A plot of the data is shown in Fig. 1. The line marked "limiting tangent" is the Debye and Hückel limiting law. The potassium chloride, magnesium chloride and magnesium sulfate curves fuse fairly well into the limiting tangent but the potassium sulfate curve shows the characteristic "hump" obtained by La Mer and Goldman for lanthanum and thallous iodates. This salt also increases the solubility of the iodate more than the others. The general deviation from the theoretical lies somewhere between the deviations of the uni- and trivalent iodates mentioned.

Summary

The activity coefficients of copper iodate have been measured by the solubility method in aqueous solutions of the chlorides and sulfates of potassium and magnesium. The solubility of copper iodate is 0.003693 mole per liter at 25°.

CEDAR RAPIDS, IOWA

NOTES

The Detection of Cobalt as Cesium Cobaltinitrites.—The oxidation of cobaltous ion in acid solution by a concentrated solution of potassium nitrite and its precipitation as the yellow cobaltinitrite are well known in the conventional scheme of analysis. The potassium salt, however, has an appreciable solubility and for low concentrations of cobaltous ion has the undesirable property of precipitating slowly. The corresponding cesium salt, on the other hand, is more insoluble and precipitates and settles much more rapidly. At 17° one cubic centimeter of saturated solution contains approximately 0.05 mg. of the cesium salt.[1] In terms of cobaltous ion the concentration is considerably less and hence serves as a very delicate test for this ion.

Procedure.—The mixture of cobalt and nickel sulfides, from the usual procedure, is dissolved in aqua regia and evaporated just to dryness. The residue is dissolved in one or two cc. of 6 *M* acetic acid. To this solution 2 cc. of 6 *M* sodium nitrite and 0.5 cc. of 0.5 *M* cesium nitrate (or 0.25 *M* cesium sulfate suggested as a reagent for aluminum)[2] are added and the yellow $Cs_2NaCo(NO_2)_6$ precipitates.

The following table illustrates the delicacy and rapidity of the test

Concn. of cobaltous ion, mg. per cc.	0.5 and greater	0.2–0.5	0.05
Time for precipitation, min.	Instantaneous	0.5	2

The sensitivity of the test may be increased by substituting potassium nitrite for the corresponding sodium salt in the previously described pro-

[1] Rosenbladt, *Ber.*, 19, 2531 (1886).

[2] Yagoda and Partridge, THIS JOURNAL, 52, 3579 (1930).

cedure. If this is done, a solution of cobaltous ion containing 0.01 mg. per cc. will yield a yellow precipitate (probably $Cs_2KCo(NO_2)_6$) in about three minutes.[3]

Considerable quantities of iron, manganese or nickel do not interfere with the cobaltinitrite precipitation.

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Inorganic Lubricants. IV. Lubricants for Temperatures Above and Below Normal. A. For Temperatures Above Normal.—Aqueous metaphosphate and metaphosphoric acid solutions yield clear, viscous lubricants capable of operating up to 120° and by selection to 160°, the operating range of temperature (Op. r.) over which any particular solution has satisfactory lubricating properties depending upon the temperature at which boiling of that solution is stopped (T. b.) Typical examples are listed in Table I.

Table I

Boiling Temperatures and Approximate Operating Temperature Ranges for Various Metaphosphate Solutions

A. Aqueous solutions of metaphosphoric acid containing approximately 20% of added orthophosphoric acid

T. b., °C.	140	150	165	185	205
Op. r., °C.	25–30	40–60	45–70	55–75	65–80
T. b.. °C.	230	260	300	350	
Op. r., °C.	70–85	80–95	105–120	Fumes	

B. Solutions of sodium metaphosphate

T. b., °C.	107 *a*	110 *a*	115	120
Op. r., °C.	25+	50–65	60–85	65–90

C. Solutions of sodium metaphosphate containing approximately 20% of borax and 10% of added orthophosphoric acid

T. b, °C.	110	115	122 *a*	118	125
Op. r., °C.	25+	60–80	70–90	50–80	90–160

a The solution was then diluted and again boiled down to avoid crystallization at the operating temperature range.

These lubricants in their respective operating ranges have properties quite similar to those of the phosphoric acid and metaphosphate lubricants

[3] *Cf.* Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York. 1927, p. 202.

previously described.[1a] In general, the operating range rises during their protracted use at elevated temperatures because of further slow dehydration.

A variety of salts melted in their water of crystallization and, at higher temperatures, certain anhydrous salts yield liquids which, when mixed with sufficient quantities of finely powdered, non-reacting, stable solids to form stiff, creamy pastes, afford lubricants similar to those obtained by mixing such solids with aqueous solutions of deliquescent substances,[1b] but having operating ranges up to their reaction or decomposition temperatures.

TABLE II

OPERATING RANGES OF MIXTURES OF FUSED SALTS WITH FINELY DIVIDED SOLIDS

Subs.	M. p., °C.	Mixed with powdered	Op. r., °C.	Remarks
$Ca(NO_3)_2 \cdot 4H_2O$	42	Graphite	45–120	Supercools
$Na_2B_2O_4 \cdot 2H_2O$	57	Graphite	55–110	Supercools
$Na_2S_2O_3 \cdot 5H_2O$	48	Graphite	70–110	SO_2 evolved
$Mg(NO_3)_2 \cdot 6H_2O$	90	Kaolin	110–200	
KSCN	172	Kaolin	175–320	
KNO_3	337	Kaolin	340–360	Decomposes above 360°

A mixture of equal parts by weight of crystallized calcium nitrate and potassium nitrate when heated to 120° and stirred until a clear solution of calcium nitrate in the potassium salt was thus obtained yielded a liquid that when mixed with kaolin gave a series of lubricants of increasing temperature ranges depending on the temperatures at which boiling the liquid was stopped.

TABLE III

BOILING TEMPERATURES OF MIXED CALCIUM AND POTASSIUM NITRATES AND OPERATING RANGES OF LUBRICANTS CONTAINING KAOLIN

T. b., °C.	150	185	200	225
Op. r., °C.	140–160	150–180	155–190	160–220
T. b., °C.	260	300	340	
Op. r., °C.	170–260	170–300	170–340	

It appears to be possible, therefore, to select a mixture of fused salt and non-reacting solid to melt under almost any required condition of high temperature inorganic lubrication. Mixtures of this kind are also useful as reversibly thermoplastic lutes.

B. Lubricants Operating at Temperatures Below Normal.—The same classes of materials in different concentrations also yield lubricants capable of operating at subnormal temperatures. Thus aqueous solutions of metaphosphoric acid boiling at the stated temperatures give approximately the following ranges of temperature for satisfactory lubrication.

[1] Boughton, THIS JOURNAL, **52**, (a) 2813; (b) 4335 (1930).

TABLE IV

BOILING TEMPERATURES AND OPERATING RANGES FOR A SOLUTION OF METAPHOSPHORIC ACID

T. b., °C.	105	110	115	120
Op. r., °C.	−75 to −65	−60 to −50	−40 to −30	−15 to 0

Sodium metaphosphate solutions have more limited usefulness as low temperature lubricants. Those boiling at 104–106° have an operating range of −25 to 0°. More dilute solutions freeze when cooled to a temperature of a few degrees below zero.

Lubricating cream mixtures of salt solutions and finely divided solids may be prepared in the usual way and can then be used at temperatures down to approximately the freezing points of the respective solutions. Thus, a 35% solution of calcium chloride mixed with kaolin may be used as a lubricating paste to temperatures as low as −20°.

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CONSTITUTION OF THE SO-CALLED DITHIOURAZOLE OF MARTIN FREUND. IV. ISOMERISM OF HYDRAZODITHIODICARBONAMIDES, IMINO-THIOL-THIOBIAZOLES AND IMINO-THIOBIAZOLONES

BY SHAHA L. JANNIAH AND P. C. GUHA

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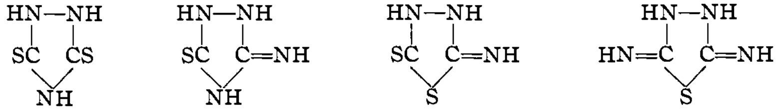
The ring-closing action of various reagents upon hydrazodithiodicarbonamides and their alkyl and aryl substituted derivatives has been studied by a number of workers, *viz.*, by Freund, Busch, Arndt, Fromm, Guha and their collaborators beginning from the year 1893, and all the possible four types of triazoles and thio-biazole compounds, I, II, III and IV, obtainable from the hydrazides, have been isolated.



I II III IV

A careful survey of the literature reveals the fact that various authors attribute different melting points to one and the same substance. As an example, to imino-thio-tetrahydro-4,1,2-thiodiazole, Freund[1] gives the

[1] Freund, *Ber.*, **28**, 946 (1895).