PA 18T91

YATSIMIRSKII, K. B.

USSR/Chemistry - Entropy
    Chemistry - Ions

May 1947

"The Standard Entropies of Ions in the Crystalline
State," K. B. Yatsimirskii, Chemical-Technological
Institute, Ivanovo, 2 pp

"Zhur Fiz Khim" Vol XXI, No 5

Lists the values as discovered by E. N. Gapon and the
different values derived by later experimentation.
Published 17 Dec 1946.

18T91

USSR/Chemistry - Ions
    Chemistry - Cations   Dec 1947

"Thermochemical Radii of Ions in Solution," K. B. Yatsimirskiy, 4 pp

"Dok Akad Nauk SSSR, Nova Ser"   Vol LVIII, No 7

Uses method of calculating radii of ions from thermo-
chemical data to calculate this data for several ion
solutions. Method consists of finding magnitude of en-
ergy of a lattice from thermochemical and spectroscopic
data, according to the equation
    $U = -\Delta H_{K} - \Delta H_{x} - \Delta H_{Kx}$,
where U is the energy of the lattice,
    $-\Delta H_{K}, - \Delta H_{x}$ and $-2 U$

                                                60T10

USSR/Chemistry - Ions   (Contd)
                                           Dec 1947

and $-\Delta H_{Kx}$ are the heat of formation of a gaseous
cation, a gaseous anion, and hard salt. Submitted by
Academician I. I. Chernyayev, 18 Jun 1947.

                                                60T10

ACCESSION AND PROPERTIES NOTE

2

The hexachlorostannate series. K. B. Yatsimirskii (N. S. Kurnakov Inst. Gen. Inorg. Chem. Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1948, 263-5; cf. *ibid.* 1946, 461.— The heat of the reaction $SnCl_4 + 2Cl^- \to SnCl_6^{--}$, in the gaseous state, is taken = 17.3 kcal./mole, and the radius of the $SnCl_6^{--}$ anion = 2.98 A. (from the K_2SnCl_6 lattice). Then by Kapustinskii's equation for the lattice energy (*C.A.* 38, 5705) the heat of formation Q of the complex salt from the simple salt and the addend = $[287.3 + 2(n + m)Z_b/(r_b + 2.98)][1 - [0.345/(r_b + 2.98)]] - [287.3 Z_b (Z_b + 1)/(r_b + 1.81)][1 - [0.345/(r_b + 1.81)]] - 17.3]$, where r_b = radius of the cation, 1.81 = radius of Cl^-, Z_b = charge of the cation, n = no. of cations, m = no. of $SnCl_6^{--}$ anions in the mol. Numerical solution of this equation gives the conditions of stability of hexachlorostannates, namely, for salts of the type M_2SnCl_6, $Q > 0$ if $r_b > 0.4$ A., for salts of the type $M^{II}SnCl_6$, $Q > 0$ if $r_b > 1.8$ A., and for salts of the type $M_2^{II}(SnCl_6)_3$, $Q > 0$ if $r_b > 3.7$ A. It accounts satisfactorily for the fact that, although chlorostannates of $[M^{II}(H_2O)_6]^{++}$ aquo cations are stable, those of the anhyd. simple cations M^{II} are not, as the latter do not attain the crit. size of 1.8 A. There are no chlorostannates of Ba^{++} or Pb^{++}, as these cations form no stable aquo ions. It further becomes evident why chlorostannates of big cations such as $[M(CO-N_2H_4)_6]^{++}$ are stable. The following chlorostannates were prepd.: By mixing the stoichiometric amts. of $FeCl_2$,

$CO(NH_2)_2$, and $SnCl_4$ and evapg. on a water bath to beginning crysta., one obtains $[Fe(CON_2H_4)_6](Cl)(SnCl_6) \cdot 3H_2O$, readily sol. in H_2O, stable in air, losing H_2O at 70-80°; with excess $SnCl_4$, one gets the yellowish $[(CON_2H_4)_6]_2(SnCl_6)_3 \cdot 15H_2O$. On mixing concd. solns. of $[Cr(CON_2H_4)_6]Cl_3$ and $SnCl_4$, one obtains a ppt. of light-green crystals $[Cr(CON_2H_4)_6](Cl)(SnCl_6)$, stable in air, losing H_2O at 90-100°. When the calcd. amts. of $CaCl_2 \cdot 6H_2O$ and of $CO(NH_2)_2$ are dissolved in a 60% aq. soln. of $SnCl_4$, and the soln. is heated 10-20 min. on a water bath and left in a desiccator over H_2SO_4 for 5-6 days, the salt $[Ca(CON_2H_4)_6](SnCl_6)$ is pptd. $[Mg(CON_2H_4)_6](SnCl_6)$ is obtained in an analogous way.   N. Thon

METALLURGICAL LITERATURE CLASSIFICATION

YATSIMIRSKIY, K.B.

Yatsemirskiy, K.B. and Zaslavskiy, I.I. "Classification of diagrams in volumetric analysis of liquid double systems," (reference), Soobshch. o nauch. rabotakh chlenov Vsesoyuz. khim. o-va im. Mendleyeva, 1948, Issue 2, p. 23

SO: U-2888, Letopis Zhurnal'nykh Statey, No. 1, 1949

PA 8/49T13

USSR/Chemistry - Heat of Hydration, Of Ions   Jul/Aug 48
     Chemistry - Thermochemistry

"Thermochemical Radii and Heats of Hydration of Ions,"
K. B. Yatsimirskiy, Inst Gen and Inorg Chem imeni N. S.
Kurnakov, Acad Sci USSR, $7\frac{1}{2}$ pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk"   No 4

Calculates thermochemical radii and heats of formation
in the gaseous state of the ions: JO_3', BrO_3', CNO';
$C_6H_2(NO_2)_3O'$ and $[Co(NH_3)_5Cl]''$
Calculates heats of hydration of the ions:
ClO_4', $C_6H_2(NO_2)_3O'$, ClO_3', BrO_3', NO_3', HCO_3', CNO',..
H_2COO', NO_2', CNS', CN', $[N(CH_3)_4]$ and $[Co(NH_3)_5Cl]''$
Shows relation between heat of hydration and magnitude
                                                        8/49T13

USSR/Chemistry - Heat of Hydration, Of Ions   Jul/Aug 48
                    (Contd)

of thermochemical radius. This relation for anions of
the type RO_n' is somewhat different from that for other
anions. Shows applicability of Kapustinskiy's
equation for calculating the entropies of RO_n' type
ions in aqueous solution.   Presents   heat
of solution of salts as a function of the ion radii
which form the particular salt. Establishes general
relationship between alteration of heat of solution and
the magnitude of the ion radii. Submitted 11 Jun 1947.

                                                        8/49T13

USSR/Chemistry - Lanthanium Compounds   Sep/Oct 48
     Chemistry - Ionization, Potential of

"Calculation of the Potentials of Ionization for
Some Lanthanides by Means of Kapustinskiy's
Equation," K. B. Yatsmirskly, Inst Gen and Inorg
Chem imeni N. S. Kurnakov, Acad Sci USSR, Ivanovo
Chem Eng Inst, 2 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 5

Found a regular increase in the ionization potential
of the lanthanide series, Ce-37.1 ev, Pr-37.7 ev,
Nd-38.2 ev, Sm-38.2 ev, and Er-40.0 ev. Submitted
5 Apr 48.

                                        27/49T32

USSR/Chemistry - Synthesis   Nov/Dec 48
      Chemistry - Energy, Lattice, of Metal Salts

"The Lattice Energy of Metal Salts of Secondary
Groups in a Periodic System," K. B. Yatsimirskiy,
Inst Gen and Inorg Chem imeni N. S. Kurnakov,
Acad Sci USSR, 11 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 6

Studies condensation of 2-formoxybutadiene, 2-
methoxybutadiene, and chloroprene with divinylke-
tones (5-methyl-1,4-hexadiene-3-onium and 5-
methyl-1,4-octadiene-3-onium). Shows that re-
action takes place easily according to general

                                              33/49T20

USSR/Chemistry - Synthesis (Contd)   Nov/Dec 48

diagram of diene synthesis with formation of
corresponding pair-substituted derivatives of
cyclohexenylketones. Submitted 10 Nov 47.

                                              33/49T20

YATSIMIRSKIY, K. B.

USSR/Chemistry - Salts, Ammine   Dec 48
                    Cobalt

"Thermochemistry of Cobalt Acidopentammine Salts,"
K. B. Yatsimirskiy, L. L. Pankova, Chair of
Inorg Chem, Ivanovo Chemicotechnol Inst, 7½ pp

"Zhur Obshch Khim" Vol XVIII, No 12

Determined heats of formation and heats of
solution for a large number of salts such as
$(Co(NH_3)_5Cl)Br_2$, $(Co(NH_3)_5SO_4)I$, etc. Made a
study of the thermochemistry of their ions.

                                        67/49T40

C A

2

Extreme points on property curves of binary systems in volume analysis. I. I. Zaslavskii and K. B. Yatsimirskii. Zhur. Obshchei Khim. (J. Gen. Chem.) 18, 1755-9(1948); cf. C.A. 43, 930d.—For ideal binary systems, the d. d_m and the at. concn. (total no. of g. atoms in 1 l.) A_m are additive if the compn. is expressed in vol. %, thus, $d_m = d_1V_1 + d_2V_2$ and $A_m = A_1V_1 + A_2V_2$. In real systems, the deviations ΔA and Δd of the real A and d from the ideal A_m and d_m are related by $0.5A/\partial V_1 = \Delta d(\partial/\partial V_1)$ $(A_m/d_m) - (A_m/d_m)(\partial\Delta d/\partial V_1)$. It follows from this expression that ΔA and Δd can have extreme values at the same point only if $M_1/n_1 = M_2/n_2$, where $M = $ mol. wt., $n = $ no. of atoms in the mol., and, further, that the max. of ΔA will be shifted, relative to the max. of Δd, in the direction of the component with the smaller "mean at. wt." M/n. By an analogous consideration, the contractions C and Δd can have an extreme value at the same point only if the sp. grs. of the 2 components are equal; in the general case, the max. of C is shifted, relative to the max. of Δd, in the direction of the component of lower sp. gr. Δd and C have an extreme value at the same point only if $A_1 = A_2$; in the general case, the max. of ΔA is shifted, relative to the max. of C, in the direction of the component of higher A. As an illustration, $H_2SO_4 + H_2O$, at 20°, has a max. of ΔA at 73 wt. % H_2SO_4, C at 76%, Δd at 80%; $HNO_3 + H_2O$, at 20°, max. ΔA at 54%, C at 55%, Δd at 60 wt. % HNO_3; $EtOH + H_2O$, at 15°, max. ΔA at 46, C at 48–49, Δd at 42 wt. % EtOH. In all 3 cases, the max. of ΔA corresponds to a rational compn.; thus, resp., $H_2SO_4.2H_2O$ (between 0 and 100°), $HNO_3.3H_2O$ (between 5 and 30°), $EtOH.3H_2O$ (between 15 and 40°), whereas the positions of the max. of C and of Δd are irrational.

N. Thom

26

Entropies of Ions in Crystals and Solubility of Salts.
(In Russian.) A. F. Kapustinskii and K. B. Yatsi-
mirskii. Zhurnal Fizicheskoi Khimii (Journal of
Physical Chemistry), v. 22, ct. 1948, p. 1271-1279.
Presents results of experimental and theoretical
study. Data are tabulated and charted. 15 ref.

IATSIMIRSKII, K. B.

I. I. Zaslovskii and K. B. Iatsimirskii,   Unusual points on the curves of pro-
perties of binary systems during volumetric analysis.   p. 1755

    Mathematical analysis has established the following for 2-compound systems
by chemical reaction: The maximum deviation of atomic concentration from the
average of calculated value (ΔA) is shifted in regards to the maximum deviation
of specific gravity from the average calculated value (Δd) toward the component
with the smaller average atomic weight. The maximum ΔA is shifted in regard
to the compression maximum C toward the component with the largest atomic con-
centration. The maximum Δd is shifted in regards to the maximum C toward the
component with the largest specific gravity.

√ Chair of Inorganic Chemistry of the Ivanov Chemico Technological Institute
  July 17, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 10 (1948):

YAKIMIRSKIY, K. B.,

K. B. Iakimirskii and L. L. Pankova, Thermo-chemistry of acido-pentaammine salts of cobalt. p. 2051.

The heat of reaction is determined with a 0.26 in solution of $Na_2 S$ and from this is calculated the heat of formation of 15 compounds and the heat of solution of 13 compounds. The heat of formation is calculated for a series of complex acido-penta-ammino colbalt-ions in a water solution. From this is calculated the heat of formation of certain salts.

Chair of Inorganic Chemistry of the
Ivanov Chemico-Technological
Institute
June 28, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 12, (1948)

YATSIMIRSKIY, K.B.

29573

Ie istorii analitichyeskoy khimii v rossii. Uspyekhi Khimii,
1949, vyp.5, s.623-28. Bibliogr: s.628

4. Gyeologo-Gyeorafichyeskiye Nauki
   (Palyeontologiya - Sm. XV, 5 B)
a. Gyeologo-Gyeografichyeskiye Nauki b Tsyelom. Gyeologiya. Pyetrografiya.
Minyeralogiya. Kristallografiya.

SO: LETOPIS' NO. 40

3014   The Energetics of the Lanthanide Ions. K. B.
        Yatsimirskii. Izvest. Akad. Nauk S.S.S.R., Otd.
        Khim. Nauk, No. 6, 648-51(1949)(in Russian).
    Thermochemical characteristics of rare earths, such
as ionization potentials, and hydration and formation heats,
of their trivalent ions, were determined by using the equation
of Kapustinskii (Zhur. Obshchei Khim. 13, 497(1943)) and the
known thermochemical data. Thus, the formation heats $-H_R$
of the gaseous ions La^{+3}, Ce^{+3}, Pr^{+3}, Nd^{+3}, Gd^{+3}, Dy^{+3}, Ho^{+3},

Er^{+3}, Tm^{+3}, and Lu^{+3} were found from $-H_R = 3H_{Cl^-} - U_{RCl_3}$
$-H_{RCl_3}$, where H_{Cl^-} and $-H_{RCl_3}$ are formation heats of
the gaseous Cl^- and the solid salt, respectively, and U_{RCl_3}
is the energy of the latter's lattice, calculated from Kapustin-
skii's equation. Since the formation heat of a gaseous ion is
the sum of the metal's sublimation and ionisation heats, and
since the ionization heat is approximately equal to the ioni-
zation potential I, the latter can be calculated, by using the
value 90 kcal for the sublimation heat of the lanthanides.
The values found satisfy the equation $I = 43.18 \log Z - 38.9$,
from which the ionization potential of the element 61, Eu^{+3},
Tb^{+3}, and Yb^{+3}, can be calculated. Further, the hydration
heats $L_R = -H_{aq} + H_R - 3 \times 101$, where 101 kcal is the heat
of formation of a H ion in water solution, and the difference
$H_{aq} - 303$ is the heat of formation of a trivalent lanthanide
ion in water solution. The values thus calculated satisfy the
equation $L_R = 382 + 515/r$, where r is the ion radius. By
using the material obtained in the present work, an estima-
tion can be made of the heats of formation of various com-
pounds, such as chlorides, hydroxides, oxides, nitrates,
sulfates, etc., of the lanthanides.

C. A.

Diagrams of the type ionic radii-property. K. B. Yatsimirskiĭ (Ivanovo Chem.-Technol., Inst., Ivanovo, U.S.S.R.). *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshcheĭ i Neorg. Khim., Akad. Nauk S.S.S.R.* No. 19, 203–10(1949). —For this type of diagram where the properties are lattice energy, heat of soln., and soly. cf. C.A. 42, 4800e, 8004e, and 43, 1241i. Analogous diagrams were constructed for ionic radii vs. m. ps. The diagram ionic radii-crystal structure differed from the preceding ones. When values of r_a were plotted as abscissas and r_c as ordinates, where c and a designate cation and anion, resp., and when line AB was drawn for $r_c/r_a > 0.87$ and line CD for $r_c/r_a = 0.41$, it could be expected, according to Magnus and to Goldschmidt, that to the right of AB the crystal structure would be that of CsCl, yet out of 19 salts 9 crystd. as expected, 9 were of the NaCl type, and 7 had both structures. Similarly, between AB and CD the NaCl type of structure was expected, yet NH₄I having both types of structure was located there. The diagram showed that the CsCl structure appeared where $r_a > 1.6$ A. and $r_c > 1.9$ A. Both CsCl and NaCl types occurred where $r_a > 1.35$ A. and $r_c > 1.7$ A. Thus, the type of crystal structure depended on the abs. value of r.   M. Hoseh

CA

Thermochemistry of complex cobaltic salts with neutral additives. K. B. Yatsimirskii and I. L. Pankova (Ivanovo Inst. Chem. Technol.). J. Gen. Chem. U.S.S.R. 19, 569-75(1949)(English translation).— See C.A. 43, 7813g. R. J. C.

C 9

2

Thermochemical relations in the Werner-Kiselev series for complex cobaltic compounds. K. B. Yatsimir skii and I. L. Perkova (Ivanovo Inst. Chem. Technol.). J. Gen. Chem. U.S.S.R. 19, 877-88 (1949)(English translation).—See C.A. 43, 7806d.

E. J. C.

Thermochemical radii and energies of tetrahedral and triangular ions. A. F. Kapustinskii and K. B. Yatsimirskii (Acad. Sci. U.S.S.R., Moscow). Zhur. Obshchei Khim. (J. Gen. Chem.) 19, 2191–2200(1949).—(1) Thermochem. radii r calcd. for a given anion by K.'s equation (C.A. 38, 3709) from the lattice energy U, show very slight variations, of the order of 3%, depending on the nature of the cation of the salt, in the sense that r of the nonspherical anion increases when it is assocd. with a larger cation;

e.g., NO_3^-, r varies from 1.86 in $CsNO_3$ to 1.94 A. in $[Co(NH_3)_6]Cl](NO_3)_2$; ClO_3^-, from 1.98 in $RbClO_3$ to 2.05 A. in $[Ni(H_2O)_6](ClO_3)_2$; HCO_3^-, from 1.56 in [Zn(NH_3)_6](HCO_3)_2 to 1.60 in $[Cu(NH_3)_6](HCO_3)_2$; SO_4^{--}, from 2.36 in $CaSO_4$ to 2.83 in $[Co(NH_3)_6Cl]SO_4$; CrO_4^{--}, from 2.37 in $[Co(NH_3)_6]Br]CrO_4$ to 2.42 in $[Co(NH_3)_6]$, $NO_3]CrO_4$; O_2^{--}, 1.79 in BaO_2, 1.80 in CaO_2 and SrO_2. A smaller cation penetrates more deeply into recesses of the anion and thus brings about a decrease of its r. (2). In heats of hydration Q of anhyd. salts, calcd. by $Q = U_h - U + W$, where $U_h = $ lattice energy of the hydrated salt, the heat of formation W of the gaseous aquo ion from the gaseous central ion and gaseous H_2O remains const. in the case of salts of spherical anions (F^-, Cl^-, Br^-, I^-) but anomalies appear with nonspherical anions; thus, instead of increasing with the size of the anion, Q is greater for chlorides than for nitrates, and the same reversal

is found between bromides and chlorates. This reversal is due to a decrease of the "penetration effect," present in the case of polyat. anions, as a result of the hydration of the cation. Illustrative data of Q, in kcal./mole, are: $[Li(H_2O)_4]Cl$ 42.3, $[Li(H_2O)_4]NO_3$ 40.0, $[Mg(H_2O)_6]Cl_2$ 36.9, $[Mg(H_2O)_6](NO_3)_2$ 28.8, $[Mg(H_2O)_6]Cl_2$ 96.3, $[Ca(H_2O)_6]Cl_2$ 11.8, $[Ca(H_2O)_6](NO_3)_2$ 14.0, $[Ca(H_2O)_6]Cl_2$ 68.4, $[Ca(H_2O)_6](NO_3)_2$ 54.4, $[Ba(H_2O)_6]Br_2$ 16.6, $[Ba(H_2O)_6](ClO_3)_2$ 14.4, $[Ba(H_2O)_6]Cl_2$ 15.3, $[Ba(H_2O)_6](IO_3)_2$ 12.7. (3) The value of r lies somewhere between the min. distance of max. penetration and the radius of the circumscribed sphere. The distance d between the central atom of the complex anion and the cation is not equal to the sum of the thermochem. radii r calcd. for an octahedral surrounding, but, for a given lattice type, the ratio of d and the sum of r is a const.; thus, for the barite type ($BaSO_4$, $SrSO_4$, $PbSO_4$), that ratio = 1.05, and for the calcite type ($CaCO_3$, $MnCO_3$, $NaNO_3$), 0.90. For a given type of anion, the ratio of r and the radius of the circumscribed sphere is a const., thus, for triangular ions (NO_3^-, CO_3^{--}) it is = 0.67; for tetrahedral ions (ClO_4^-, MnO_4^-, BF_4^-, SO_4^{--}, CrO_4^{--}, MoO_4^{--}) it varies between 0.76 and 0.81, mean 0.79 ± 0.03. This relation permits calcu.

of r for anions for which the radius of the circumscribed sphere is known; thus, for BO_4^{---}, r (calcd.) = 1.91, BeF_4^{--} 2.45, IO_4^- 2.49, SeO_4^{--} 2.43, TeO_4^{--} 2.54, PO_4^{---} 2.36, AsO_4^{---} 2.48, SbO_4^{---} 2.60, BiO_4^{---} 2.68 A. (4) In groups of the periodic system, the r of anions of analogous structure increase regularly with increasing at. no. of the elements. (5) Heats of formation of the gaseous anion are calcd. by $-\Delta H_A = \Delta H_C - \Delta H_{CA} - U_{CA}$, where the subscripts A, C, and CA refer to the gaseous anion, the gaseous cation, and the solid salt, resp., and the ΔH's are calcd. from the ionization potentials and the heats of sublimation of the metals; for TeO_4^{--} and SbO_4^{---}, the ΔH_A were calcd. from the heats of formation of the ions in soln., and their heats of hydration Q. Values of r, ΔH_A, and Q, are: NO_3^- 1.89, 80.0, 70.7; ClO_3^- 2.00, 57.8, 64; ClO_4^- 2.36, 91.5, 50; MnO_4^- 2.40, 174, 49; IO_4^- 2.49, 99, (40); CO_3^{--} 1.85, 47, 317; CrO_4^{--} 2.4, 182, 229; SO_4^{--} 2.3, 178, 241; SeO_4^{--} 2.43, 124, 224; MoO_4^{--} 2.54, 230, 216; TeO_4^{--} 2.54, 155, (216); WO_4^{--} 2.57, 266, 202; BO_4^{---} 1.91, -240, 760; PO_4^{---} 2.36, 50, 550; AsO_4^{---} 2.48, -20, 550; SbO_4^{---} 2.60, -20, (515); BiO_4^{---} 2.4, (-330), —. (6) The calcd. values of $-\Delta H_A$ permit a decision between the Kossel scheme representing the structure of the SO_4^{--} ion by ionic bonds between a cen-

tral S^{6+} ion and 4 O^{--} ions, and the Lewis scheme involving covalent bonds between S^{++} and 4 O^-. The energy of the process $S^{6+} + 4 O^{--} = SO_4^{--}$ is calcd. to be 4660 kcal., that of $S^{++} + 4 O^- = SO_4^{--}$ (to be 725, as against 7340 and 1000 kcal., resp., from the ΔH_A data. Consequently, the Lewis structure is distinctly predominating. The same holds for the anions ClO_4^-, PO_4^{---}, SiO_4^{----}, AsO_4^{---}, SbO_4^{---}, NO_3^-, CO_3^{--}, BO_4^{---}, ClO_4^-, all of which prove to be predominantly built of singly charged O^- ions covalently bonded with the central ion. The Kossel structures become somewhat more probable as the degree of oxidation of the central ion decreases, but their share never becomes significant. (7) Exptl. detn. of the heat of soln. of $NaIO_4$ in H_2O at 25° gave -5910 cal.; with the

heat of formation of $NaIO_4$ in aq. soln. = 96.1 kcal.; this gives for solid $NaIO_4$, $\Delta H_{298} = -104.0$ kcal.

N. Thon

CA

2

Thermochemistry of aqua salts of manganese. K. B.
Yatsimirskii and A. A. Astashova (Ivanovskii Khim.-
Tekhnol. Inst.). Doklady Akad. Nauk S.S.S.R. 66,
381-3(1949); cf. ibid. 59, 1407(1947). C.A. 43, 3166d.—
Owing to the difficulty of prepg. [Mn(H₂O)₄]Cl₂ with
exactly 4 H₂O, the heat of soln. in H₂O, at 25 ± 0.06°,
is reported as a mean of 11 detns. made on prepns. with
4.3, 4.05, 4.08, 3.98, and 3.7 H₂O; the av. values inter-
polated to 4 H₂O is 3660 cal. different from the figures of
Thomsen and of Person (C.A. 36, 5539³). This gives
for the heat of formation ΔH°₂₉₈ = −396.7 kcal. Further
detns. of heats of soln. gave: [Mn(H₂O)₄]Br₂ 4020 cal.,
ΔH°₂₉₈ = −376.1 kcal.; [Mn(H₂O)₄]I₂ 5460 cal., ΔH°₂₉₈ =
−341.0 kcal.; [Mn(H₂O)₄]Br₂ at 0° (because of the
decompn. above 15°), −400 cal., ΔH°₂₉₈ = −517.2 kcal.
With the previously detd. heat of addn. of 6 H₂O (gas) to
Mn⁺⁺ (gas), −350 kcal., and Mn⁺⁺ (gas) +4 H₂O (gas)
= [Mn(H₂O)₄]⁺⁺ (gas) −180 kcal., based on the calcns. of
Eley and Evans (C.A. 32, 8277⁴), the heat of formation of
the gaseous ion [Mn(H₂O)₄]⁺⁺ is ΔH₂₉₈ = 177 kcal.
Hence, by the energy difference of the solid salt and the
gaseous ions, the lattice energy of solid [Mn(H₂O)₄]Cl₂ is
480.7 kcal.; and, by the equation of Kapustinskii (C.A.
33, 5709⁶), the thermochem. radius of [Mn(H₂O)₄]⁺⁺ is
1.63 A. The calcd. ΔH°₂₉₈ values are in very good agreement
with the exptl. values, but differ by 11.4–12.7 kcal., from
the figures of Bichowsky and Rossini, which are based on
old erroneous data of Lescoeur (Ann. chim. phys. 25, 423
(1893)).   N. Thon

Classification of diagrams in volume analysis of liquid binary systems. K. B. Yatsimirskii and I. I. Zaslavskii (Ivanovo Chem. Technol. Inst.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 301-6(1950).—Diagrams of the at. concn. Δ as a function of the compn. are of 4 types: In ideal systems of noninteracting liquids of unchanging degree of assocn., Δ is a linear function of the compn., and the deviation ΔΔ from additivity is zero throughout. In systems with one assocd. component which, in soln., dissocs. into simpler units, the curve of ΔΔ is convex to the axis of compn., and ΔΔ is always neg. In systems where the components form chem. compds., ΔΔ is concave to the axis of the compn. In systems involving both compd. formation and dissocn. of one or both assocd. components, the ΔΔ curve is slightly concave to the axis of abscissas; the abs. values of ΔΔ are relatively low, and the max. of ΔΔ may not correspond to the compn. of the compd. Examples of ideal systems are EtI-AcOEt, C₆H₆-CCl₄, C₆H₆-PhBr, AcOMe-HCO₂Et, C₆H₆-PhCl, C₆H₆-PhMe, CCl₄-PhMe, CCl₄-C₆H₅Br, C₆H₆-C₆H₅Br, etc.; for all these systems, plots of ΔΔ and of the sp. gr. against the compn. in mole fractions are linear, although the viscosity isotherms may show a min. or a max. Linear plots of ΔΔ may be found also with systems of assocd. but chemically close substances, as MeOH-PrOH and HCO₂H-AcOH. Very slight deviations from additivity, with consistently neg. ΔΔ, are exhibited by CCl₄-CS₂, PhMe-CS₂, CHCl₃-CS₂, C₆H₅Br-CS₂, C₆H₆-CS₂, CCl₄-CHCl₃, C₆H₆-Et₂O, C₆H₆-C₆H₅Br, etc.; very small pos. ΔΔ is found in C₆H₅Br-CHCl₃ and CS₂-PhBr. The 2nd type, with dis-

tinctly neg. ΔΔ, is exemplified by C₆H₆-AcOH, CCl₄-Me₂CO, CS₂-Me₂CO, EtBr-AcOH, PhMe-AcOH, CCl₄-PrOH, MeI-Me₂CO, CS₂-PrOH, etc.; viscosity isotherms of some of these systems may have either a min. or a max., and are, consequently, less informative than the ΔΔ plots. In the 3rd type, the ΔΔ curve consists of 2 branches intersecting at the max.; depending on whether, along a branch, Δ and ΔΔ are symbatic, antibatic, or const., the branch is convex to the axis of compn., concave to it, or rectilinear. One single compd. is indicated by a singular point, whereas in the case of presence of several compds., the max. is rounded, as in HClO₄-H₂O, HNO₃-H₂O, HF-H₂O, H₂SO₄-H₂O, H₃PO₄-H₂O, N₂H₄-H₂O, H₂SO₄-Et₂O, etc. "Irrational" systems of the 4th type, showing a flat diffuse max., are illustrated by PhOH-PhNH₂, Me₂CO-HCOₐH, C₆H₆(NO₂), BuOH, etc. In the systems AcOH-H₂O, MeOH-H₂O, Me₂CO-AcOH, PhOH-Me₂CO, the max. corresponds to no stoichiometric ratio of the components and to no definite compd. An S-shaped ΔΔ curve, resulting from the predominance of the dissocn. of an assocd. component along part of the curve, and of compd. formation along another part, is exemplified by the systems SbCl₃-C₆H₆, SbCl₃, ClIPh₃, and SbCl₃-C₆H₆, where, again, the max. corresponds to no stoichiometric ratio of the components.

N. Thon

CA

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Classification of complex-forming elements and addends on the basis of energy characteristics. K. B. Yatsimirskii. (Ivanov Chem.-Technol. Inst.). Zhur. Obshchei Khim. (J. Gen. Chem.) 20, 1401-7(1950). In the general case, the energy of formation H' of a complex ion from the gaseous central ion and the gaseous addends ("energy of addn.") is composed of electrostatic and covalent terms; specifically, if n is the no. of donor-acceptor covalent bonds in the complex ion, $W = I - nE - nD + U$, where I = total ionization potential, E = electron affinity of the addend, D = energy of the covalent bond between the central ion and the addend, and U = resonance energy of the given structure. On that basis, both complex-forming central elements and addends can be classified, roughly, in 4 groups: (1) "electrostatic," characterized by a high elec. charge, small radius r, high dipole moment, relatively low I, and high E: examples of central atoms are Al^{++}, Ti^{+}, Zr^{+}, Ill^{+}, and of addends, F^{-}, H_2O, ROH, CO_3^{--}, SO_4^{--}; (2) "covalent," characterized by high I, low E, low electrostatic characteristics; examples of central atoms are Au^{+}, Hg^{++}, Pb^{++}, Bi^{++}, Tl^{+}, addends $S_2O_3^{--}$, I^{-}, CNS^{-}, Br^{-}, CSN_2H_4; (3) "universal," characterized by high I, low E, high elec. charge and small r; examples are Co^{++}, Pt^{++}, Rh^{++}, Ir^{++}, Cr^{++}, Cu^{++}, and the addends $C_2O_4^{--}$, $C_4H_4O_6^{--}$, CN^{-}; (4) "intermediate," characterized by medium values of all energy characteristics; examples are Ni^{++}, Zn^{++}, Co^{++}, Fe^{++}, Ag^{+}, Cu^{+}, Cd^{++}, and the addends NH_3, $C_5H_5(NH_2)_2$, NO_3^{-}, HCO_3^{-}. Phenomena of group-selectivity in complex formation and differences of stability of complex ions in soln. can be interpreted from this point of view.

N. Thon

YATSIMIRSKIY, K. B.

C A

Formatopentammine salts of cobalt(III). K. B. Yatsimirskii. Zhur. Obshchei Khim. (J. Gen. Chem.) 20, 1408-11(1950).—Two new complex salts of Co(III) were synthesized. [Co(NH_3)$_5$$HCO_3$]I$_2$ (I), red crystals, was obtained with a 95% yield by 40-min. heating 5 g. of Co purpureochloride, [Co(NH_3)$_5$Cl]Cl$_2$, with 100 ml. of a concd. soln. of HCO_3K contg. approx. an 8-fold excess of HCO_3K, subsequent mixing of the cooled red soln. with an equal vol. of satd. KI, and washing the ppt. with ice water, aq. alc., and finally 96% alc. With a satd. soln. of NH_4NO_3 instead of KI, a red ppt. of [Co-(NH_3)$_5$$HCO_3$]($NO_3$)$_2$ (II) was obtained in a 90% yield. The heats of reaction with a 0.26 M soln. of Na$_2$S at 25° were detd., for I, to be −3110 cal., and for II, to be −4560 cal./mole. The heats of soln. in H$_2$O were detd. to be 14780 and 16380 cal./mole, resp. Hence, and with the use of the thermochem. data of Bichowsky and Rossini, the standard heats of formation ΔH°_{298} of the solid salts were calcd. to be I −261.2, II −334.3 kcal./mole, and for the ion [Co(NH_3)$_5$$HCO_3$]$^{++}$ in aq. soln., −219.7 kcal./mole. For the gaseous ion [Co(NH_3)$_5$$HCO_3$]$^{++}$, the heat of formation was calcd. to be 194 kcal./mole with the aid of the Kapustinskii equation for the lattice energy, with the thermochem. radius of the ion assumed = 2.36 Å. Hence, the heat of the reaction Co^{+++} (gas) + 5NH$_3$ (gas) + HCO$_2$$^-$ (gas) = [Co(NH_3)$_5$$HCO_3$]$^{--}$ (gas) + W is x − 357 kcal., where x = heat of formation of the gaseous Co^{+++}. Consequently, the thermal stability of the gaseous [Co(NH_3)$_5$$HCO_3$]$^{++}$ is greater than the stability of all other acidopentammine Co(III) ions, with the exception of [Co(NH_3)$_5$$NO_2$]$^{++}$. The stability of these complex ions decreases in the order $NO_2$$^-$ > $HCO_3$$^-$ > CNS$^-$ > I$^-$, Cl$^-$ > Br$^-$ > $NO_3$$^-$. N. Thon

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THE PROBLEM OF SOLUBILITY OF COMPLEX SALTS.
K. B. Yatsimirskii. Zhur. Obshchei Khim. 20, 2123-8(1950)
Dec. (in Russian)

Using a theoretical approach that has led to the discovery of
certain regularities in the solubility of simple ionic com-
pounds (Kapustinskii and Yatsimirskii, Zhur. Fiz. Khim. 22,
1271(1948)), an analysis is made of fundamental factors that
determine the solubility of complex salts, viz., dimensions
of ions, their charges, and the presence of polar or hydro-
philous groups in their compositions. Regularities are de-

duced permitting an explanation of differences in the solubility
of certain groups of complex salts, and conditions are set
forth under which difficultly soluble complexes can be ob-
tained. It can be stated that in order to obtain a difficultly
soluble compound of a given complex ion, or, more generally,
of a given large ion ($r > 2$ A), another sufficiently large ion of
opposite sign, and with a maximal possible charge, must be
selected, the sizes of both standing in a certain optimal rela-
tion to each other; the given ion must not contain hydrophilous
groups, while a well-expressed polarity within that ion is
desirable.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

YATSIMIRSKIY, K. B.

Thermochemistry of complex compounds with ethylene-diamine. K. B. Yatsimirskii and A. A. Astasheva (Chem. Tech. Inst., Ivanovo). Zhur. Obshchei Khim. (J. Gen. Chem.) 20, 2130-43(1950)).—Calorimetric measurements at 25° gave for the heats of the reaction of the complex salts with 1 N HCl the following values (en = $NH_2CH_2CH_2NH_2$): [Cd en$_3$]Cl$_2$ 40.43;   [Cd en$_3$]Br$_2$ 39.2;   [Ni en$_3$]Cl$_3$.2H$_2$O 39.00;   [Ni e$_3$]Br$_3$ 37.64;   [Ni en$_3$]I$_3$ 35.41 kcal./mole. From [M en$_3$]X$_2$ (cryst.) + 6HCl.aq. → M^{++} aq. + 3 en H$_2^{++}$.aq. + 6Cl$^-$.aq. + 2X$^-$.aq. + Q_1, and detns. of the heats of soln., the heats of formation of the complex salts in the standard state were calcd. to: [Cd en$_3$]Cl$_2$ 168.8, [Cd en$_3$]Br$_2$ 149.0, [Ni en$_3$]Cl$_2$ 163.1, [Ni en$_3$]Br$_2$ 148.0, [Ni en$_3$]I$_3$ 119.6, [Ni en$_3$]Cl$_3$.2H$_2$O 309.7, [Ni en$_3$]Br$_3$.2H$_2$O 290.4 [Ni en$_3$]I$_3$.2H$_2$O 269.9, [Cd en$_3$]$^{++}$.aq. 78.3, [Ni en$_3$]$^{++}$.aq. 81.6 kcal./mole. The energy, W, of binding of gaseous en by the gaseous metal ion M^{++}, to form the gaseous complex ion [M en$_3$]$^{++}$, is estd. from the lattice energy U of the cryst. complex salts, [M en$_3$]X$_2$ (cryst.) = [M en$_3$]$^{++}$ (gaseous) + 2X$^-$ (gaseous) − U, where U is calcd. by Kapustinskii's equation ($C.A.$ 38, 5705^4), with the thermo-chem. radii of all complex ions [M en$_3$]$^{++}$ = 2.7 A. This gives for W, Ni^{++} 383, Zn^{++} 372, Co^{++} 372, Fe^{++} 342, Cd^{++} 323 kcal./mole. The order of the heats of binding of 3 en by these ions is the same as that of the heats of binding of 6 NH$_3$; the latter are lower by 5-13 kcal. From the difference of the heats of formation of the anhyd. and the hydrated salts, the heats of hydration are calcd. to [Ni en$_3$]Cl$_2$.2H$_2$O 10.8, [Ni en$_3$]Br$_3$.2H$_2$O 5.9, [Ni en$_3$]I$_3$.2H$_2$O 3.6. The abnormal increase of the heats of hydration from the iodide to the chloride can be explained by assuming hydration of the anion rather than the cation.   N. T

CA

The solubility of complex salts. K. B. Yatsimirskii
(Chem.-Technol. Inst., Ivanovo). J. Gen. Chem. U.S.S.R.
20. 2213-17(1950)(Engl. translation). See C.I. 45.
[illegible].
B. L. M.

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CA

Energetics of complex compounds. K. B. Yatsimirskii (Chem. Technol. Inst., Ivanovo). Izvit. Sektora Platiny i Drugikh Blagorod. Metal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R. No. 25, 6-2X(1951).—An extensive discussion of previous work (C.A. 42, 4880c, 8448c). M. Hoch

1951

Thermochemistry of the trans influence. — K. B. Yatsimirskii, (Ivanov Chem.-Technol. Inst.). *Doklady Akad. Nauk S.S.S.R.* **72**, 307-10(1950). — With the heat of formation of the hydrated Co⁺⁺⁺ ion assumed to be $\Delta H_{298} = -22$ kcal. (from the free energy, with the entropy of the ion in soln. taken equal to that of Fe⁺⁺⁺), the following heats of formation of the complex ion in soln. (from the hydrated neutral ion and addend) are calcd.: [Co(NH₃)₆]⁺⁺⁺ (I) 0.0; [Co(NH₃)₅NO₂]⁺⁺ (II) 51.1; [Co(NH₃)₅Cl]⁺⁺ (III) 41.7; [Co(NH₃)₅H₂O]⁺⁺⁺ (IV) 45.0; 1,6-[Co(NH₃)₄(NO₂)₂]⁺ (V) 53.1; 1,2-[Co(NH₃)₄(NO₂)₂]⁺ (VII) 32.0; [NO₂]⁻ (VI) 51.0; 1,6-[Co(NH₃)₄Cl₂]⁺ (VIII) 40.2; 1,6-[Co(NH₃)₄(NO₂)-Cl]⁺ (IX) 45.0; 1,2-[Co(NH₃)₄Cl₂]⁺ (XI) 47.0; [Co(NO₂)₆]⁻ (XII); [Co(NH₃)₄(NO₂)₂] ... From these data, the heats of displacement of NO₂ by NH₃ are: V → II, 0.0; VI → II, −0.8; II → I, 28.1 kcal. ... XII → VI, −1.3; X → IV, −0.6; IX → III, −7.0; +18.9; XI → VI, +6.9; VI → I, −2.0 kcal. Heats of displacement of NO₂ by H₂O are, V → X, −7.5; II → IV, −8.1. Heats of displacement of NO₂ by Cl are, V → IX, −3.8; II → III, −11.4; IX → VII, −17.3 kcal. Heats of displacement of NH₃ by Cl: II → IX, −3.8; I → III, −10.2; III → VII, −0.7; III → X, −7.5; I → IV, −6.9. Displacement of NH₃ by H₂O: II → X, −7.5; IV → III, −11.5. Displacement of H₂O by Cl: X → IX, +3.7; IV → III, −3.3 kcal. These figures illustrate the possibility of thermochem. measurement of the trans influence. In the case of Co⁺⁺⁺ complexes, the series is NO₂⁻ > NH₃ > H₂O > Cl⁻. The susceptibility to trans-influence decreases in that order, i.e. the heat effect accompanying the

displacement of NO₂ is greatest when the trans position is occupied by NO₂, somewhat smaller if it is occupied by NH₃ or H₂O, and smallest with Cl in the trans position. In the displacement of 2 NO₂, the thermal effect is greatest with XII, smaller with XI, and neg. with NH₃ in trans position to NO₂. The same rules apply to displacement of NH₃ and H₂O by Cl⁻; the heat is greater with NO₂ in trans position to NH₃ or H₂O than with NH₃ or Cl⁻ in that position. This order is reversed in the displacement of Cl⁻, NH₃ or H₂O by NO₂⁻, and in the displacement of NH₃ or H₂O by NO₂⁻. These facts can be by any of the addends considered. These facts can be interpreted by assuming that, of the two d-, one π-, and three p-bonds of the octahedron, the d-bonds are the most and the p-bonds the least stable, and that the different addends have unequal tendency to occupy a d bond. This tendency appears to decrease in the order NO₂⁻ > NH₃, H₂O > Cl⁻. For NO₂, the bond strength differs greatly, depending on whether the NO₂ group is bound by p- or by d-bonds; this difference is less pronounced for NH₃ and H₂O, and seems to disappear completely for Cl⁻. This conclusion is borne out by the heats of formation ΔH of geometric isomers. Croceo-ions, with one NO₂ group bound by a p-bond, the other by a d-bond, have a lower ΔH than flavo-ions, with both NO₂ groups d-bonded. In the case of praseo- and violeo-salts, the trans isomer, with the Cl⁻ ions bound by d- and p-bonds, has the higher ΔH, probably as a result of the ionogenic nature of the bond. — N. Thon

YATSIMIRSKIY, K. B.

Thermochemistry of complex compounds Moskva, Izd-vo Akademii nauk
SSSR, 1951. (Mic 53-843 Collation of the original: 250 p.

Microfilm T-14

YATSIMIRSKIY, K. B.

USSR/Chemistry - Analytical Reactions   Jul/Aug 51
                and Reagents

"Classification of Analytical Reactions and Rea-
gents on the Basis of the Energy Characteristics
of Ions," K. B. Yatsimirskiy, Ivanovo Chem-Technol
Inst

"Zhur Analit Khim" Vol VI, No 4, pp 211-217

"Covalent characteristic" of given ion, or tendency
of ion to form covalent bond (calcd as difference
between ion's ionization potential and its heat of
hydration), electron charge, and ionic radius pro-
vide data for classification of ions for analyt
                                          183T24

USSR/Chemistry - Analytical Reactions   Jul/Aug 51
                and Reagents (Contd)

purposes. Gives tables of above values for many
anions and gen rules for prediction of soly when
particular anion and cation are present in soln.

                                          183T24

LC

Complex compounds with anions of aromatic sulfonic acids in the outer sphere. K. B. Yatsimirski, K. E. Prik, T. L. Zyirskaya, and V. V. Starostin [Chem.-Technol. Inst., Ivanovsk]. Zhur. Obshchei Khim. (J. Gen. Chem.) 21, 486-90(1951). Mixing 1% solns. of aromatic sulfonates (Na salts) with satd. aq. solns. of [Co(NH₃)₆]Cl₃ (I), [Cr(NH₃)₆]Cl₃ (III), (NH₄)₃(NO₂)₆ (II), or [Cr(CON₂H₄)₆]Cl₃ usually gave ppts. of the corresponding complex salts. p-Me₃C₆H₄SO₃Na gave with I and III ppts. having compns. of the type; soly. of the Co salt is 0.0037 mole/l. at 20°. [Co(NH₃)₆][C₆NH₄₃SO₃]₃. The soly. does not give ppts. 2,4-ClMeC₆H₃SO₃Na gives ppts. with I, II, and III; [Co(NH₃)₆]-[C₆H₄ClSO₃]₃, yellow; [Cr(CON₂H₄)₆][C₆H₄ClSO₃]₃, green. The 2-nitro analog gives ppts. with I, II, and III; [Co(NH₃)₆]-[C₆H₃NSO₃]₃, yellow; [Cr(NH₃)₆][C₆H₃NSO₃]₃, yellow, soly. 0.0087 mole/l. at 40°; [Cr(CON₂H₄)₆][C₆H₃NSO₃]₃, green, soly. 0.0033 mole/l. at 20°. The 2-Chloro-5-nitro analog also gives ppts. with I, II, and III; [Cr(NH₃)₆][C₆H₃ClNSO₃]₃, green. Na 3-yellow; [Cr(CON₂H₄)₆][C₆H₃ClNSO₃]₃, green. carbazolesulfonate gives ppts. even in rather dil. solns. with I, II, and III. Even less sol. are the salts of 6-nitro-3-carbazolesulfonic acid; [Co(NH₃)₆][C₁₂H₆N₂SO₃]₃, yellow; [Cr(CON₂H₄)₆][C₁₂H₆N₂SO₃]₃, yellow; poorly sol. salts also form with derivs. of Cu, Zn, Ni, and Cd. Especially poorly sol. are salts of alizarinsulfonates; salts with I and II are especially mentioned but are not further characterized.

Generally, the soly. declines with increased size of the anion and with introduction of polar groups into it. Introduction of OH, NH₂, or CO₂H groups into the sulfonate radical, sharply raises the soly. of the complex salts. Sepn. of some sulfonic acids by such means may be feasible.　G. M. K.

Unsaturated cyclic hydrocarbons and their halogen deriva-tives. X. Transformations ...

USSR/Chemistry - Analytical   Feb 51

"Problem of the Variation of Free Energy and Entropy in Reactions of Formation of Complexes," K. B. Yatsimirskiy, Chair of Analyt Chem, Chemicotech Inst, Ivanovo

"Zhur Fiz Khim" Vol XXV, No 2, pp 221-223

Advances hypothesis, based on entropy data for RO_n^{2-} ions (i.e., CC_3^{2-}, MoO_4^{2-}), that only thermochem radius determines entropy of single-type complex ions (i.e., those having equal number of same groups combined to cen ion). Shows difference between heat effect and free energy to be const in single-type

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complex formation. Arranges anions and cations by decreasing stability, latter assumed to be detd by difference between ionization potential of cen atom and heat of hydration of ion formed.

184T33

CA

Stability constants of some complex compounds of lead. K. B. Yatsimirskii (Chem.-Tech. Inst., Ivanovo). Zhur. Fiz. Khim. 25, 475-9(1951).—Earlier theoretical predictions (C.A. 45, 6110f) concerning the relative stability of complexes in soln. are verified by expts. leading to the detn. at 25° of the stability consts. $K_1 = [Pb(S_2O_3)]^-]/[Pb^{++}][S_2O_3^-]^2$, $K_2 = [Pb(S_2O_3)]^-]/[Pb^{++}][S_2O_3^-]^2$ and $K = [Pb(CNS)_2^-]/[Pb^{++}][CNS^-]^2$. The values $K_1 = 1.35 \times 10^6$ and $K_2 = 2.21 \times 10^6$ are obtained by measuring the soly. of PbS_2O_3 in aq. solns. of $Na_2S_2O_3$. The soly. product of PbS_2O_3 is also calcd.: 3.99×10^{-7}. The value $K = 0.8$ is found by measuring the soly. of $Pb(CNS)_2$ in aq. solns. of KCNS. The soly. product of $Pb(CNS)_2$ is 2.00×10^{-5}. Finally, the stability const. K' $PbBr_4^-$ is estd. from the data of Burrage (C.1. 20, 3402); it is approx. 2×10^6. These values of K_1, K_2, K and K' confirm the theory.   Michel Boudart

...plex information in

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Complex compounds with anions as coördination centers. K. B. Yatsimirskii (Ivanovo Chem.-Technol. Inst.). *Dok. lady Akad. Nauk S.S.S.R.* 77, 819-22(1951).—Favorable conditions for the formation of complex ions with cations as addends to an anion as central atoms are low electron affinity of the anion and high electron affinity of the cation, i.e. low and high ionization potentials, resp., of the corresponding atoms. In aq. soln., the detg. magnitude is the difference of electron affinity and energy of hydration; consequently, favored addends will be cations with both high electron affinity and large radius, particularly Au^+, Ag^+, Hg^{++}, Cd^{++}, and Pb^{++}. The double salts found in the systems $AgCl$-$AgNO_3$, $AgBr$-$AgNO_3$, and AgI-$AgNO_3$, should thus be formulated $[Ag_2I]NO_3$, $[Ag_3I](NO_3)_2$, $[Ag_2Br]NO_3$, and $[Ag_2Cl]NO_3$. From data of Hellwig (Z. anorg. Chem. 25, 157(1900)) on the soly. of Ag halides in solns. of $AgNO_3$, the following equil. consts. are estd.: $[Ag^+][I^-]/[Ag_2I^+] \sim 2 \times 10^{-4}$, $\sim 0.8 \times 10^{-10}$; $[Ag^+][Br^-]/[Ag_2Br^+] \sim 2 \times 10^{-4}$, $[Ag^+][Cl^-]/[Ag_2Cl^+] \sim 2 \times 10^{-4}$. Thus, the stability of these complexes increases with decreasing ionization po-

tential of the anion element, i.e. from chloride to iodine. In the search for analogous complexes with addend cations other than Ag^+, detns. were made of the soly. of HgI_2 in aq. solns. of $Hg(NO_3)_2$: selected data are, for $Hg(NO_3)_2$ 0.1780, 0.7210, 1.2123, 1.4534, 1.8587 moles/1000 g. H_2O, HgI_2 14.5, 55.8, 110.3, 148.0, 299.3 millimoles/1000 g. H_2O. The fast increase of the soly. indicates presence not only of HgI_2 but also of HgI^+. From the soly. data, the equil. consts. are $[Hg^{++}][I^-]/[HgI^+] \sim 4.4 \times 10^{-8}$, $[Hg^{++}][I^-]/[HgI_2] \sim 2.4 \times 10^{-8}$. Further complexes of this type are double salts variously described in the old literature, which should be formulated $[Hg_2S]X_2$, $[Cd_2S]X_2$, $[Hg_2S](ClO_4)_2$, $[Pb_2S]X_2$, $[Ag_2S]NO_3$, $[Hg_2Se]Cl_2$, $[Hg_2Se]Br_2$; there are also more highly complex ions, such as $[Hg_2S]X_2$. Examples of complexes with a 5th-group element as central atom are the complexes described by Poleck and Thümmel (Ber. 16, 2435(1883)), $[Ag_3P](NO_3)_3$, $[Ag_3As](NO_3)_3$, and $[Ag_3Sb](NO_3)_3$.   N. Thon

1951

The periodic law of D. I. Mendeleev and the stability of complex compounds. A. A. Grinberg and K. B. Yatsimir-skii. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1952, 211–17.—The tendency to complex formation is characterised quantitatively by the energies of formation of the gaseous complex ions, and by the instability const. K of the complex; the latter magnitude actually expresses the difference of the stability of the complex ion and of the corresponding aquo ion. From a thermochem. cycle involving the formation of a complex ion $[MA_n]^{++}$ from $M^{++} + nA$, the heat is $\Delta H = (W_1 - W_2) + (l_a - l_n) + n(\lambda_1 - \lambda_2)$, where W_1 and W_2 are the energies of addn. of H_2O and of A. resp., to the gaseous M^{++}, l_a and l_n are the heats of hydration of $[MA_n]^{++}$ and $[M(H_2O)_n]^{++}$, resp., and λ_1 and λ_2 the heat of evapn. of H_2O and of hydration of A. resp. The latter term being const. for reactions of one type, and the middle term approx. const., $\Delta H = (W_1 - W_2) + C$ (const.), and $RT \ln K = (W_1 - W_2) + C'$ (const.). This gives the relation between the 3 characteristics of the tendency to complex formation. This relation is verified by data for $[Mg(NH_3)_6]^{++}$, $[Co(NH_3)_6]^{++}$, $[Ni(NH_3)_6]^{++}$, $[Co\,en_3]^{++}$, $[Ni\,en_3]^{++}$, and $[Zn\,en]^{++}$. In application to ions with an inert-gas structure of the outer electron shell, but different charge and radius, this leads to the conclusion

that the stability of complexes increases from left to right in the period and decreases from top to bottom in the groups of the periodic system. For ions with 18-electron shells, the complex stability ought to decrease with increasing at. no. In the groups if the bond is predominantly ionic; with predominantly covalent bonding, elements of the 6th period should form particularly stable complexes. As a result of the 2 antagonistic factors, the heat of formation of gaseous complex ions within a subgroup may pass through a min.; examples are, for complex ions $[M(NH_3)_6]^+$, $M = Cu$ 131, Ag 104, Au 166 kcal./mole, and for ions $[M(NH_3)_4]^{++}$, $M = Zn$ 366, Cd 311, Hg 376 kcal./mole. The same is found for the free-energy change $\Delta F = RT \ln K$ of formation of complex ions in aq. soln. The more pronounced the covalent character of the bond, the more marked is the increase of the stability (ΔF) of the complex ions from top to bottom; this is illustrated by comparison of ΔF for complex chlorides, bromides, and iodides, the latter showing the most marked change of ΔF from Cu to Au or from Zn to Hg, and the chlorides the least marked. In series of complex ions formed by central ions with the same charge, but with different outer-electron shell structures, the complex sta-

YATSIMIRSKIY, K.B.; ASTASHEVA, A.A.

Slightly soluble complex compounds of thiourea and their use in analysis.
J. Anal. Chem. U.S.S.R. 7, 45-9 '52 [Engl. translation].
(CA 47 no.19:9849 '53)

YATSIMIRSKIY, K. B.

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Analytical Chemistry

Thermodynamic criteria for the applicability of chemical reactions to volumetric analysis. K. B. Yatsimirskii (Ivanovo Chem. Tech. Inst.). J. Inst. Chem. (U.S.S.R.) 7, 23-25(1952)(Engl. translation).—See C.A. 47, 1529h.   H. L. H.

YATSIMIRSKIY, K. B., SHUTOV, A. A.

Mercury Compounds

Instability constants of complex mercury-iodide compounds. Zhur. fiz. khim. 16 no. 6, 1952

YATSIMIRSKIY, K.B.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
Inorganic Chemistry

③

Some ternary complexes of copper and silver. K. B. Yatsimirskii and V. E. Panova (Ivanovo Inst. Chem. Technol.). J. Gen. Chem. U.S.S.R. 22, 1329-33(1952) (Engl. translation); Zhur. Obshchei Khim. 22, 1284-9 (1952).—When halides of Cu (I) and Ag dissolve in solns. of $S_2O_3^{--}$, mixed complexes of the type $[MeXS_2O_3]^{--}$ are formed. The solubilities of CuI and CuCNS in thiosulfate solns. were measured at various temps., and the stability consts. were calcd. for the resultant $[CuIS_2O_3]^{--}$ and $[Cu(CNS)S_2O_3]^{--}$ as 3.1×10^{-14} and 1.3×10^{-11}, resp. On the basis of literature data for the solubilities of Ag halides in thiocyanate and thiosulfate solns., the following stability consts. were calcd.: $[Ag(CNS)_2]^{---}$, $1.0 \pm 0.5 \times 10^{-11}$; $[AgICNS]^{-}$, 7.1×10^{-13}; $[AgClS_2O_3]^{--}$, 0.7×10^{-9}; $[AgBrS_2O_3]^{--}$, 4.1×10^{-11}; $[AgIS_2O_3]^{--}$, 2.7×10^{-13}.

Bernard Rubin

YATJMIRSKIY, K.B.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
General and Physical Chemistry

The absolute contraction constant and the periodic law.
I. I. Zaslavskii and K. B. Yatsimirskii. J. Gen. Chem.
(U.S.S.R.) 22, 1753-6(1962)(Engl. translation).—See C.A.
47. 1098c.

YATSIMIRSKIY, K. B.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
General and Physical Chemistry

Thermochemistry of nickel-ammonia complexes in aqueous solution. K. B. Yatsimirskii and Z. M. Grafova. *J. Gen. Chem.* (U.S.S.R.) 22, 1705-9(1952)(Engl. translation).—See *C.A.* 47, 2030c. H. L. H.

YATSIMIRSKIY, K. B.

Compounds, Complex

"Thermochemistry of complex compounds."
Reviewed by O. Ye. Zvyagintsev. Zhur. prikl.
khim, 25, No. 7, 1952.

Monthly List of Russian Accessions, Library of Congress, November 1952, UNCLASSIFIED.

YATSIMIRSKIY, K. B.

USSR/Chemistry - Cadmium and Lead   Feb 52
                    Compounds

"Entropy Changes During Formation of Complex Halides
in Aqueous Solutions," K. B. Yatsimirskiy, A. A.
Astasheva, Ivanovo Chem-Technol Inst

"Zhur Fiz Khim" Vol XXVI, No 2, pp 239-243

Calcd entropy changes occurring during formation of
some halide and cyanide complexes as well as std
entropies for 11 complex ions and mols in aq soln
(2 tables). Detd heats of mixing of $Cd(NO_3)_2$ and
$Pb(NO_3)_2$ solns with KI solns. On the basis of exptl
data, calcd heat effects of formation of ions

                                                211T49

CdI_4^- , PbI_4^- , CdI_3^- in aq soln as well as contin-
gent entropy changes. Showed that published re-
sults on heats of formation of $CdCl_2$ and PbI_4^- are
in need of correction.

                                                211T49

Inorganic Chemistry

Constants of instability of mercury-iodine complex compounds. C. B. Yatsimirskii and A. A. Shutov (Chem. Technol. Inst., Ivanovo). *Zhur. Fis. Khim.* 26, 842-7 (1952).—The soly. S of HgI_2 in 0.036 M, 0.090 M, 0.368 M, 0.593 M, 0.844 M, 1.058 M, 1.345 M, and 1.551 M $Hg(NO_3)_2$ at 25° is 19, 85, 275, 443, 684, 928, 1290, and 1538 $\times 10^{-4}$ mole/l. Except the last two, these values can be represented by $S = 0.0224$ $c^{1/2} + 0.0895$ $c^{1/2}$, in which c is the concn. of Hg^{2+}, complete dissocn. being assumed. The increase of S with c cannot be explained by the ionic strength J of the soln., as S increases with c also when J remains const. (in mixts. of $Mg(NO_3)_2$ and $Hg(NO_3)_2$ at $J = 6$). As S contains terms in $c^{1/2}$ and $c^{1/2}$, the increase of S is due to formation of $[HgI]^+$ and $[Hg_2I]^{1+}$ ions. From the above equation $A_2K_1 = 0.0224$ and $A_1K_0 = 0.0895$; A_0 is the soly. product of $HgI_2 = 10^{-9})$, $K_1 = 7.06 \times 10^{-10}$ is the instability const. of $[HgI]^+$, and $K_0 = 1.77 \times 10^{-10}$ the instability const. of $[Hg_2I]^{1+}$. The soly. was detd. in the usual manner and also by titrating $Hg(NO_3)_2$ solns. with KI to opalescence.
J. J. Bikerman .

YATSIMIRSKIY, K.P.

Investigation of bismuth halide complexes by the solu-
bility method. K. B. Yatsimirski (Chem.-Technol. Inst...

X 10⁻² for (BiCl⁺⁺)/(H⁺) and for the corresponding bro-
mide, resp. The curve log S vs. log [HNO₃] for BiONO₃ is
a straight line at low HNO₃ concns., and in this range the

YATSIMIRSKIY, K. B.

The calculation of the dissociation constants of stepwise complex formation from polarographic data. K. B. Yatsimirskii (Chem.-Technol. Inst., Ivanovo), *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.* 1, 193-9(1953).— The standard equations used for the calcn. of equil. consts. from polarographic data are derived on the assumption of a single equil. reaction, $MX_p^{z-p} \rightleftarrows M^{z+} + pX^{a-}$. When stepwise complex formation occurs, it is necessary to add another equil.: $MX_{p+1}^{z+} = MX_p^{z-p} + X^{a-}$ (for notations cf. Stromberg, et al., C.A. 43, 6691e). This leads to relations that, upon differentiation and limitation to the case where the concn. of both complex ions is the same, become $\partial \Delta E / \partial \log C_a = A(p + 0.5)$ and $\Delta E = A(\log C_a^{z+} - \log K_{p+1} + \log 2)$, where $A = 0.059/n$. The tangent for $p = 1, 2$, etc., is drawn to the ΔE vs. $\log c$ curve, and thus p, ΔE, and $\log C_a$ are obtained. Dissocn. consts. of known complexes calcd. by this method agree with, or are of the same order of magnitude as, those calcd. by the older, simplified method.   I. Bencowitz

YATSIMIRSKIY, K.B.

Stability of different degrees of oxidation of the elements.
K. B. Yatsimirskii (Chem. Technol. Inst., Ivanovo)

YATSIMIRSKII, K. B.

Chemical Abst.
Vol. 48 No. 4
Feb. 25, 1954
Analytical Chemistry

The nature of the so-called "weighting effect." K. B. Yatsimirskii (Ivanov Chem.-Technol. Inst.), Zhur. Anal. Khim. 8, 314-20(1953).—The "weighting effect" first proposed by Feigl (C.A. 19, 1108) according to which an increase in the mol. wt. of a reagent increases the sensitivity of the latter toward a given reaction is not strictly true. The analysis outlined in C.A. 43, 1241i and 45, 3089e is applied here to org. reagents. It is shown that addn. of various groups into an analytical reagent causes a change in the free energy of its lattice. Replacement of H in a C—H group by some other group causes a change in the log of soly. (Δ log S) by approx. the same value. For OH, Δ log $S \sim 1.5$, i.e. the soly. increases approx. 30 times. For other groups Δ log S is for CH_3, −0.60, C_2H_5 −2.1, Cl −0.4, Br −0.5, and I −1.0. The effect of added CH_2 groups was studied on Li, Ca, and Ba fatty acid salts. For these salts −Δ log S/n was calcd. where n is the no. of CH_2 groups. Each addnl. CH_2 caused the log S to decrease by an av. of 0.25. Addn. of aromatic rings caused a greater decrease in the soly. Addn. of hydrophobic groups causes a decrease in the soly. of the ppt. but at the same time reduces the soly. of the reagent which leads to a reduction of its sensitivity.   M. Hosch

YATSIMIRSKIY, K.B.

Stability of complex compounds in aqueous solutions. Uspekhi Khim.22,
410-44 '53.   (MIRA 6:4)
(CA 47 no.19:9841 '53)

YATSIMIRSKIY, K.B.

U S S R.

...adii and ionization potentials   K. B. Yatsimirskii

more extensive   The following results for ionic radii ...
were obtained   ...
...
to ...
CrCl₃, ... VCl₃, and ... nCl₃, and the results were in satis-
factory agreement with exptl. values. Regularities in the
change of ionic radius with at. no. were described.
J. J. Casey.

YATSIMIRSKIY, K.B.;   GRAFOVA, Z.M.

Thermochemistry of cuprammonium complexes in water solution.   Zhur.ob.
khim. 23 no.5:717-720 My '53.   (MLRA 6:5)

1. Ivanovskiy khimiko-tekhnologicheskiy institut.
                                        (Thermochemistry) (Compounds, Complex)

YATSIMIRSKIY, K.B.

(2)

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Inorganic Chemistry

Nickel-dimethylglyoxime complexes. K. B. Yatsimirskii and Z. M. Graiova. Zhur. Obshchei Khim. 23, 936-41 (1953).—The reaction between NiSO₄ and dimethylglyoxime in ammoniacal soln. in the presence of atm. O₂, yielded a colored (I) and a colorless (II) complex compd. The ratio of Ni:dimethylglyoxime in I was 1:3; in II, 1:1. The calcd. equil. const. checked well with the exptl., obtained by measuring the optical density of I at different concns.   A. P. Kotloby

YATSIMIRSKIY, K.B.

Instability constants of iodide-cadmium and iodide-lead complexes. K. B. Yatsimirskii and A. A. Shutov (Chem.-Technol. Inst., Ivanovo). Zhur. Fiz. Khim. 27, 782-9 (1953); cf. C.A. 46, 11002d.—The calcd. instability consts. of the complex ions $(Cd_2I)^{+++}$, $(CdI)^+$, $(Pb_2I)^{+++}$, and $(PbI)^+$ at 25° were 8.16×10^{-2}, 8.41×10^{-4}, 2.16×10^{-1}, and 5.05×10^{-4}, resp., by measurement of the soly. (S) of PbI_2 in aq. solns. of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ of various concns. S depended on the cation concns. according to the empirical equations $S_1 = 0.057[Cd]^{1/2} + 0.0236[Cd]^{1/4}$ and $S_2 = 0.0032[Pb]^{1/2} + 0.00075[Pb]^{1/4}$. The calcd. relative activity coeffs. (γ) of PbI_2 in aq. solns. of Ca, Mg, and Zn nitrates are tabulated for concns. of the latter from 0.2 to 2.4M; values of γ for 1M solns. are 0.225, 0.309, and 0.319, resp., where γ for PbI_2 in satd. aq. soln. is arbitrarily equal to unity. The soly. product of PbI_2, calcd. from exptl. data by the method of Kapustinskii (C.A. 38, 2870^1), is 1.05×10^{-4}. I. W. Lowehere, Ir.

Thermochemistry of anthranilates. K. B. Yatsimirskii and V. V. Kharitonov (Chem.-Technol. Inst., Ivanovo). Zhur. Fiz. Khim. 27. Zal.tha(1953) cf. C. A. 45, 6363c.— The heat of reaction (H) of a 24.8 HCl soln. (I) with anthranilic acid. FeAn, III; ... An, IV; NiAn, V; CoAn, VI; ZnAn, VII; ... anthranilic acid, was measured in an illustrated microcalorimeter at 25°. Values of H for II to VIII are -16.00, -11.11, -14.89, -11.58, -8.60, -8.46, and -13.42 kcal./mole, resp. Measured values of the heat of soln. at 25° in 1 of cryst. $FeCl_3.4H_2O$, $FeCl_2$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, ... $ZnCl_2$, and ... H_2O are ... ... , ... , ... and ... kcal./mole, resp. The ... ... of anthranilic ... ... A, where A is ... ... 2HCl An ... The calcd. lattice energies of II to VIII have the value $B + A$, where $B =$ ... ... , ... , 684, 690.4, 683.3, and 627.1 kcal./mole, resp., and K_1 is the heat of formation of the An anion.   J. W. Loweberg, Jr.

USSR/Chemistry - Cadmium, Palladium,   Oct 53
                    and Bismuth Compounds

"Thermochemistry of Complex Thiourea Compounds
in Aqueous Solutions," K. B. Yatsimirskiy, A. A.
Astasheva, Ivanovo Chem-Technol Inst

Detd the heat of mixing of solns of the salts
$AgNO_3$, $Hg(NO_3)_2$, $Cd(NO_3)_2$, $CdBr_2$, CdI_2, $Pd(NO_3)_2$,
$Bi(NO_3)_3$, and CuCNS with thiourea solns of dif-
ferent concns. Detd the changes of enthalpy

272T12

and entropy in connection with the formation of
complex ions from Ag^+, Cu^+, Cd^{2+}, and Pb^{2+} with
thiourea. Estimated the constant of instability K of
$[Hg(thiourea)_4]^{2+}$ to be 1.1×10^{-33} on the basis
of thermochemical data.

272T12

YATSIMIRSKIY, K. B.

USSR .

Use of dimethylphenylbenzylammonium as reagent for large anions. K. B. Yatsimirskii and Z. I. Blagoveshchenskaya. Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 5(8) 90–3(1954); cf. Emde, C.A. 3, 2470.—The Me$_2$(Ph)(PhCH$_2$)N (I) ion was added to solns. of different anions. I pptd. Cr$_2$O$_7^{--}$, S$_2$O$_4^{--}$, [Fe(CN)$_6$]$^{4-}$, [Fe(CN)$_6$]$^{4-}$, and iodide. Sensitivity of these reactions was detd. The crystals were photographed. A M soln. of ICl was mixed with 0.5 M solns. of salts of the anions. With S$_2$O$_4^{--}$ white dendrites pptd. from concd. solns. (above 0.5%). Dil. solns. gave crystals. A M ICl soln. did not form a ppt. in solns. contg. <0.1% S$_2$O$_4^{--}$ but when a ICl crystal was added to 1 drop of such dil. S$_2$O$_4^{--}$ soln., crystals of I$_2$S$_2$O$_4$ formed rapidly. Min. concn. was 1:2000, detectable min. 0.5 γ (vol. of drop is 0.001 ml.). Soly. of I$_2$S$_2$O$_4$ increased greatly by heating. The salt was recrystd. from hot H$_2$O, dried over H$_2$SO$_4$, and analyzed for S and N. With [Fe(CN)$_6$]$^{4-}$ yellow crystals, I$_4$Fe(CN)$_6$.3H$_2$O, formed. Min. concn. was 1:2000, detectable min. 0.5 γ. Compn. was confirmed by N and [Fe(CN)$_6$]$^{4-}$ detns. With Cr$_2$O$_7^{--}$ yellow crystals with an unusual form pptd. from very dil. soln. Min. concn. was 1:2000, detectable min. 0.36 γ. Analysis for Cr$_2$O$_7^{--}$ confirmed the formula I$_2$Cr$_2$O$_7$. With [Fe(CN)$_6$]$^{4-}$, ICl gave a ppt. only in the presence of acid. These fine greenish cubes are much less sol. in H$_2$O than the ferricyanide salt. Min. concn. was 1:17,000, detectable min. 0.059 γ. Detn. of N and [Fe(CN)$_6$]$^{4-}$ confirmed the formula IH$_3$Fe(CN)$_6$.3H$_2$O. From iodide solns. a crystal of ICl pptd. I iodide as confirmed by analysis. Min. concn. was 1:400, detectable min. 2.5 γ.   Eurilla Mayerle

USSR/Chemistry

Card 1/1   Pub. 145 – 5/10

Authors

Title   : Energy characteristics and analytical classification of ions

Periodical : Zhur. anal. khim. 9/5, 282–292, Sep–Oct 1954

Abstract   : The basic energy characteristics of ions, which determine mainly
their behavior in a solution and the electro–affinity of the ion
in an aqueous solution, are explained. Judging by the magnitude
of electro–affinity all cations can be divided into three groups;
ions with low electro–affinity forming water–soluble sulfides;
ions with mean electro–affinity values forming sulfides soluble
in acids but not in water, and ions with high electro–affinity
forming non–soluble sulfides. All three groups belong to mono–,
di– and tri–charge ions with an electro–affinity of 30, 70 and 190
kcal. Five USSR references (1950–1952). Tables.

Institution : ......

Submitted : November 26, 1953

YA tsiMiRskiy, K. B

USSR/Chemistry

Card 1/1   Pub. 151 - 10/36

Authors   : Yatsimirskiy, K. B., and Yasinskene, E. I.

Title   : The kinetics of aquation of Cr urea complexes

Periodical   : Zhur. ob. khim. 24/1, 55-61, Jan 1954

Abstract   : The constants of the rate of reaction leading to the aquation of hexaurea-
                chromion in an aqueous solution were measured at 30, 40, 50 and 60° tempera-
                tures. The activation energy was computed. The rate of reaction of hexaurea-
                chromion activation was also investigated by an optical method and the re-
                sults are listed. Seven references: 4-USA; 2-USSR and 1-German (1903-1952).
                Tables; graphs.

Institution : The Chemical-Technological Institute, Ivanovo

Submitted   : September 14, 1953

YATSIMIRSKIY, K. B.

USSR/Chemistry

Card   1/1   :   Pub. 151 - 5/42

Authors   :   Yatsimirskiy, K. B.

Title   :   Factors determining the stability of certain complex compound groups in aqueous solutions

Periodical   :   Zhur. ob. khim. 24/9, 1498-1507, Sep 1954

Abstract   :   The effect of increased central ion charge on the stability of complexes in aqueous solutions, especially in the case of addenda-anions with small radii or high charges, is explained. The stability of complexes with large addenda increases with the increase in radius of the central ion; the stability of complexes with small addenda and amino-acids decreases with increase in radius of the complex forming cation. The polarizing effect of isochoric ions was characterized by means of instability constants. Fifteen references: 4-USSR; 11-USA (1948-1953). Tables; graphs.

Institution   :   Chemical Technological Institute, Ivanov

Submitted   :   March 25, 1954

YATSIMIRSKIY, K.B.

USSR/ Chemistry - Physical chemistry

Card 1/1   Pub. 147 - 6/26

Authors   :   Yatsimirskiy , K. B., and Shutov, A. A.

Title   :   On the thermochemistry of certain iodide complexes

Periodical   :   Zhur. fiz. khim. 28/1, 30-35, Jan 1954

Abstract   :   The change in the heat content and entropy which occurs during the formation of complex ions $[HgJ]^+$, $[CdJ]^+$ and $[PbJ]^+$ was established from the experimental data regarding the heats of blending KI solutions with $Hg(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ solutions. The specific heats of these solutions were established. The heats of formation of the iodide complexes were estimated on the basis of the heats of decomposition of solid complex $[Ag_3J](NO_3)_2$ and $[HgJ]NO_3$ salts with water and Na_2S solutions. Six references 5-USSR and 1-French (1876-1953). Tables.

Institution   :   The Chemical Technological Institute, Ivanovo

Submitted   :   February 16, 1953

YATSIMIRSKIY, K.B.

GRINBERG, A.A. (Leningrad); BABAYEVA, A.V.(Moscow); YATSIMIRSKIY, K.B.
(Ivanovo); GOREMYKIN, V.I. (Moscow); BOLIY, G.B. (Moscow); FIAL-
KOV, Ya.A. (Kiyev); YAKSHIN, M.M. (Moscow); KEDROV, B.M. (Moscow);
GEL'MAN, A.D. (Moscow); FEDOROV, I.A. (Moscow); MAKSIMYUK, Ye.A.
(Leningrad); VOL'KENSHTEYN, M.V. (Leningrad); ZHDANOV, G.S. (Moscow);
PTITSYN, B.V. (Leningrad); ABLOV, A.V. (Kishinev); VOLSHTEYN, L.M.
(Dnepropetrovsk); TROITSKAYA, A.D. (Kazan'); KLOCHKO, M.A. (Moscow);
BABAYEVA, A.V.; TRONEV, V.G. (Moscow); RUBINSHTEYN, A.M.(Moscow)
CHERNYAYEV, I.I.; GRINBERG, A.A.; TANANAYEV, I.V.

Explanation of the transeffect. Izv.Sekt.plat.i blag.met. no.28:
                                                        (MLRA 7:9)
56-126 '54.
       (Compounds, Complex) (Platinum)

YATSIMIRSKIY, K. B.

USSR/ Chemistry - Physical Chemistry

Card   : 1/1   Pub. 147 - 17/25

Authors   : Yatsimirskiy, K. B., and Zolotarev, E. K.

Title   : On the thermodynamics of oxalate complexes

Periodical : Zhur. fiz. khim. 28/7, 1292 - 1298, July 1954

Abstract   : Experimental data on the thermodynamics of oxalate complexes. The heat
              of blending solutions of homologous salts, with potassium and ammonium
              oxalate solutions, was determined for the purpose of estimating the
              enthalpy changes of such complexes. The instability constants of
              complex ions: Mn, Co, Ni, Cu, Zn $(C_2O_4)_2^{2-}$ and Fe $(C_2O_4)_3^{3-}$, were
              determined. Nineteen references: 8 USA; 7 USSR; 1 Italian and 3 German
              (1903 - 1952). Tables; graph.

Institution : Chemical-Technological Institute, Ivanov

Submitted   : November 16, 1953

YATSIMIRSKIY K. B

A new method for the

YATSIMIRSKIY, K. B.

Quantitative characteristics which determine the suitability of complex compounds for volumetric analysis. CH. K. B. Yatsimirskiy (Inst. Chem. Technol., Ivanovo). Zhur. Anal. Khim. 10, 64-9(1955); J. Anal. Chem. U.S.S.R. 10, 85-9(1955)(Engl. translation).—In titration of complex-forming metals and in titration with such metals the max. degree of accuracy is detd. by the dissocn. const. of the complex formed and by the initial concns. of the reactants. The accuracy of a titration is considered to be detd. by the ratio of the concn. of the given substance at the equivalence point to its initial concn. (cf. C.A. 47, 1620b). The inverse logarithm of this ratio, designated by pT, is referred to as the index of titration accuracy. For a reaction of the type $M + A = MA$ a relation contg. pK (the inverse log of the dissocn. const. of MA) is derived, under the assumptions that the initial concns. of M and A are equal and that the changes in vol. upon titration are negligible. Where dissocn. occurs in more than 1 step, the equation is somewhat more complex. The min. pH at which a titration with a certain degree of required accuracy can be carried out can be calcd. Fixing or masking accompanying elements into complexes is essential in certain cases of titration. The completeness of masking is detd. by the ratio of the equil. consts. of the masked and masking reactions and by the concns. of the reactants. A set of equations is derived which express the completeness of masking. In certain procedures of volumetric analysis the sought ion is first converted into a complex ion and then pptd. The applicability of this method depends primarily on the sol. product of the complex salt formed. Conditions for suitability of colored end-point indicators are derived. M. Hoch
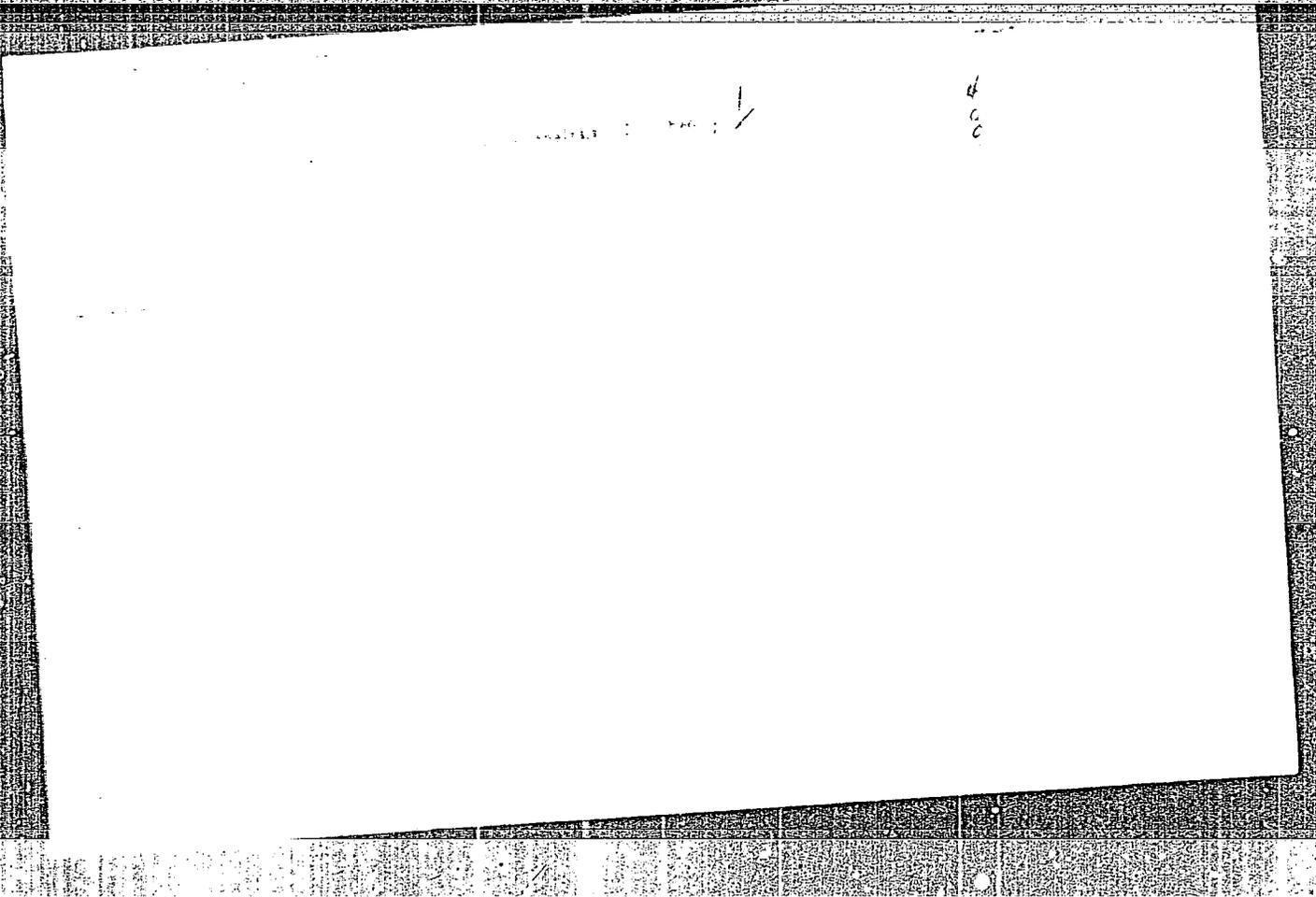
Use of complexones in analytical chemistry

YATSIMIRSKIY, K.B.

/Application of complexons in analytical chemistry. II.
Zav. Lab. 21, 1276-80(1955);

YATSIMIRSKIY, K.B.

VASIL'YEV,V.P.; YATSIMIRSKIY,K.B.

On E.A.Ukshe and A.I.Levin's article "Composition and properties of a complex electrolyte in a copper-pyrophosphate bath." Zhur. ob.khim.25 no.6:1233-1235 Je '55.
(MIRA 8:12)

1. Ivanovskiy khimiko-tekhnologicheskiy institut.
(Electrolytes) (Ukshe, E.A.) (Levin, A.I.)

YATSIMIRSKIY, K.V. (Ivanovo)

Thermodynamics of complex compounds of elements from the middle
of the fourth period of Mendeleev's system. Uch.zap.Kaz.un. 115
no.10:50-51 '55.   (MLRA 10:5)

                    (Compounds, Complex)

YATSIMIRSKIY, K. B.

Yatsimirskiy, K. B.

B-3

USSR/Physical Chemistry - Atom

Abs Jour: Ref Zhur-Khimiya, No 5, 1957, 14336

Author : Yatsimirskiy K. B.

Inst   :

Title   : Special characteristics of thirteen-electron ions

Orig Pub: Zh. neorgan. khimii, 1956, 1, No. 1, 96-99

Abstract: An examination is made of the relationship between the characteristics of bi-and trivalent ions of elements of the fourth period from Sc to Ga and the structure of the electron shells. It is shown that, in the series Ti^{2+}, V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Sc^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Cu^{3+}, $Ga^{3+} d^5$ (thirteen pelectron), the ions Mn^{2+}, Fe^{3+} disturb the monotonous nature of the variation of certain characteristics: ionization potentials, oxidation potentials, ionic radii, heats of hydration, strength of compounds formed by these ions, vapor pressures of halide dissociation, crystalline structure of sulfides and

Card 1/2   Chemical Technol. Inst., Ivanovo.

USSR/Physical Chemistry - Atom   B-3

Abs Jour: Ref Zhur-Khimiya, No 5, 1957, 14336

Abstract: selenides of the type MX, rates of formation and de-
           composition of complex compounds. Disturbances of the
           monotony take place also in the case of Zn^{2+} and Ga^{3+}.
           All the disturbances are explained by the order in
           which the d-nuclei are filled by the electrons.

Card 2/2   .

YATSIMIRSKIY K. B.

USSR/Inorganic Chemistry - Complex Compounds, C

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 678

Author: Yatsimirskiy, K. B.

Institution: None

Title: Concerning Certain Functions Characteristic of Stepwise Complex Formation in Solutions

Original
Periodical: Zh. neorgan. khimii, 1956, Vol 1, No 3, 412-421

Abstract: The basic functions which characterize stepwise complex formation in solutions are discussed: the "formation function" $\bar{n}$, the "degree of complex binding" ϕ (giving the ratio of the total concentration of the metal to the concentration of free metal ions), the "fraction of the given complex" α_m (giving the ratio of the concentration of a given complex (MA_m) to the sum of the concentration of all complexes and the free metal ions). The relationships between $\bar{n}$, ϕ, and α_m have been established, and the method for calculating any one of these functions from the others is indicated; $\bar{n}$, ϕ, and α_m can be calculated from the

Card 1/2

USSR/Inorganic Chemistry - Complex Compounds, C

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 678

Abstract: experimental data obtained during the study of stepwise complex forma-
tion by the solubility method, the distribution coefficient, ion ex-
change, by the potentiometric method, by the polarographic method,
etc. Formulas are given relating the functions under discussion to
experimentally measured values. From a series of values of $\bar{n}$, ϕ, and
α_m it is possible to calculate the equilibrium constant for each step.
Current methods for calculating the equilibrium constants are dis-
cussed and an improvement of a method previously proposed by the author
is presented (Referat Zhur - Khimiya, 1954, 41064, 46234).

Card 2/2

YATSIMIRSKIY, K.B

/ The kinetics and mechanism of the formation of urea]

USSR/Inorganic Chemistry.   Complex Compounds.

YATSIMIRSKIY, K.B.

Abs Jour : Referat. Zhurnal Khimiya, No 6, 1957, 18847

Author   : K.B. Yatsimirskiy, I.I. Alekseyeva.

Inst   :

Title   : Study of Oxalate and Phosphate Complexes of Moly-
             bdenum by the Kinetic Method

Orig Pub : Zh. Neorgan. Khimii, 1956, 1, No 5, 952-957

Abstract : The equilibrium in solutions of oxalate and phos-
             phate complexes of Mo was studied on the basis of the
             measurement of the speed of the reaction of iodide
             oxidation by hydrogen peroxyde in an acid medium.
             This reaction is catalyzed by molybdic acid (I)
             (RZHKhim, 1956 78453). A decrease of the concentra-
             tion of I in consequence of the formation of complex-
             es causes a corresponding decrease of the reaction
             speed. Oxalic and phosphoric acids were used in ex-
             cessive amounts as complex producing reagents. The
             concentration of the H^+ ions was 0.144 M. The kine-
             tic study showed that I reacted with oxalic acid ac-
             cording to the equation: $H_2MoO_4 + H_2C_2O_4 = [MoO_2C_2O_4]$

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Card 1/2

YATSIMIRSKIY, K.B.

YATSIMIRSKIY, K.B.

YATSIMIRSKIY, K.B.

Kinetic methods of quantitative analysis. III. Deter- 2

made with 1.2-0.1 X 10... mole or 0.11-0.57 γ. mre per 10

ЧATSIMIRSKIY, K.B.

G-1

USSR/ Analytical Chemistry - General Questions

Abs Jour   : Referat Zhur - Khimiya, No 4, 1957, 11981

Author   : Yatsimirskiy K.B., Astasheva A.A.
Title   : Use fo Solutions of Thiourea in Volumetric Analysis
               (Thiocarbamidometry)

Orig Pub   : Zh. analit. khimii, 1956, 11, No 4, 442-446

Abstract   : To 10-25 ml 0.025-0.2 M solution of thiourea (I) is added
               an indicator (15-20 drops of satureted solution of diphe-
               nylcarbazide (II) in alcohol or 10 drops of an analogous so-
               lution of   -nitroso- α-naphthol (III)), the mixture is
               diluted to 100-150 ml and titrated with a solution of
               $Hg(NO_3)_2$. On addition of II the solution acquires, at the
               transition point, a blue-violet coloration, while on addi-
               tion of III it changes color from yellowish-green to yello-
               wish-orange. Mean quadratic deviation is of 0.2-0.3% with
               II, and 0.1-0.2% with III. Back titration is also possible,
               although it is more appropriate, in the determiantion of Hg,

Card 1/2

G-1

to add a predetermined excess of I, and to titrate it the-
reafter with a solution of $Hg(NO_3)_2$. A pH value of 2 is op-
timal. Ag^+, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Mg^+, NH_4^+,

CH_3COO^-, SO_4^{2-}, NO_3^- and PO_4^{3-} do not interfere. I is used
also in the determination of Cd. To 20 ml of Cd-salt under
study (0.01-0.05 M) are added 20 ml 0.25 M solution of I,
30-40 ml of saturated solution of picric acid, and the volu-
me is brouhgt up to 100 ml. After 15-20 minutes it is fil-
tered through a dry filter and an aliquot portion (20 ml)
is titrated with 0.25-0.05 M solution of $Hg(NO_3)_2$, using II
as indicator. Mean quadratic deviation 0.23%. Lowest limit
of determination $5 \cdot 10^{-4}$M. Determination is interfered
with by Hg, Bi, Ag, Cu, Tl and large amounts of Pb. A 1000-
fold excess of Zn does not decrease the accuracy, but de-
lays substantially separation of precipitate.

YATSIMIRSKIY, K.B

USSR/Analytical Chemistry - General Questions, G-1

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61780

Author: Yatsimirskiy, K. B., Gruin, I. P., Kashirina, F. D.

Institution: None

Title: Determination of the pH of Alkaline Solutions by Means of Light Filters

Original
Periodical: Zavod laboratoriya, 1956, 22, No 3, 271-273

Abstract: For determination of pH of alkaline solutions by means of a set of indicators and a photometer with light filters (Referat Zhur - Khimiya, 1955, 21380) the following indicators are suitable: tropeolin 000, eosin, 2,4-nitrophenyl-azo-1-naphthol-4,8-disulfonic acid Na salt, alizarine red and tropeolin 0. The pH interval is 7.5-13.4. Error of the method ~0.1. At very high values of pH the presence in the solution of ions carrying a large charge interferes.

Card 1/1

VATSIEUREKIV K.B

YATSIMIRSKIY, K. B.

USSR/Physical Chemistry - Crystals, B-5

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 195

Author: Kapustinskiy, A. F., and Yatsimirskiy, K. B.

Institution: None

Title: Lattice Energy of Salts Formed by Ions with 8-Electron Outer Shells

Original Periodical: Zh. obshst. khimii, 1956, Vol 26, No 4, 941-948

Abstract: In the formula for the calculation of the energy of the crystal lattice $U = 287.2 \left[\sum n Z_K Z_A / (r_K + r_A)\right]\left[1 - \rho/(r_K + r_A)\right]$ (Kapustinskiy, Zh. obshst. khimii, 1943, Vol 13, 497) the value of the repulsion coefficient ρ depends on the sum of the ionic radii $\rho = 0.345 - 0.00870 (r_K + r_A)^2$. Using this empirical expression the following equation can be obtained: $U = 287.2 \times \left[\sum n Z_K Z_A / (r_K + r_A)\right]\left[1 - 0.345/(r_K + r_A) + 0.00870 \times (r_K + r_A)\right]$, which gives values of U which agree with experimental values within 2% for salts of the type MX and MX$_2$. The equation also gives satisfactory results for salts of the type MX$_3$. Considerable deviations are observed in the calculation of U for salts in

Card 1/2

USSR/Physical Chemistry - Crystals, B-5

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 195

Abstract: which the cations are highly polarized. The value of U has been cal-
culated for the oxides, sulfides, and selenides of the elements in
groups I and II of Mendeleyev's periodic system. The values of the
electron affinity of the atoms O, Se, and S have also been calculated.

Card 2/2

YATSIMIRSKIY, K. B.

C

Category: USSR

Abs Jour: RZh--Kh, No 3, 1957, 7802

Author : Yatsimirskiy, K. B.
Inst : Not given
Title : On the Question of Step-By-Step Complex Formation

Orig Pub: Zh. Obshch. Khimii, 1956, Vol 26, No 7, 2083-2084

Abstract: A review article. See RZhKhim, 1956, 19015.

Card : 1/1   -23-

YATSIMIRSKIY, K. B.

USSR/Chemical - Physical chemistry

Card 1/1   Pub. 147 - 4/35

Authors   : Yatsimirskiy, K. B., and Vasil'yev, V. P.

Title   : Determination of instability constants of complexes by colorimetric measure-
             ment of the pH of the solution

Periodical : Zhur. fiz. khim. 30/1, 28-33, Jan 1956

Abstract   : A new method was developed for colorimetric determination of pH in highly
             dilute sodium pyrophosphate solutions. The method was tested on several
             series solutions containing calcium nitrate and sodium pyrophosphate and was
             found to be perfectly suitable for such type of measurements. The instability
             constant of a calcium pyrophosphate complex was computed on the basis of re-
             sults obtained by this new method. Five references: 3 USSR and 2 USA (1928-
             1954). Tables; graph.

Institution : Chemicotechnological Institute, Ivanovo

Submitted   : March 14, 1955

YATSIMIRSKIY, K. B.

Category: USSR / Physical Chemistry   B-8
Thermodynamics. Thermochemistry. Equilibrium. Physico-
chemical analysis. Phase transitions.

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 29880.

Author : Yatsimirskiy K. B., Vasil'yev V. P.
Inst   : not given
Title   : Thermochemistry of Pyrophosphate Complexes in Solution

Orig Pub: Zh. fiz. khimii, 1956, 30, No 4, 901-911

Abstract: Determination of the heat of mixing values of solutions of nitrates
of Ni, Cu, Zn and Pb with solutions of sodium pyrophosphate of differ-
ent concentration, and also of the heat of dilution of the above-
stated salts. The determinations were carried out in the previously
described calorimeter (RZhKhim, 1955, 32011) which has been improved
by the authors. From changes in heat of mixing value, with change in
concentration of sodium pyrophosphate solution, the stepwise constant
of instability of $Ni(P_2O_7)$, was calculated. Enthalpy change (ΔH)
in the reaction $Ni^{2+} aq + P_2O_7^{4-} aq = NiP_2O_7^{2-} aq$ (1) is 4.21 ± 0.04 kcal.

                                    -10-

Card   : 1/2

Category: USSR / Physical Chemistry.   B-8
Thermodynamics. Thermochemistry. Equilibrium. Physico-
chemical analysis. Phase transitions.

Abs Jour: Referat Zhur-Khimiya., No 9, 1957, 29880

Author : Yatsimirskiy K. B., Vasil'yev V. P.
Inst   : not given

In reactions of the type $M^{\cdots}aq + 2P_2O_7^{\cdots} aq = M(P_2O_7)_2^{\cdots} aq$ (2)
the $\triangle$ H for Ni, Cu, Zn and Pb is, respectively, 2.00 ± 0.02;
-0.67 ± 0.07; 2.64 ± 0.05 and -1.01 ± 0.11. Values of standard
heat of formation have been calculated for the complex ions NiP_2O
and $M(P_2O_7)_2$ (M -- Ni, Cu, Zn and Pb). For reactions of type (2)
change of isobaric thermodynamic potential and entropy have been
calculated. Entropy change in these reactions satisfies the equa-
tion: $\triangle$ S = $0.1 L_M + $ const (3), where L_M is heat of hydration of
$M^{\cdots}$ ion. Equation (3) is utilized to calculate the instability
constant of Pb (P_2O_7) ion, together with the thermochemical
data.

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Card   : 2/2
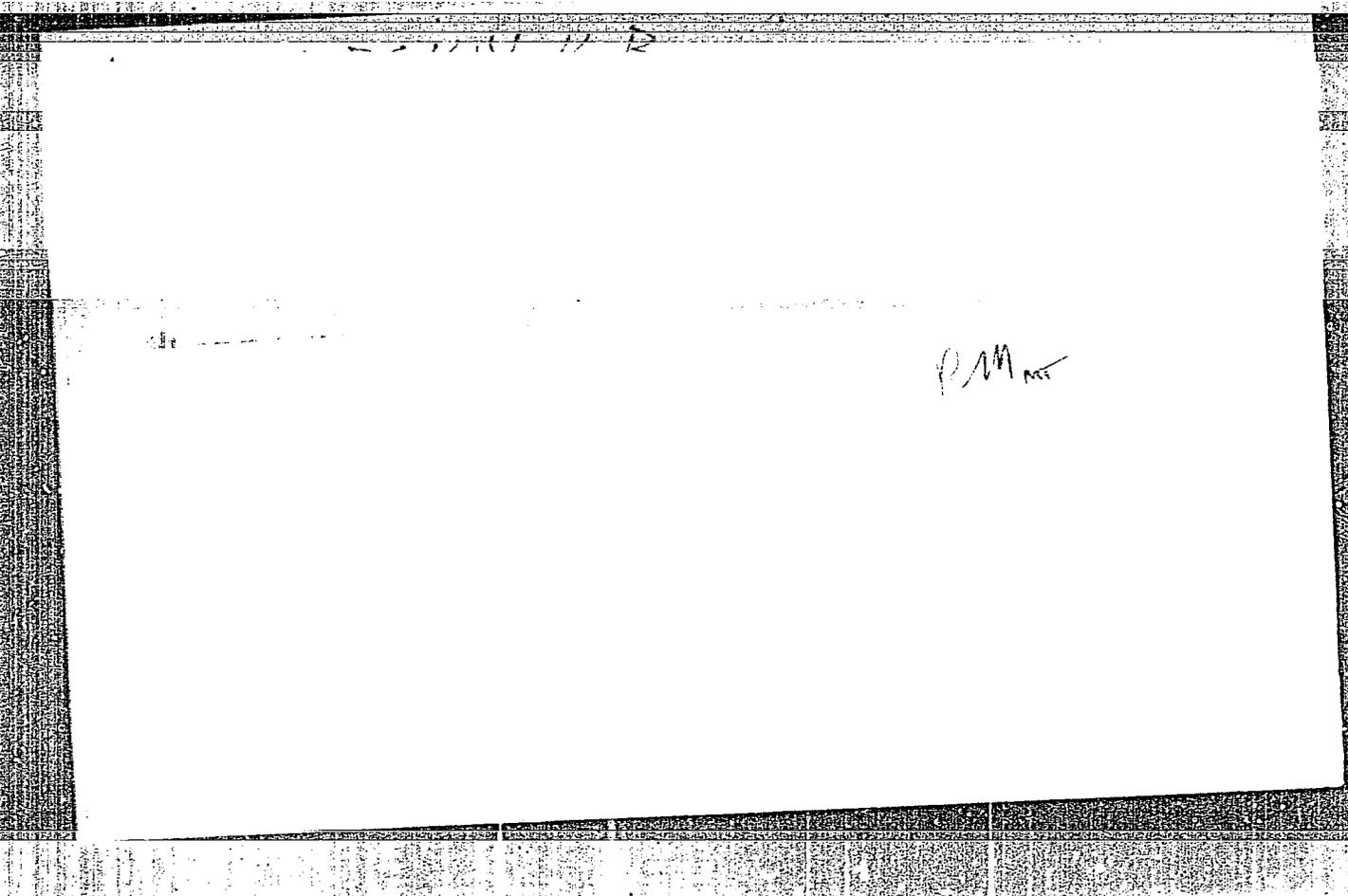
DRAKIN, S. I. and YATSIMIRSKIY, K. B.   (Ivanovo)

"The Entropy of Ion-Solvation,"

Report presented at Conference on the Effect of Solvents on the Properties of Electrolytes, Khar'kov, 14-16 Oct '57.

YATSIMIRSKIY, K. B.

"Determination of phosphate, sulfate, and molybdate."

report presented at The Use of Radioactive Isotopes in Analytical
Chemistry, Conference in Moscow, 2-4 Dec 1957
Vestnik Ak Nauk SSSR, 1958, No. 2, (author Rodin, S. S.)

YATSIMIRSKIY, K.B.

Observations on B.F. Ormont's article "Present state of the theory of complex compounds" (reports No.1 and 2). Zhur. neorg. khim. 2 no.8:1975-1977 Ag '57.

(MIRA 11:3)

(Complex compounds)
(Ormont, B.F.)

AUTHORS: Yatsimirskiy, K.B. and Tetyushkina, V.D.   566

TITLE: Influence of Ionic Force on the Instability Constants of
              Halogen and Pseudo-Halogen Complex Compounds. (O Vliyanii
              Ionnoy Sily na Konstanty Nestoykosti Galogenidnykh i Psevdogal-
              ogenidnykh Kompleksnykh Soedineniy).

PERIODICAL: "Zhurnal Neorganicheskoy Khimii" (Journal of Inorganic Chemistry,
              Vol.11, No.2, pp.320-329. (U.S.S.R.) -1957

ABSTRACT: The range of applicability of empirical equations such as that
              of Davies[9] and the concepts of ionic force is still undeci-
              ded. The research described is a contribution on this problem
              and involved the optical investigation of the thiocyanate com-
              plex of iron in the visible part of the spectrum. Relatively
              low concentrations of ferric nitrate (0.004974 mol/litre) and
              potassium thiocyanate (0.0004977 mol/litre) were used, enabling
              a wide range of ionic forces, from 0.25 to 3.5, to be covered.
              The bromide complex was also studied. Potassium, magnesium
              and aluminium nitrates were used to produce definite ionic
              forces.

              Determinations were thus made of the instability constants
              and of the influence on complex-formation equilibria in the
              systems Fe^{3+} – CNS– electrolyte and Fe^{3+} – Br– electrolyte.
              It was shown that the ionic-force concept is valid up to
              forces of the order of 1.5 if the accuracy limit for the
              instability-constant indices of the complexes is taken as ± 0.1;

Card 1/2