peared as a viscous, slightly pigmented oil. It bears no resemblance in physical properties to a crystalline product with a melting point of 69° claimed to be pure vitamin K by Doisy and co-workers [*Science*, **88**, 243 (1938)].

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Relation between Compressibility and Solubility of Metals in Acids

BY SOFRONIO BALCE

If we apply to metals the compressibility formula for compounds as given in an earlier paper,[1] the equation becomes

$$B_{calcd.} = \frac{V_a}{5.6 \times 10^{12} Z}$$

where $B_{calcd.}$ is the calculated compressibility, 5.6×10^{12} is a universal constant relating physical

TABLE I

SHOWING THE DIFFERENCES BETWEEN METALS THAT DISPLACE HYDROGEN FROM ACIDS AND THOSE THAT DO NOT

Metal	Z	Compressibility[a] in cc./atm. $B_{calcd.}$	$B_{obsd.}$	$\dfrac{B_{obsd.} - B_{calcd.}}{B_{calcd.}}$
Cs	1	12.9×10^{-6}	62×10^{-6}	3.81
Li	1	2.35	9.1	2.87
Rb	1	10.5	40.5	2.86
K	1	8.54	32.1	2.76
Na	1	4.3	15.8	2.67
Sr	2	3.05	8.1[b]	1.65
Ca	2	2.29	5.8	1.53
Mg	2	1.21	2.9	1.4
Al	3	0.61	1.34	1.2
Zn	2	.86	1.45	0.68
Cr	3	.45	0.73[c]	.64
Fe	3	.43	.654	.52
Cd	2	1.17	1.72	.47
Co	3	0.405	0.557	.375
Ni	3	.40	.542	.364
Sn	2	1.47	1.9	.29
Pb	2	1.65	2	.23
Cu	1	1.29	0.756	− .41
Ag	1	1.85	1.02	− .45
Pt	2	0.82	0.328	− .60
Au	1	1.845	.552	− .66
Ir	2	0.778	.244	− .89

[a] The figures on compressibility are from the "International Critical Tables."

[b] P. W. Bridgman, *Proc. Am. Acad.*, **70**, 285–317 (1935).

[c] T. W. Richards, "The Compressibilities of the Elements and Their Periodic Relations," Carnegie Institution of Washington, 1907.

(1) S. Balce, *Philip. J. Sci.*, **60**, 251–254 (1936) [*Chem. Zentr.*, **108**, II, 2113 (1937); British *C. A.*, A, I, 176 (1937); *C. A.*, **31**, 2881 (1937)].

properties of substances to shrinkage in volume per unit volume incident to compound formation, Z is the valence of the metal elements, and V_a the atomic volume.

This calculated compressibility, however, does not check with observed values. But when the $B_{calcd.}$ calculated compressibility is less than the $B_{obsd.}$ observed value, the metal may be said to be comparatively soft and is subject to solvent action by non-oxidizing acids; and when the calculated compressibility is greater than the observed, the metal does not displace the hydrogen.

As may be noted in the accompanying table, the order in which the metals occur in the electromotive series can be approximated by dividing the deviation, $\Delta B = B_{calcd.} - B_{obsd.}$ by $B_{calcd.}$. The units of compressibility in the table are changed to cc./atmosphere.

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Note on the Solubility of Strontium Chromate

BY T. W. DAVIS AND J. E. RICCI

In connection with an attempted study of the solubility of strontium chromate in dioxane-water mixtures as solvents, which had to be abandoned because of the extreme slowness with which equilibrium is approached, some observations were made on the solubility of this salt in water.

The figure uniformly given for the solubility of strontium chromate at room temperature is the determination of Fresenius,[1] 0.12 g. in 100 g. of solution at 15°, which was a confirmation of work by Meschtschersky.[2]

The only values for other temperatures are those of Reichard[3]: namely, 0.465% at 10°, 1.000% at 20°, 2.417% at 50° and 3.000% at 100°. The last figure for 100°, is the one quoted in the "Handbook of Chemistry and Physics,"[4] in its current editions. These incredible figures are evidently the basis for the Noyes procedure for the qualitative analysis of the alkaline earths, in which one is cautioned against much washing of the strontium chromate precipitate which is then redissolved by passing hot water through the filter paper.

(1) Fresenius, *Z. anal. Chem.*, **29**, 418 (1890).
(2) Meschtschersky, *ibid.*, **21**, 399 (1882).
(3) Reichard, *Chem. Ztg.*, **27**, 877 (1903).
(4) Chemical Rubber Publishing Co., Cleveland, Ohio.

Reichard's experimental procedure is not clear from his description, but something is unquestionably wrong with his determinations. Neither Meschtschersky nor Fresenius mentions the time allowed for attainment of equilibrium.

We have noted first of all that equilibrium is approached extremely slowly; we are in fact not prepared to give figures indicating true solubility in every case. As shown by Kohlrausch[5] for anhydrous calcium chromate, the time required for this type of salt may be a matter of years. The solubility of anhydrous calcium chromate, which he was determining, was still increasing after fifteen months. Our observations nevertheless are sufficient to show beyond doubt that the solubility of strontium chromate decreases markedly with rising temperature, which was quite unexpected, considering that the opposite had long been assumed in analytical procedure. The success of the Noyes procedure for Group IV metals must be attributed to the much greater rate of solution of the precipitate in hot as compared to cold water.

The strontium chromate used was prepared from c. p. strontium chloride and c. p. ammonium chromate; it was recrystalized from large volumes of water several times by redissolving in hydrochloric acid and reprecipitating with ammonium hydroxide. The product was finally digested in hot water for long periods, to approach a granular condition. Analysis of the solid gave 99.5% strontium chromate by iodometric titration with standard thiosulfate. This same analytical method was used in the solubility determinations themselves. The procedure for the latter was to stir an excess of solid with 200–250 cc. of water in glass-stoppered Pyrex bottles, in electrically controlled thermostats, at 15, 25 and 75°. For the 100° determination, excess solid was boiled with 1.5 liters of water in a 2-liter Pyrex flask fitted with a small reflux condenser.

The results obtained are shown in Table I. The figures for 15 and 25° probably do not represent equilibrium, although the value 0.91 g./l. at 25° is probably very close to a true solubility. The attainment of equilibrium at 15° must of course be much slower, so that it is likely that the 15° figure would have continued to rise to a value higher than that found at 25°. The 75° figure probably represents equilibrium. Here the rate of reaching equilibrium must be quite high, and

(5) Kohlrausch, *Z. physik. Chem.*, **44**, 233 (1903).

the values from undersaturation and supersaturation agree very closely. The 100° value is probably correct as far as its order of magnitude is concerned, but cannot be very precise. In this determination the continued boiling of the mixture caused an increase in the $CrO_4^=$ concentration of the solution following, after the first day or two, a linear course which was not that expected for a change approaching equilibrium in the usual logarithmic fashion, but one in accordance with the assumption that either an interchange with the glass was taking place, with a consequent increase in the $CrO_4^=$ concentration, or a progressive hydrolysis of the solid, with the same effect. To correct for this change, on the reasonable assumption that solubility equilibrium must be reached rather quickly at this temperature, duplicate experiments were run, using very different amounts of solid, in which the solution was sampled every day or two, for periods up to nine days; the values so obtained, when a rough linearity had been established, were extrapolated back to zero time, to give the saturation value without the effect of hydrolysis or exchange with glass. The most probable values of the solubility, omitting the 15° figures, are listed in Table II.

It may be added, in conclusion, that the solid phase was analyzed and found to be anhydrous,

TABLE I

Temp., °C.	Expt.	Time, days	Soly., G./l. soln.
15	1	20	0.741
		25	.788
	2	20	.779
		25	.879
25	1	3	.833
		27	.865
		31	.864
	2	18	.909
		22	.912
	3[a]	4	.883
		24	.898

			G./1000 g. soln.
75	From undersaturation	10	0.6143
	From supersaturation	10	.6150
100 (extrapolated	1		.43
to zero time)	2		.42

[a] Using residue from 100° determination.

TABLE II

Temp., °C.	Solubility
25	0.91 g./l. soln.
75	.615 g./1000 g. solution
100	.43 g./1000 g. solution

both at 25 and at 100°: at 25°, 97–98.0% strontium chromate by titration; at 100°, 96.7%.

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The Identification of Polynitro Aromatic Compounds as Addition Compounds with Naphthalene[1]

BY O. C. DERMER AND R. B. SMITH

Although polynitro aromatic compounds are not rare in industry and are common derivatives for identifying other aromatic compounds, there is no systematic procedure for their own identification. As a class they can be detected by color reactions,[2] but their derivatives generally owe their existence to the reactivity of some other functional group in the molecule. If no such group is present, recourse must be had to either (a) reduction, which is difficult to control and frequently yields polyamines requiring acylation to make them suitable derivatives, or (b) further nitration, which may be impossible.

In view of the well-known excellence of picric acid and other polynitro aromatic compounds as reagents for identifying condensed-ring aromatic compounds, the reverse procedure, suggested by Mulliken[3] and Clarke[4] and more explicitly by Reichstein[5] and Coghill and Sturtevant,[6] seemed worth systematic extension. The attractiveness of the method was increased by a literature search, which showed that 39 polynitro compounds of the 47 that had been studied form complexes with naphthalene. We retained naphthalene as the reagent because of this prior use and because it is universally available and easy to purify.

We chose for study polynitro compounds which either are commercially available and therefore

commonly encountered, or are themselves derivatives used in qualitative organic analysis. In each case the polynitro compound–naphthalene system was investigated by an application of cooling-curve technique to the method used by Baril and Hauber[7] for hydrocarbon picrates. If the curve for the equimolecular mixture indicated compound formation, the stability of the supposed compound toward recrystallization was tested. If recrystallization caused decomposition, we usually considered it necessary to construct the whole melting point–composition diagram, since a plateau on the cooling curve might represent merely the crystallization of a eutectic mixture at the fifty mole per cent. point.

Of the seventeen new derivatives thus found and described in Table I, all but four can be recrystallized without decomposition. Even these four can be used in qualitative analysis; but inasmuch as the molecular weight must be known before an equimolecular mixture can be made, this method without recrystallization is merely confirmatory

TABLE I

NEW DERIVATIVES OF POLYNITRO COMPOUNDS

M. p., °C. (corr.)	Polynitro compound	M. p. of $C_{10}H_8$ deriv., °C.[a] (corr.)
62	Isoamyl 3,5-dinitrobenzoate[b]	46–47
63	2,6-Dinitrophenol[c]	58–58.5
68	2,4,6-Trinitroanisole	69–70[i]
79	2,4,6-Trinitrophenetole	39
86	2,4-Dinitrophenetole	41[d]
86.5	3,5-Dinitro-o-cresol	94
88	1-Iodo-2,4-dinitrobenzene[e]	66–67
89	2,4-Dinitroanisole	50
93	Ethyl 3,5-dinitrobenzoate	75[f]
98	Ethyl 3,5-dinitrosalicylate	78[d,f]
106	2,4-Dinitro-6-cyclohexylphenol	73–74
106	3,5-Dinitroanisole	69[d]
117	3-Chloro-2,4,6-trinitrophenol	127
119	2,4,6-Trinitrobenzaldehyde[c]	136.5
123	3,5-Dinitroguaiacol	94
147	2,4-Dinitroresorcinol	165
171	2,4,2',4'-Tetranitrobibenzyl[g]	136[d,f,h]

[a] Capillary melting points are given unless otherwise stated. The melting points from cooling curves are generally about 2° lower. [b] Ref. 5. [c] Eastman Kodak Co. product. [d] Value obtained from the cooling curve only; compound could not be recrystallized without decomposition. [e] Körner, Gazz. chim. ital., 4, 323 (1874). [f] Result verified by melting point–composition diagram. [g] Braun and Rawicz, Ber., 49, 802 (1916). [h] Compound may melt incongruently; the temperature–composition curve was not determined accurately enough to decide the question. [i] Asahina and Shinomiya, J. Chem. Soc. Japan, 59, 341 (1938), reported 54° for this m. p.

(1) This is an abstract of a thesis submitted by R. B. Smith in partial fulfilment of the requirements for the degree of Master of Science at the Oklahoma Agricultural and Mechanical College in 1938. Nearly all this material was presented at the Milwaukee meeting of the American Chemical Society, September, 1938.

(2) Houben, "Die Methoden der organischen Chemie," G. Thieme, Leipzig, 3rd edition, Vol. IV, 1924, pp. 190–192.

(3) Mulliken, "A Method for the Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1916, Suborder II, various pages.

(4) Clarke, "A Handbook of Organic Analysis," Edward Arnold and Company, London, 1928, pp. 240–241.

(5) Reichstein, Helv. Chim. Acta, 9, 799 (1926); Sutter, ibid., 21, 1266 (1938).

(6) Coghill and Sturtevant, "An Introduction to the Preparation and Identification of Organic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1936, p. 202.

(7) Baril and Hauber, THIS JOURNAL, 53, 1087 (1931).