Grade, Commercial, Ammonium Perchlorate

Temperature, ° C.	Solubility, G./100 G. Solution	cf. Table II Values, G./100 G. Solution
10.5	14.4	14.4
18.0	17.0	17.1
20.0	17.8	17.9
30.0	21.7	21.8
33.0	22.9	22.9
36.0	24.1	24.1
39.0	25.3	25.2
41.0	26.1	26.0
45.0	27.6	27.8
50.0	29.4	29.5

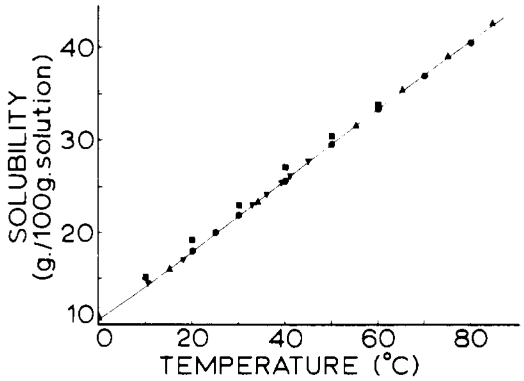

Figure 1. Variation of solubility with temperature

● Table I ■ Carlson (*1*)
▼ Table II ▲ Mazzucchelli and Rosa (*3*)

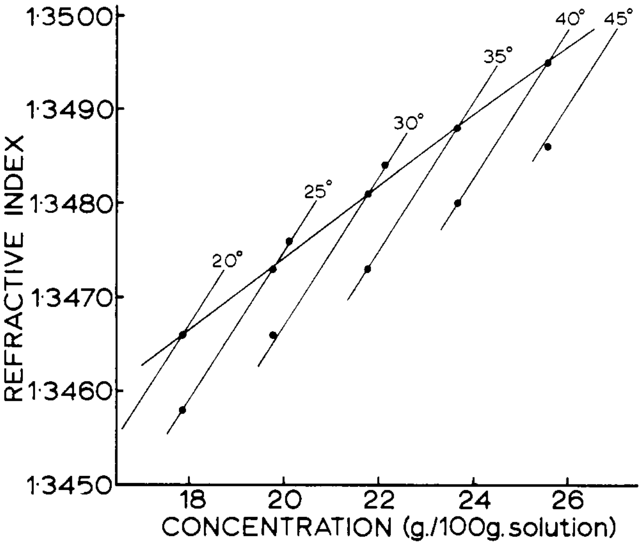

Figure 2. Refractive index *vs.* concentration

EFFECT OF POTASSIUM

Potassium perchlorate is isomorphous with ammonium perchlorate, and is found to a varying degree in all commercial samples of ammonium perchlorate. Some ammonium perchlorate with a very low potassium content, 7 p.p.m., was prepared and its solubility at 25.0° C. determined as above.

The solubilities of the low potassium content ammonium perchlorate, commercial Swedish ammonium perchlorate, and the value quoted by Mazzucchelli and Rosa (*3*) are compared in Table IV.

The higher solubility of ammonium perchlorate in a solution containing a low potassium content is only just greater than the possible experimental error. However the same magnitude of error would be expected in carrying out identical operations, so that the difference is real and is supported by refractive index measurements, which indicate an increase in concentration of 0.15 grams per 100 grams

Table IV. Comparison of Solubilities at 25.0° C.

Source	Potassium Content, P.P.M.	Solubility, G./100 G. Solution
Swedish	700	19.8
Special preparation	7	19.9
(*3*)	Not known	19.89

Table V. Refractive Index Data

Solution Temp., ° C.	Saturation Temp., ° C.	R.I.	Concn., G./100 G. Soln.	R.I., Calcd.
20	20	1.3466	17.9	1.3466
25	20	1.3458	17.9	1.3458
25	25	1.3473	19.8	1.3473
25	26	1.3476	20.1	1.3476
30	25	1.3466	19.8	1.3465
30	30	1.3481	21.8	1.3481
30	31	1.3484	22.1	1.3484
35	30	1.3473	21.8	1.3473
35	35	1.3488	23.7	1.3488
40	35	1.3480	23.7	1.3480
40	40	1.3495	25.6	1.3495
45	40	1.3486	25.6	1.3487

of solution. Potassium ions, which are not removed by recrystallization because of a strong absorption effect, appear, therefore, to depress the solubility of ammonium perchlorate.

REFRACTIVE INDEX DETERMINATION

The refractive index of undersaturated, saturated, and supersaturated solutions of ammonium perchlorate was measured in the temperature range 20° to 50° C., with a Bellingham and Stanley dipping refractometer, using the makers' calibration checked at one point against distilled water at 20.0° C. A plot of the data obtained is given in Figure 2 which shows the refractive index at points on the saturation curve at a number of temperatures between 20° and 50° C. Values obtained above and below the saturation curves are also given and these values show no discontinuity in passing through the saturation point in either direction, and show a linear plot.

It is, therefore, possible to express the information in the form of an empirical equation applicable within the limits of 20° to 50° C. and supersaturation or undersaturations of at least 5° C. The equation is

$$\text{R.I.} = 1.3325 + 0.00079c - 0.00016\,(t - 20)$$

where c = solution concentration g./100 g. solution

t = solution temperature, ° C.

LITERATURE CITED

(1) Carlson, B., "Tables Annuelles," p. 379, J. & A. Churchill, London, 1910.

(2) Freeth, F.A., *Rec. Trav. Chim.* **43**, 475 (1924).

(3) Mazzucchelli, A., Rosa, A., *Atti Accad. Nazl. Lincei* **30** (5), 270 (1921).

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The Ternary System Indium Telluride–Indium Antimonide–Antimony

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The liquidus and solidus surfaces of the system InTe-InSb-Sb have been determined by thermal analysis, metallographic, and x-ray procedures. InTe is the primary phase of precipitation over most of the system. An intermediate phase, beta, in the InTe-InSb system extends into this ternary and is stable between 511° and 420° C. At the lower temperature, the system decomposes into InTe and alpha, a solid solution of InTe in InSb. A ternary eutectic of antimony, alpha, and beta melts at 486° C. and contains 7 wt.% InTe, 59.5 wt.% InSb, and 33.5 wt.% Sb. Liquidus isotherms are presented in a figure, and a schematic space model is illustrated.

SOME ALLOYS in the InTe-InSb-Sb subternary system of the indium-tellurium-antimony system have been studied by Wooley, Gillet, and Evans (*6*). They measured the solid solubility along the InSb-In_2Te_3 section, a portion of which lies in the subternary under discussion. InSb and In_2Te_3 do not form a quasibinary section, but InTe and Sb do, as reported by Stegman and Peretti (*4*). Rosenberg and Strauss (*3*) measured the liquidus of the InSb-Te and InSb-In_2Te_3 isopleths, portions of which lie in the InTe-InSb-Sb ternary area. Goryunova, Radautson, and Kiosse (*1*) first reported the existence of a semiconducting compound on the InSb-InTe tie line; it has a sodium chloride structure and a lattice parameter of 6.128 A.

The InTe-Sb quasibinary diagram (*4*) is a simple eutectic type with very small solid solubility in either phase. The alloys form a eutectic at 571.5° C., containing 72.5 wt. % Sb and 27.5% InTe. Indium telluride melts at 696° C. and forms solid solutions with InSb, which melts at 525° C.

According to Stegman and Peretti (*5*), the intermediate phase formed by InTe and InSb has the composition 2InTe·InSb. This phase melts incongruently at 553.5° C. and decomposes below 420° C. into InTe and α(InSb). The solid solubility of InSb, in either the intermediate phase or InTe, is immeasurably small; on the other hand, InTe dissolves in solid InSb to the extent of 9.9 wt.% at 500° C.

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