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# Science & Technology

## USSR: Chemistry

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### CONTENTS

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#### Aerosols

- UHF-Dielcometry—New Method for Studying Aerosols  
 [A. Ya. Simonov, A. G. Sutugin; *KOLLOIDNYY ZHURNAL*, Vol 50 No 1, Jan-Feb 88] ..... 1

#### Analytical Chemistry

- EPR Study of Spacial Distribution of Copper (II) in Complex-Forming Polymers  
 [A. I. Kokorin, A. A. Shubin; *KHIMICHESKAYA FIZIKA*, Vol 7 No 8, Aug 88] ..... 2
- Rapid Orientational Movements of Molecules in Organic Glasses  
 [S. A. Dzyuba, O. A. Shushakov, et al.; *KHIMICHESKAYA FIZIKA*, Vol 7 No 8, Aug 88] ..... 2
- Effect of Various Agromeasures on Gas Exchange Rate in Grey Forest Soil  
 [A. A. Larionova, L. N. Rozonova, et al.; *GENETIKA*, No 9, Sep 88] ..... 2
- Resolution of Raman Spectra into Constituent Components  
 [R. Ya. Yuga, Yu. L. Khaldna; *ZHURNAL ANALITICHESKOY KHIMII*, Vol 43 No 9, Sep 88] ..... 2
- Determination of Tropospheric Water Vapor on Venus  
 [Yu. A. Surkov, O. P. Shcheglov, et al.; *ZHURNAL ANALITICHESKOY KHIMII*, Vol 43 No 9, Sep 88] .. 3

#### Catalysis

- Study of Radicals Desorbing From Surface of Deep Oxidation Catalysts in Reactions of Alcohols  
 With Oxygen [V. K. Yermolayev, S. N. Pak, et al.; *KHIMICHESKAYA FIZIKA*, Vol 7 No 8, Aug 88] ..... 4
- Laser Magnetic Resonance Study of Heterogenous Loss of HO<sub>2</sub> Radical as a Function of Temperature  
 [Ye. V. Antsupov; *KHIMICHESKAYA FIZIKA*, Vol 7 No 8, Aug 88] ..... 4
- Low Temperature Reaction of Hydrogen With Individual and Palladium-Promoted Cobalt  
 Monoxide-Oxide  
 [V. M. Belousov, I. V. Bacherikova, et al.; *UKRAINSKIY KHIMICHESKIY ZHURNAL*,  
 Vol 54 No 8, Aug 88] ..... 4
- Conjugated Catalytic Oxidation of n-Pentane and Propylene  
 [S. P. Prokopchuk, V. U. Shevchuk, et al.; *UKRAINSKIY KHIMICHESKIY ZHURNAL*,  
 Vol 54 No 8, Aug 88] ..... 4
- Structure of Active Surface of Heterogeneous Catalysts Based on Chemically Deposited Metal Complexes  
 [V. V. Berentsveyg, Chan Bik Nga, et al.; *VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA*,  
 Vol 29 No 4, Jul-Aug 88] ..... 5
- Synthesis of Deposited Ni- and Co- Containing Catalysts in an Accelerated Electron Beam  
 [B. Ya. Adigamov, V. V. Lunin, et al.; *VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA*,  
 Vol 29 No 4, Jul-Aug 88] ..... 5
- Hydrogenation of Pyrocondensate Over Palladium Catalyst  
 [Ye. Ye. Kugucheva, L. I. Lakhman, et al.; *NEFTEKHIMIYA*, Vol 28 No 4, Jul-Aug 88] ..... 5
- Catalytic Poisons of Hexene-1 Metathesis Reaction on Aluminum-Rhenium Catalyst  
 [B. S. Strelchik, M. L. Gringolts, et al.; *NEFTEKHIMIYA*, Vol 28 No 4, Jul-Aug 88] ..... 5
- Selectivity of Camphor Hydrogenation and Hydroamination Over Molten Iron Catalyst  
 [L. S. Glebov, G. A. Klinger, et al.; *NEFTEKHIMIYA*, Vol 28 No 4, Jul-Aug 88] ..... 6
- Conversion of Synthesis Gas Over Bimetallic Ruthenium-Containing Catalysts  
 [G. D. Zakumbayeva, L. B. Shapovalova, et al.; *NEFTEKHIMIYA*, Vol 28 No 4, Jul-Aug 88] ..... 6
- Conversion of Carbon Monoxide and Hydrogen Into Aliphatic Alcohols Over Modified  
 Zinc-Chromium-Potassium Catalyst  
 [V. Ye. Leonov, L. P. Gerich, et al.; *NEFTEKHIMIYA*, Vol 28 No 4, Jul-Aug 88] ..... 6
- Catalytic Gassification of Thermal Soot With Steam in Presence of Calcium Compounds  
 [A. M. Brodskiy, G. L. Stolyar, et al.; *NEFTEKHIMIYA*, Vol 28 No 4, Jul-Aug 88] ..... 6
- Acoustoelectrostimulated Catalysis on Semiconductor Surface  
 [R. N. Giryunene, A. Y. Yutsis; *ZHURNAL FIZICHESKOY KHIMII*, Vol 62 No 8, Aug 88] ..... 7
- Remote 'Catalytic' Effect in Thermal Oxidation of Silicon  
 [Ya. A. Ugay, L. A. Malevskaya, et al.; *ZHURNAL FIZICHESKOY KHIMII*, Vol 62 No 8, Aug 88] ..... 7

- Effect of Solvent Nature on Catalytic Properties of Pd(II):Poly-2-Vinylpyridine Complex  
[D. V. Sokolskiy, A. K. Zharmagambetova, et al.; *ZHURNAL FIZICHESKOY KHIMII*,  
Vol 62 No 8, Aug 88] ..... 7

### Electrochemistry

- Mechanism of Action of Amine Type Corrosion Inhibitors With Elongated Hydrocarbon Chain  
[B. M. Larkin, G. F. Bebikh; *VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA*,  
Vol 29 No 4, Jul-Aug 88] ..... 8
- Exoemission During Pitting Corrosion of Stainless Steel  
[I. V. Krylova, Ye. V. Lumin; *ZHURNAL FIZICHESKOY KHIMII*, Vol 62 No 8, Aug 88] ..... 8

### Environmental Chemistry

- Identification of Petroleum Products Detected in Biologically Purified Effluents at Petroleum  
Processing Plants [A. I. Sumskeya, D. F. Varfolomeyev; *NEFTEKHIMIYA*, Vol 28 No 4, Jul-Aug 88] ..... 9
- Mechanism of Action of Organic Coagulant During Purification of Effluent From Textile Plants  
[A. A. Mamontova, V. V. Teleskin, et al.; *KHIMIYA I TEKHOLOGIYA VODY*,  
Vol 10 No 4, Jul-Aug 88] ..... 9
- Adsorption of Lanthanum and Neodymium Ions on Alkaline Earth Metal Carbonates  
[V. I. Maksin, N. Ya. Gudz, et al.; *KHIMIYA I TEKHOLOGIYA VODY*, Vol 10 No 4, Jul-Aug 88] ..... 9
- Extraction Methods for Regeneration of Adsorbents  
[V. V. Podlesnyuk, N. A. Klimenko; *KHIMIYA I TEKHOLOGIYA VODY*, Vol 10 No 4, Jul-Aug 88] ..... 9
- Adsorption of Hydroxylated SAS on Porous Acetatecellulose Membrane From Aqueous Solutions  
[N. A. Klimenko, N. A. Yaroshenko, et al.; *KHIMIYA I TEKHOLOGIYA VODY*,  
Vol 10 No 4, Jul-Aug 88] ..... 10
- Adsorption of Anionic Dyes on Carbon-Mineral Adsorbents  
[Yu. I. Tarasevich, V. Ye. Doroshenko, et al.; *KHIMIYA I TEKHOLOGIYA VODY*,  
Vol 10 No 4, Jul-Aug 88] ..... 10
- Oxidation of EDTA With Oxone in Aqueous Solution  
[M. A. Grachok, S. A. Prokudina, et al.; *KHIMIYA I TEKHOLOGIYA VODY*,  
Vol 10 No 4, Jul-Aug 88] ..... 10
- Effective Use of Calcium Gamma-Orthosilicate as Component of Composition Coagulants  
[L. A. Kulskiy, A. A. Pashchenko, et al.; *KHIMIYA I TEKHOLOGIYA VODY*,  
Vol 10 No 4, Jul-Aug 88] ..... 11
- Role of Electrokinetic Properties of Hydrolysis Products of Basic Aluminum Salts in Water Purification  
[N. G. Gerasimenko, I. M. Solomentseva, et al.; *KHIMIYA I TEKHOLOGIYA VODY*,  
Vol 10 No 4, Jul-Aug 88] ..... 11

### Fertilizers

- Corn for Grain in Crop Rotation and in Permanent Seeding Under Systematic Use of Fertilizers  
in Central Chernozem Zone [A. F. Stulin; *GENETIKA*, No 9, Sep 88] ..... 12
- Iodine Content in Altai Plants [M. A. Malgin; *GENETIKA*, No 9, Sep 88] ..... 12

### Inorganic Compounds

- Reaction and Properties of Intermediate Phases in System Iron-Titanium-Molybdenum at 900°  
[Ye. M. Sokolovskaya, Ye. F. Kazakova, et al.; *VESTNIK MOSKOVSKOGO UNIVERSITETA:*  
*KHIMIYA*, Vol 29 No 4, Jul-Aug 88] ..... 13
- Velocity of Sound and Compressibility of Germanate Glasses Containing Lead and Bismuth Oxides  
[A. I. Rabukhin, M. M. Smirnova; *IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY:*  
*KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA*, Vol 30 No 12, Dec 87] ..... 13
- Magnetic Properties of MgCl<sub>2</sub> Alloys With Alkali Metal Chlorides  
[S. G. Bakhvalov, A. A. Cheremisin, et al.; *ZHURNAL FIZICHESKOY KHIMII*, Vol 62 No 8, Aug 88] .. 13

### Laser Materials

- Effective Two-Frequency IR-Laser Synthesis of (CF<sub>3</sub>)<sub>3</sub>Cl Molecules  
[V. N. Bagratashvili, V. N. Burimov, et al.; *KHIMIYA VYSOKIKH ENERGIY*,  
Vol 22 No 4, Jul-Aug 88] ..... 14

|                                                                                                                                                                                                                              |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Role of Adsorption in Surface Photopolymerization of Styrene Exposed to Laser UV-Radiation<br>[A. V. Shaposhnik, G. A. Grigoryeva, et al.; <i>KHIMIYA VYSOKIKH ENERGIY</i> ,<br>Vol 22 No 4, Jul-Aug 88]                     | 14 |
| Effect of Critical Cross-Sectional Venturi Height on Gas Stream Characteristics of Reacting Mixture<br>N <sub>2</sub> O Plus CO Plus He<br>[S. V. Kulikov, O. V. Skrebkov; <i>KHIMICHESKAYA FIZIKA</i> , Vol 7 No 2, Feb 88] | 14 |

### Organophosphorous Compounds

|                                                                                                                                                                         |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Addition of Phosphoric Acid to 1,4-Dihydronicotinamides<br>[T. K. Nikolayenko, A. B. Uziyenko, et al.; <i>UKRAINSKIY KHIMICHESKIY ZHURNAL</i> ,<br>Vol 54 No 8, Aug 88] | 15 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

### Petroleum, Coal Processing

|                                                                                                                                                                                                                                                                                 |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Sulfides and Thiophenes From Diesel Fraction of Mordovo-Karmal Crude Oil Extracted by Different<br>Methods From Bituminous Rock<br>[N. V. Yegorova, A. N. Sadykov, et al.; <i>NEFTEKHIMIYA</i> , Vol 28 No 4, Jul-Aug 88]                                                       | 16 |
| Some Characteristics of Synthetic Oils Obtained by Oligoalkylation of Benzene (Toluene) With Ethylene<br>in Presence of Titanium Containing Systems Modified With Metal Dithiocarbamates<br>[A. G. Azizov, A. B. Aliyev, et al.; <i>NEFTEKHIMIYA</i> , Vol 28 No 4, Jul-Aug 88] | 16 |
| Formation of Liquid-Phase Precipitates in Reactive Fuels<br>[B. G. Bedrik, V. N. Golubushkin, et al.; <i>KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL</i> ,<br>No 8, Aug 88]                                                                                                            | 16 |
| Catalytic Effect of Copper on Oxidation of Petroleum Oil With Additives<br>[A. B. Vippper, G. M. Balak, et al.; <i>KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL</i> , No 8, Aug 88]                                                                                                     | 16 |

### Polymers, Rubber

|                                                                                                                                                                                                                                                                       |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Study of Reaction of para-Aminosalicylic Acid With Polyacrylic and Polymethacrylic Acids<br>in Aqueous Solutions<br>[V. A. Frolova, S. Ye. Kudaybergenov, et al.; <i>IZVESTIYA AKADEMIYA NAUK KAZAKHSKOY SSR</i> :<br><i>SERIYA KHIMICHESKAYA</i> , No 1, Jan-Feb 88] | 18 |
| Effects of Modification Method on Bonding Strength of Metal-Polymer Composite<br>[A. V. Viksne, I. I. Tiltinya, et al.; <i>IZVESTIYA AKADEMII NAUK LATVIYSKOY SSSR</i> :<br><i>SERIYA KHIMICHESKAYA</i> , No 5, Sep-Oct 87]                                           | 18 |

### Radiation Chemistry

|                                                                                                                                                                                                                                                             |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Hydrogen Formation in Thermo-Radiation Processes During Hypothetical Coolant Escape Accidents<br>at Nuclear Power Plant With Water Moderated Reactors<br>[S. A. Kabakchi, M. A. Budayev, et al.; <i>KHIMIYA VYSOKIKH ENERGIY</i> , Vol 22 No 4, Jul-Aug 88] | 19 |
| Catalysis of Radiation-Induced Chain Decomposition of Hydrogen Peroxide and Its Reaction With<br>Phosphonic Acid<br>[M. B. Muratbekov, S. P. Nazarbekova; <i>KHIMIYA VYSOKIKH ENERGIY</i> , Vol 22 No 4, Jul-Aug 88]                                        | 19 |
| Effect of OH Groups on Optical Properties of Irradiated Quartz Glass<br>[G. N. Pirogova, A. I. Ryabov, et al.; <i>KHIMIYA VYSOKIKH ENERGIY</i> , Vol 22 No 4, Jul-Aug 88]                                                                                   | 19 |
| Formation and Stabilization of Free Radicals During Radiolysis of Hexafluoropropylene<br>[S. R. Allayarov, I. M. Barkalov, et al.; <i>KHIMIYA VYSOKIKH ENERGIY</i> , Vol 22 No 4, Jul-Aug 88]                                                               | 19 |
| Degradation of Methanol in Aqueous Solution in Microdischarge at Rectifier Anode<br>[Ye. G. Volf, L. T. Bugayenko, et al.; <i>KHIMIYA VYSOKIKH ENERGIY</i> , Vol 22 No 4, Jul-Aug 88]                                                                       | 20 |
| Uranium (VI) Adsorption by Cryogranulated Hydroxides of Divalent Metals<br>[V. S. Pakholkov, V. I. Zelenin; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                                                                                                  | 20 |
| Synthesis and Ion Exchange Properties of Cryogranulated Hydroxides of Divalent Metals<br>[V. S. Pakholkov, V. I. Zelenin; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                                                                                    | 20 |
| Potential for Use of VPK and VP-IAP Ion Exchange Resins in Separation of Americium in<br>Environmental Samples<br>[G. N. Romanov, T. A. Grigoryeva; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                                                          | 20 |
| Use of Ion Exchange Resin in Isolation and Separation of U, Np and Pu From Other Elements Out<br>of Sulfuric and Phosphoric Acid Solutions<br>[L. I. Guseva, G. S. Tikhomirova, et al.; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                      | 21 |

|                                                                                                                                                                                                                                                                                            |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Effect of Characteristics of Extraction System Component Used in Separation of Radionuclides Upon Interphase Tension. Part 12, Sodium Salts of Carboxylic and Organophosphorus Acids in Tributylphosphate Containing System [S. D. Nikitin; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88] | 21 |
| Study of Bk <sup>(III)</sup> and Bk <sup>(IV)</sup> Complex Formation and Stability of Bk <sup>(IV)</sup> in Acetonitrile Solutions of Phosphoric Acid [S. A. Perevalov, I. A. Lebedev, et al.; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                                             | 21 |
| Reaction of Uranium (VI) Ions With Cryogranulated Titanium, Zirconium and Niobium Hydroxides During Adsorption [V. S. Pakholkov, V. I. Zelenin; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                                                                                             | 21 |
| Synthesis of Tritium-Tagged Prostaglandins F and Their Methyl Ethers [V. P. Shevchneko, T. Yu. Lazurkina, et al.; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                                                                                                                           | 22 |
| Determination of Atomic Ratio of Oxygen to Metal in Uranium-Plutonium Mixed Oxide Fuel [A. Ya. Kuperman, S. I. Korolev, et al.; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                                                                                                             | 22 |
| Nuclear-Chemical Synthesis of Tritiated Phenyl Onium Derivatives of Oxygen, Sulfur, Selenium and Tellurium [V. D. Nefedov, M. A. Toropova, et al.; <i>RADIOKHIMIYA</i> , Vol 30 No 4, Jul-Aug 88]                                                                                          | 22 |
| Isotope-Selective Dissociation of BCl <sub>3</sub> in Dual Frequency IR Laser Field [V. B. Laptev, Ye. A. Ryabov; <i>KHIMICHESKAYA FIZIKA</i> Vol 7 No 2, Feb 88]                                                                                                                          | 22 |

### Miscellaneous

|                                                                                                                                                                                                      |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Solid State Photolysis of Aromatic Azides [L. N. Karyakina, V. V. Kurenkova, et al.; <i>KHIMIYA VYSOKIKH ENERGIY</i> , Vol 22 No 4, Jul-Aug 88]                                                      | 23 |
| Crystal Structure and Electrophysical Properties of Dimethylethylenedithiotetrathiafulvalene Perchlorate [T. G. Takhirov, O. N. Krasochka, et al.; <i>KHIMICHESKAYA FIZIKA</i> , Vol 7 No 2, Feb 88] | 23 |

UDC 541.182.2/3.18.02

**UHF-Dielcometry—New Method for Studying Aerosols**

18410290b Moscow KOLLOIDNYY ZHURNAL in Russian Vol 50 No 1, Jan-Feb 88 (manuscript received 5 Feb 86) pp 164-166

[Article by A. Ya. Simonov and A. G. Sutugin, Physical Chemistry SRI imeni L.Ya. Karpov, Moscow]

[Abstract] Electromagnetic radiation in the optical range ( $10^{14}$  Hz) has been used widely to study the electrophysical properties of aerosols. A major shortcoming of these methods lies in the difficulty in establishing a well-defined relationship between the measured intensity of the weakening or scattering of radiation and the mass concentration of the aerosol. This makes it urgent to search for new methods of studying aerosol formations that do not require particle settling. Radiation between  $10^9$  and  $10^{10}$  Hz is used widely in meteorology

to study clouds having large-sized droplets, but references to the use of these radiations to study aerosols having a particle size of  $10^{-6}$  meter or less are nonexistent. This is apparently related to the extremely small cross sectional area of interaction of these particles with the electromagnetic field, as follows from Rayleigh's formula. However, the availability of very highly sensitive radiofrequency methods, and the theoretical prediction of the existence of resonance phenomena at which the scattering cross sectional area may be several orders greater than that prescribed by Rayleigh's formula, make it possible to employ ultrahigh frequencies to study aerosols and pose questions which these studies could provide answers to. In the present work UHF-dielectrometry was used for the laboratory scale measurement of the dielectric permeability of an aerosol mixture to sixth decimal place accuracy. Dielectric permeability measurements were made of eight model aerosols (diethylamine in HCl, ammonia in HCl, aluminum, titanium, and ferromagnetic powders) and compared with theoretical values. The dielectric permeability of irregularly shaped aerosols differed markedly from theoretically derived values for spherical particles. References 3 (Russian).

UDC 541.49:539.2

**EPR Study of Spatial Distribution of Copper (II) in Complex-Forming Polymers**

18410013a Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 7 No 8, Aug 88 (manuscript received  
3 Sep 87) pp 1018-1022

[Article by A. I. Kokorin and A. A. Shubin, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] Spatial distribution of Cu(II) ions coordinated by complex forming polymers was studied. Four distinct distribution types were noted: 1) random distribution throughout the entire polymer, 2) general increase of locally concentrated Cu, 3) mixed type where, along with constant local concentration of metal complexes, highly concentrated foci appear, and 4) formation of more than two types of structures. The first type occurs at small degrees of filling with macromolecules with relatively-dispersed coordinating groups. The second type was observed with linear macromolecules (polyethylenamine). The third type of distribution was observed in solid polymer matrixes of anion exchange resins in which the amino and imino groups are on the side chains of the main polymer. The fourth type was most complex; it occurred in systems coordinated with methyl carboxyl groups in which copper complexes appeared as isolated mononuclear types, cluster type aggregates with strong dipole-dipole interactions, and clusters with strong antiferromagnetic interactions. At small concentrations, in general, uniform distribution of these complexes occurred; at high concentrations the spatial distribution could vary. Figures 4; references 16: 15 Russian, 1 Western.

UDC 538.113

**Rapid Orientational Movements of Molecules in Organic Glasses**

18410013b Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 7 No 8, Aug 88 (manuscript received  
3 Sep 87) pp 1023-1028

[Article by S. A. Dzyuba, O. A. Shushakov, and Yu. D. Tsvetkov, Institute of Chemical Kinetics and Combustion, Siberian Department, USSR Academy of Sciences, Novosibirsk]

[Abstract] An attempt was made to compare published qualitative and quantitative results of various studies of rapid molecular movements in glasses and to analyze the frequency of molecular movement of admixtures expressed as a function of their concentrations. Data obtained by the following methods were compared: dielectric and NMR relaxation, electron spin echo with transmission of magnetization (ESETM) and EPR in the third and fourth bands. It was shown that the difference in movement times could be explained by distribution of these times. Data obtained by NMR and ESETM methods showed that the movement of admixture molecules is not a function of their concentration up to the level of

several percent. An assumption was expressed that rapid molecular mobility is a rather general property of the amorphous state. Figures 3; references 23: 8 Russian, 15 Western (2 by Russian authors).

UDC 631.5:631.445

**Effect of Various Agromeasures on Gas Exchange Rate in Grey Forest Soil**

18410050b Moscow *GENETIKA* in Russian  
No 9, Sep 88 (manuscript received 18 Dec 87) pp 75-87

[Article by A. A. Larionova, L. N. Rozonova, V. I. Strekozova and T. I. Samoylov, Institute of Soil Science and Photosynthesis, USSR Academy of Sciences, Pushchino, Moscow Oblast]

[Abstract] The effect of various agromeasures on the intensity of CO<sub>2</sub> generation and on absorption of O<sub>2</sub> by the grey forest soil was investigated. Agromeasures included soil tilling, use of mineral and organic fertilizers, crop rotation, etc. The different grain cultures planted affected generation of CO<sub>2</sub> in the soil and duration of soil "respiration". Application of mineral fertilizers (NPK) diminished soil respiration for long periods, slowing down decomposition of organic matter in the soil. This could be counterbalanced by addition of carbon substrates to the soil. Tilling appears to have had no effect on soil respiration. Addition of organic fertilizers in autumn, under the basic soil workup had also no effect on soil respiration during the following vegetative period because of rapid mineralization of carbon from organic fertilizers. Figures 4; references 25: 15 Russian, 10 Western.

UDC 543.424:519.65

**Resolution of Raman Spectra into Constituent Components**

18410058b Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 43 No 9, Sep 88 (manuscript received 15 Jul 87) pp 1564-1568

[Article by R. Ya. Yuga and Yu. L. Khaldna, Institute of Chemistry, Estonian SSR Academy of Sciences, Tallin]

[Abstract] A RAMAN program has been written in FORTRAN IV for computer-based resolution of Raman spectra into its constituent component bands, with the intensity of the individual spectra corresponding to the concentration of individual molecular components in the sample under analysis. In this approach the overall spectrum is regarded as superimposition of individual bands, with the shape of each spectrum described by the Voigt function in the Kielkopf approximation, assuming a Gaussian distribution. Each separate spectrum is a function of three variables (amplitude, wavelength maximum, shape coefficient), on the basis of which each is defined in the entire spectrum. This approach was successfully applied to the analysis of sulfuric acid solutions,

with the resolution of the Raman spectrum into 7 individual bands. Figures 1; references 13: 2 Russian, 11 Western.

UDC 535.24:523.42

**Determination of Tropospheric Water Vapor on Venus**

18410058c Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Vol 43 No 9, Sep 88 (manuscript received 22 Jun 87) pp 1601-1609

[Article by Yu. A. Surkov, O. P. Shcheglov, M. L. Ryvkin, D. M. Sheynin and N. A. Davydov, Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow]

[Abstract] Description is provided of the instrumentation and techniques used in determination of tropospheric

water vapor on Venus as part of Vega 1 and 2 space probes. Direct measurements were made by coulometric and thermoelectrolytic sensors in VM-4 apparatus, yielding water vapor data over an altitude span of 25 to 60 km at temperatures ranging from -10 to 270 degrees C and pressures spanning 0.02 to 1.6 MPa. In general, good agreement was obtained between the data provided by the two different sensors. At 60 to 52 km the water vapor ranged from 0.4 to 0.22 percent by vol., at 50-47 km values of 0.08-0.09 percent by vol. were obtained, and at 45-25 km the values corresponded to 0.04 to 0.01-0.012 percent by vol. However, significant fluctuation in the levels of water vapor were detected at the 45-50 km span. The relative errors in the determinations due to lag times and temperature pressure effects were estimated to be on the order of 40 percent at 45-60 km, and 20 percent at 25-45 km. Figures 6; references 4: 3 Russian, 1 Western.

UDC 541.128:54.024

**Study of Radicals Desorbing From Surface of Deep Oxidation Catalysts in Reactions of Alcohols With Oxygen**

18410013f Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 7 No 8, Aug 88 (manuscript received  
3 Sep 87) pp 1141-1146

[Article by V. K. Yermolayev, S. N. Pak, L. G. Krish-topa, Z. R. Ismagilov, and K. I. Zamarayev, Institute of Catalysis, Siberian Department, USSR Academy of Sci-ences, Novosibirsk]

[Abstract] Selected results were reported on the experi-mental program devoted to study of radicals desorbing from the surface of deep oxidation catalysts in reactions of hydrocarbons, amines and alcohols with oxygen, spe-cial attention being given to  $C_1$ - $C_6$  normal alcohols. These desorbing radicals are registered as  $RO_2$ ; to obtain information on starting  $R$ , photolysis of  $RO_2$  frozen out on a  $CO_2$  support was carried out. The rate of the formation of peroxide radicals was studied as a function of relative oxygen concentration in the reaction mixture; for catalysts  $\gamma-Al_2O_3$ ,  $Cr_2O_3$ ,  $CuCr_2O_4/\gamma-Al_2O_3$ ,  $Pt/\gamma-Al_2O_3$  a zero order was observed, converting to a negative order when the amount of oxygen in the reac-tion mixture began to exceed the amount of alcohol. The rate of the accumulation of radicals and effective ener-gies of activation in the temperature range 450-900 K are similar for all alcohols studied (80-125 kJ/mole). A possible formation diagram was presented for  $RO_2$  radicals involving adsorbed forms of the alcohol, the alkoxides and surface oxygen. Figures 7; references 16: 10 Russian, 6 Western (1 by Russian authors).

UDC 541.127+543.42

**Laser Magnetic Resonance Study of Heterogenous Loss of  $HO_2$  Radical as a Function of Temperature**

18410013e Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 7 No 8, Aug 88 (manuscript received  
21 Jul 87) pp 1082-1086

[Article by Ye. V. Antsupov, Kazakh State University imeni S. M. Kirov]

[Abstract] Heterogenous loss of radicals is an important phenomenon in catalytic studies, in space exploration, atmospheric photochemistry, combustion of hydrocar-bon fuels, etc. In the present work, surface pretreatment along with adsorption of reagents and reaction products on the surface was studied as they affected the loss of  $HO_2$  radicals forming in oxidation of allyl and ethyl alcohols. Several surfaces were investigated and coeffi-cients of heterogenous loss of  $HO_2$  radicals were deter-mined for quartz, quartz with adsorbed water, quartz with sodium chloride, boric acid and molybdenum in the temperature range 300 to 365 K. The quartz reactor was pretreated with hydrofluoric acid, resulting in lower loss

of  $HO_2$  radicals with temperature increase. Adsorption of water on the reactor surface also lowered loss of radicals. In general, the extent and temperature function of the coefficient of heterogenous radical loss are deter-mined by the preparatory treatment of the reactor sur-face, by adsorption of the reagents and reaction products on this surface and the relationship between effective activation energy and heat of adsorption. Figure 1; references 7: 5 Russian, 2 Western.

UDC 541.183.5+541.183.03

**Low Temperature Reaction of Hydrogen With Individual and Palladium-Promoted Cobalt Monoxide-Oxide**

18410016a Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 54 No 8, Aug 88  
(manuscript received 12 Mar 87) pp 833-837

[Article by V. M. Belousov, I. V. Bacherikova, E. V. Rozhkova, L. V. Lyashenko, and Ye. Stokh, Institute of Physical Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] Kinetic characteristics and hydrogen reac-tions with individual cobalt monoxide-oxide and with addition of 0.5 percent Pd were studied at low temper-atures (195-300 K) and pressures (0.01-0.7 kPa). An attempt was made to elucidate the promoting action of palladium. In parallel experiments, it was shown that an irreversible chemical binding of hydrogen occurs during its reaction with individual or Pd-promoted  $Co_3O_4$  at 77-293 K. It was shown that with individual  $Co_3O_4$ , the hydrogen reaction occurs on the  $Co^{3+}$  ions with partici-pation of poorly-bound nonstoichiometric oxygen, pos-sibly by a tunnel mechanism. On palladium-promoted  $Co_3O_4$ , molecular hydrogen reacts with  $Co_3O_4$  and with PdO forming the true catalyst  $(PdO)_{red}$  which then acts as the catalyst for the reduction of  $Co_3O_4$ . Hence, this process is catalytic in nature. The catalytic action of  $(PdO)_{red}$  consists of activation of hydrogen molecules through atomization. Figures 1; references 8: 6 Russian, 2 Western.

UDC 542.943-547.292

**Conjugated Catalytic Oxidation of n-Pentane and Propylene**

18410016b Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 54 No 8, Aug 88  
(manuscript received 31 Mar 87) pp 840-843

[Article by S. P. Prokopchuk, V. U. Shevchuk, and B. V. Ivakh, Lvov Polytechnic Institute]

[Abstract] Conjugated oxidation of n-pentane and propylene with atmospheric oxygen was studied in pres-ence of cobalt, manganese, and molybdenum at 150°C and 5MPa pressure. The principal products included propylene oxide, amyl alcohols,  $C_5$ -ketones and carboxy-lic acids (mostly formic and acetic acids). Effects of the

three catalysts on individual product yields was analyzed. Best results were obtained with manganese and molybdenum, the latter proving to be the most practical agent. It was shown that introduction of propylene into the zone of liquid phase oxidation of n-pentane led to faster formation of amyl alcohol and C-5 ketone from the hydroperoxide; in conjugated oxidation of n-pentane and propylene, propylene oxide is formed by epoxidation with the hydroperoxide. Possible mechanism for this conversion is presented. Figure 1; references: 4 (Russian).

UDC 541.128 + 541.49

**Structure of Active Surface of Heterogeneous Catalysts Based on Chemically Deposited Metal Complexes**

18410023a Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 29 No 4, Jul-Aug 88 (manuscript received 3 Apr 87) pp 390-395

[Article by V. V. Berentsveyg, Chan Bik Nga and B. V. Rozentuller, Department of Petroleum Chemistry and Organic Catalysis]

[Abstract] In spite of many papers devoted to catalytic properties of heterogeneous catalysts based on chemically-deposited metal complexes, little has been written about the structure of the active surface of such systems. This paper reports study of catalysts obtained by deposition of transition metal complexes (Co, Mn, V) with iminodiacetate on the surface of silicon (Silichrom C-120 and C-80) and aluminum oxide. The active surface of such catalysts was analyzed by Kobozev's theory of "active assemblies". Unfortunately, it was not possible to express the general and specific activity as a function of the degree of catalyst surface-filling with transition metal ions. The effect of the carriers was related to their structure which affected the distribution of complex-forming groups, their average number in the zone of fixation and the density of grafts. These parameters are responsible for the specificity of heterogeneous catalyst properties. Figures 4; references 13: 12 Russian, 1 Western.

UDC 541.127.542.98:546.654

**Synthesis of Deposited Ni- and Co- Containing Catalysts in an Accelerated Electron Beam**

18410023b Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 29 No 4, Jul-Aug 88 (manuscript received 27 Mar 87) pp 395-398

[Article by B. Ya. Adigamov, V. V. Lunin, I. I. Miroshnichenko, Yu. I. Solovetskiy, Yu. V. Taletskiy and N. G. Chulkov, Department of Petroleum Chemistry and Organic Catalysis, Belgorod Technologic Institute of Construction Materials imeni I. A. Grishman]

[Abstract] A novel synthetic method is proposed for metal-deposited catalysts which avoids the difficult, time consuming, multistage traditional methods. Aluminum silicate material was used as the catalyst basis (72

percent  $Al_2O_3$ , 27 percent  $SiO_2$ ). The carrier granules were saturated with a 10 percent ethanol solution of  $Ni(NO_3)_2 \cdot 6H_2O$ . The alcohol was evaporated at 55-60°C and the sample dried in vacuum at 40°C. Thus-prepared support was transferred to a crucible making a 10 mm layer and then it was exposed to a beam of accelerated electrons with 1.3 MeV energy. For a period of 10-60 s the sample temperature reached 400-600°C. This resulted in ionization and complete breakdown of nitrates throughout the entire sample. The material was then reduced in hydrogen at 350°C for 30 min. Its properties were evaluated on hydrogenation of hexene-1. The nickel catalyst was active even at 80-100°C; best results with the cobalt catalyst were obtained at 200-250°C. Figure 1; references 3: 2 Russian, 1 Western.

UDC 547.313:542.941.7:66.094.173

**Hydrogenation of Pyrocondensate Over Palladium Catalyst**

18410024c Moscow NEFTEKHIMIYA in Russian Vol 28 No 4, Jul-Aug 88 (manuscript received 20 Jan 88) pp 468-471

[Article by Ye. Ye. Kugucheva, L. I. Lakhman and A. D. Berents, All-Union Scientific Research Institute of Organic Synthesis, Moscow]

[Abstract] Changes in group and individual composition of the pyrocondensate were studied during its hydrogenation on industrial setup in presence of palladium catalyst (PK-25) in an effort to obtain a stable high octane gasoline component. The starting material and the hydrogenation product were analyzed by highly effective capillary gas chromatographic method coupled with chromat-mass spectroscopy. About 170 peaks were identified, 100 of which were individual compounds. It was shown that hydrogenation of pyrocondensate led to extensive reduction of vinylaromatic hydrocarbons; diene hydrocarbons were hydrogenated quantitatively; only nonconjugated double bonds reacted less completely (66 percent). References 4 (Russian).

UDC 547.313:542.97.1.3

**Catalytic Poisons of Hexene-1 Metathesis Reaction on Aluminum-Rhenium Catalyst**

18410024b Moscow NEFTEKHIMIYA in Russian Vol 28 No 4, Jul-Aug 88 (manuscript received 29 Jan 88) pp 457-459

[Article by B. S. Strelchik, M. L. Gringolts, O. V. Lysova, Ye. B. Portnykh, Ye. Sh. Finkelshteyn and S. P. Chernykh, Novokuybyshev Branch of All-Union Scientific Research Institute of Organic Synthesis; Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences]

[Abstract] Trimethylethylene, isoprene, piperilene, acetylene, allene, dimethylallene and methanol were examined as they affected the activity of aluminum-rhenium

catalyst on metathesis of hexene-1—in an attempt to determine their maximum permissible concentration in the starting materials, because most metathesis catalysts are very sensitive to oxygen containing compounds, to dienes and to acetylenes. All of these additives, with exception of trimethylethylene, inhibited, to the same extent, the metathesis of hexene-1. "Critical" concentration of each compound was different. Acetylenes and allenes exhibited the most inhibiting activity. Figure 1; references 8: 5 Russian, 3 Western.

UDC 547.599.6:[542.941+542.958.3]

**Selectivity of Camphor Hydrogenation and Hydroamination Over Molten Iron Catalyst**

18410024d Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 4, Jul-Aug 88 (manuscript received  
18 Mar 88) pp 472-477

[Article by L. S. Glebov, G. A. Kliger, V. D. Oppengeym, A. N. Shuykin, A. Ye. Yatsenko, V. G. Zaikin and S. M. Loktev, Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences, Moscow]

[Abstract] Stereoselectivity of hydrogenation of hydroamination of camphor over reduced molten iron catalyst was studied. This catalyst is highly effective in synthesis of alicyclic alcohols and amines from respective ketones. It was shown that in the temperature range 230-280°C camphor yielded 80 percent of bornylamines with a 1.4-1.8:1 ratio of endo:exo isomers. Hydrogenation of camphor at 190°C gave a 70-95 percent yield of borneol with about the same ratio of endo:exo isomers. The selectivity in this case was 84-92 percent. A reaction mechanism for this stereoselective conversion was proposed involving tautomeric conversion of camphor or its amine. The endo:exo mixture of borneols and bornylamines could be separated by highly effective gas-liquid chromatography. References 15: 6 Russian, 9 Western (1 by Russian authors).

UDC 66-092.514:546.96:54-44

**Conversion of Synthesis Gas Over Bimetallic Ruthenium-Containing Catalysts**

18410024e Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 4, Jul-Aug 88 (manuscript received  
17 Aug 87) pp 507-512

[Article by G. D. Zakumbayeva, L. B. Shapovalova, Zh. T. Omarov, E. N. Litvyakova and A. Sh. Kuanyshev, Institute of Organic Catalysis and Electrochemistry, KaSSR Academy of Sciences, Alma-Ata]

[Abstract] Catalysts containing 5 percent Ru-Cu/Al<sub>2</sub>O<sub>3</sub> with different ratios of Ru:Cu were studied in an attempt to explain the effect of the structure of active centers on the direction of catalytic conversion of synthesis gas. It was shown that introduction of copper into the ruthenium catalyst led to significant changes in the activity and direction of carbon monoxide hydrogenation: higher hydrocarbons were formed in presence of Cu but the extent of CO conversion dropped. Data of electron microscopic diffraction studies showed that the structure of

Ru-Cu/Al<sub>2</sub>O<sub>3</sub> is rather complex: the particle sizes ranged from 40 to 800 Angstrom, ruthenium exists as Ru<sup>0</sup> and copper as Cu<sup>0</sup> and CuO; cluster-associates of Ru-Cu formed in which Cu was segregated on the surface of Ru. In isolated cases a monolayer of Cu over Ru was achieved and because Cu/Al<sub>2</sub>O<sub>3</sub> catalysts do not adsorb hydrogen, the formation of cluster-associates led to a reduced number of active centers capable of adsorbing hydrogen and hence lower reactivity. Figure 1; references 15: 7 Russian, 8 Western.

UDC 546.262.3-31:547.26.057:542.97

**Conversion of Carbon Monoxide and Hydrogen Into Aliphatic Alcohols Over Modified Zinc-Chromium-Potassium Catalyst**

18410024f Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 4, Jul-Aug 88 (manuscript received  
23 Oct 87) pp 513-518

[Article by V. Ye. Leonov, L. P. Gerich and L. V. Pavliy, State Scientific Research Institute of Methanol Projects]

[Abstract] The goal of this work was to investigate the routes of carbon monoxide hydrogenation over zinc-chromium-potassium catalyst to yield aliphatic alcohols. The study covered two approaches: a kinetic one based on the change in relative selectivity as a function of the time of contact and an impulse approach based on introduction of aliphatic alcohols and water into the synthesis gas. It was shown that this introduction without catalyst led to higher yields of alcohols, hydrocarbons and water. When the C<sub>1</sub>-C<sub>3</sub> alcohols were introduced in presence of modified Zn-Cr-K catalyst, the yield of aliphatic C<sub>2</sub>-C<sub>4+</sub> alcohols was also increased. The selectivity towards higher alcohols increased with the number of carbon atoms in the molecule. The yield of isobutanol was affected by the following order: n-propanolisopropanolethanolmethanol. Synthesis of C<sub>2</sub>-C<sub>4+</sub> alcohols occurred in a gradual manner with precursor alcohols participating in the reaction; their formation was limited by delta-addition of the carbon atom. Steam exhibited a negative effect on the yield of C<sub>2+</sub> alcohols; their formation rate was a function of the reaction-conversion rate of CO. Figures 2; references 8 (Russian).

UDC 665.777.2:542.971.3

**Catalytic Gassification of Thermal Soot With Steam in Presence of Calcium Compounds**

Moscow NEFTEKHIMIYA in Russian Vol 28 No 4,  
Jul-Aug 88 (manuscript received 31 Jul 87) pp 535-540

[Article by A. M. Brodskiy, G. L. Stolyar, V. L. Mashinskiy, T. Ye. Rodionova, L. M. Grundel and M. A. Margulis, All-Union Scientific Research Institute of Organic Synthesis]

[Abstract] Principal kinetic patterns of the gassification of thermal soot with steam were studied by the thermogravimetric method in presence of various calcium compounds: acetate, carbonate, hydroxide, and oxide in the temperature range of 800-930°C. Under reaction conditions specified in a previous paper, a zero order reaction

was observed with respect to carbon both in the catalyzed and non-catalyzed gassification. Study of the catalyst by the derivatographic method showed that the final stable form of the catalyst, at temperatures exceeding 850°C, was calcium oxide. It was assumed that during soot gassification with catalytic addition of calcium oxide a structure is formed representing a polyradical surface resulting from thermolysis of calcium compounds and this surface expresses catalytic activity during the polymerization process. Figures 4; references 10: 7 Russian (1 by Western author), 3 Western.

UDC 542.97:534.23

**Acoustoelectrostimulated Catalysis  
on Semiconductor Surface**

18410025a Moscow *ZHURNAL FIZICHESKOY  
KHIMII* in Russian Vol 62 No 8, Aug 88 (manuscript  
received 18 Mar 87) pp 2047-2052

[Article by R. N. Giryunene and A. Y. Yutsis, Vilnius  
State University imeni V. Kapsukas]

[Abstract] The goal of this work was to study, in a layered system of lithium niobate- gas gap - cadmium sulfide, the possibility of increasing catalytic activity of the surface of semiconducting catalyst by acoustoelectric fields during heterogenic catalytic breakdown of hydrogen peroxide. Also, control characteristics of this reaction were studied using surface acoustic waves in an impulse regimen. Determination of transverse acoustic-electric tension developing in the semiconductor made it possible to monitor surface conductivity and photoconductivity of the semiconductor catalyst. It was shown that both the high frequency and constant acoustic-electric fields created by surface acoustic waves increased catalytic activity of the surface of a semiconducting catalyst. The results obtained were analyzed in light of the electronic theory of catalysis and acoustic-electronics. Figures 3; references: 10 (Russian).

UDC 542.97:621.315.592.4

**Remote 'Catalytic' Effect in Thermal Oxidation  
of Silicon**

Moscow *ZHURNAL FIZICHESKOY KHIMII*  
in Russian Vol 62 No 8, Aug 88 (manuscript received  
20 Apr 87) pp 2053-2055

[Article by Ya. A. Ugay, L. A. Malevskaya, I. Yu.  
Mittova, V. Z. Anokhin and V. V. Pukhova, Voronezh  
State University imeni Lenin Comsomol]

[Abstract] Mutual interaction of silicon plates during thermooxidation without application of an external electric

field was studied by a "sandwich" method with two silicon plates separated by  $2 \cdot 10^{-4}$  m. Oxidation was carried out at 900, 950, 1000, 1050 and 1100°C in a medium of steam. It was shown that the plate sides facing each other were oxidized 1.5-2 times faster than the normally oxidized silicon. This interaction of silicon plates was shown to be due to the positive charge in the oxide (resulting from  $V_{2O_5}$ ,  $H_3O^+$  and  $H^+$ ) leading to the appearance of a negative charge in silicon at the border of Si-SiO. This distance effect diminished when water content in the gas phase was lowered; in case of a specifically dried oxygen, the rate of the film growth in the "sandwich" was practically the same as in direct oxidation. Figures 2; references 2 (Russian).

UDC 541.128;678.744

**Effect of Solvent Nature on Catalytic Properties  
of Pd(II):Poly-2-Vinylpyridine Complex**

18410025c Moscow *ZHURNAL FIZICHESKOY  
KHIMII* in Russian Vol 62 No 8, Aug 88 (manuscript  
received 12 Aug 87) pp 2056-2059

[Article by D. V. Sokolskiy (deceased), A. K. Zharmagambetova, A. Ye. Bektorov, Ye. A. Bektorov and G. S. Kanapyanova, Institute of Organic Catalysis and Electrochemistry imeni D. V. Sokolskiy, KazSSR Academy of Sciences, Alma-Ata]

[Abstract] Hydrogenation of allyl alcohol over a complex of Pd(II) with poly-2-vinylpyridine (P2VP-Pd) was studied in various solvents: hexane, water methanol, ethanol, propanol, butanol and aqueous alcohol mixtures. The process was carried out at atmospheric pressure of hydrogen and 25°C. The activity of this polymer complex in hydrogenation reaction increased in the following order: hexane and, within the alcohol group: butanol. In dilute aqueous solutions the reaction rates were similar to those found with water; when alcohol concentration reached 50 percent and higher, the alcohol pattern became decisive. These results can be explained partially by the state of the polymer complex: in low alcohol concentrations the polymer is insoluble and the complex does not swell, therefore the results in such dilute alcohols resemble the results found in water. Thus the ability of the polymer complex to swell in a given solution is the determining factor in such reactions. Figures 3; references 11: 8 Russian (2 by Western authors), 3 Western (2 by Russian authors).

UDC 547.298.1

**Mechanism of Action of Amine Type Corrosion Inhibitors With Elongated Hydrocarbon Chain**

18410023d Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 29 No 4, Jul-Aug 88 (manuscript received 28 May 87) pp 414-418

[Article by B. M. Larkin and G. F. Bebikh, Department of Radiochemistry and Chemical Technology]

[Abstract] Amine type corrosion inhibitors are widely used to slow corrosion of ferrous and non-ferrous metals in acid, neutral and hydrocarbon media because of their ability to participate in donor-acceptor reactions with the surface of the protected metal. This mechanism implies that, to be effective, a protector should be a good electron donor. In such a process, an amine is adsorbed on an iron cation donating its unshared electron pair to iron and itself becoming positively charged. The field formed by all cations-anions retards the flow of iron cations towards the oxidizer-electrolyte border. This model has come inadequately considered aspects which the authors analyzed. One aspect is that the adsorbed amine cannot be viewed always as a positively-charged cation. The authors view the corrosion process as one consisting of two connected mechanisms; one anodic and one cathodic. Electron flow in metal oxide should be symbatic with the rate of the cathode process and thus the electroconductivity of oxides should determine the rate of corrosion. In this interpretation, electroconductivity changes in relation to donor-acceptor activity of the complexes formed by adsorbed amines. To retard the corrosion process, a negative change is required in the area of the surface charge which actually occurs with donor and acceptor type inhibitors. Based on some of these considerations, the charges of  $\text{Fe}^{3+}$  in a cluster

$\text{FeO}_6^{9-}$  and on N in  $\text{NH}_2(\text{CH}_2)_p\text{CH}_3$  were calculated for  $p = 1$  to 17. It was concluded that corrosion is retarded effectively with odd  $p$ . [ $p$  = parameter] References: 11 (Russian)

7813/12223

UDC 537.533

**Exoemission During Pitting Corrosion of Stainless Steel**

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 62 No 8, Aug 88 (manuscript received 26 Oct 87) pp 2252-2256

[Article by I. V. Krylova and Ye. V. Lumin, Chemistry Faculty, Moscow State University imeni M. V. Lomonosov]

[Abstract] Steel resistance to corrosive breakdown can be determined by the properties of surface oxide films, by the degree of deviation from stoichiometry and by pinpoint defects. Electrochemical corrosion is accompanied by transfer of electrons and ions which can be detected by physical-chemical processes occurring in the oxide films. Exoemission from several samples of stainless steel VNS-2 is studied after prolonged exposure to standard solution of sea water. Analysis of the data leads to the conclusion that the frequency of occurrence and the intensity of emission impulse current reflect the number and the extent of pinpoint damage (pitting) in the oxide film. Pitting formation results in separation of charges on the metal-oxide border, causes appearance of ions weakly bound to the surface, and leads to their diffusion and emission at the expense of the energy generated during the pitting. Figures 4; references 9: 5 Russian, 4 Western.

**Identification of Petroleum Products Detected in Biologically Purified Effluents at Petroleum Processing Plants**

*Moscow NEFTEKHIMIYA in Russian Vol 28 No 4, Jul-Aug 88 (manuscript received 16 Jun 87) pp 567-574*

[Article by A. I. Sumskaya and D. F. Varfolomeyev, Bashkir Scientific Research Institute of Petroleum Processing]

[Abstract] The goal of this study was to examine the composition of petroleum products found in effluents from petro-processing plants (PPP) after they were subjected to a biodegradation procedure. Carbon tetrachloride was used to extract these reagents from the waste water. The overall isolation and separation procedure included distillation and chromatography. Because of the effectiveness of the biodegradation process, the most resistant to oxidation hydrocarbons of the naphthalene series, boiling in the range of 250-400°C, were found in the effluent. These residual petrochemicals amounted to 0.5-5 mg/l level and appeared to differ substantially from the original petroleum components entering the water system. The principal contaminants consisted of intermediate oxidation products: neutral or acidic tarry substances. These residual products, consisting of tars and elemental sulfur, formed complexes and stable colloidal particles. It was shown that the structural composition of hydrocarbon radicals of these tarry substances isolated from biologically-purified effluents of PPP is very similar. The degree of their oxidation varies widely, which means that the intensity and the duration of the biodegradation process is also different. References 13 (Russian).

UDC 628.34 + 541.18

**Mechanism of Action of Organic Coagulant During Purification of Effluent From Textile Plants**

*18410048a Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 40 No 4, Jul-Aug 88 (manuscript received 12 May 87) pp 327-329*

[Article by A. A. Mamontova, V. V. Teleskin, V. N. Moraru and N. A. Klimenko, Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Increased demand for pure water by households and industrial utilization necessitates development of improved purification methods. One approach is based on the use of high molecular weight flocculants. Recently, a new such reagent was proposed, highly effective in application to multicomponent effluent from textile plants. An attempt was made to explain the mechanism of action of this reagent and to study its colloidal-chemical properties by laser spectroscopic and electrophoretic methodology. Highly dispersed state of its aqueous suspension and considerable positive charge

on its particles make it possible for this reagent to purify the effluent from the dissolved substances without any additional reagents. Figures 3; references 7 (Russian).

UDC 541.15+541.183+536.658.2

**Adsorption of Lanthanum and Neodymium Ions on Alkaline Earth Metal Carbonates**

*18410048b Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 10 No 4, Jul-Aug 88 (manuscript received 26 Jan 87) pp 318-321*

[Article by V. I. Maksin, N. Ya. Gudz and O. Z. Standrichuk, Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Adsorption of lanthanum and neodymium was studied on calcium, barium and magnesium carbonates from 1.2 and 4.4 M solution of sodium chloride at 298 and 310 K. Analysis of adsorption kinetics data showed that  $MgCO_3$  was the best adsorbent followed by  $BaCO_3$  and  $CaCO_3$ . Adsorption curves were S-shaped and increased with the rise in temperature. Possible adsorption mechanism for these systems was discussed. A relationship was discovered between the degree of adsorption, static volume capacity of the sorbents studied and energy characteristics of the crystalline lattice of the solvents and exchange ions. Figures 4; references 10: 9 Russian (1 by Western authors), 1 Western.

UDC 541.183.5 + 628.31

**Extraction Methods for Regeneration of Adsorbents**

*18410048c Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 10 No 4, Jul-Aug 88 (manuscript received 15 Dec 87) pp 303-311*

[Article by V. V. Podlesnyuk and N. A. Klimenko, Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] One of the principal conditions for an effective utilization of adsorbents in purification of industrial effluent is their repetitive use by regeneration of their activity. There are two most effective methods for recovery of original activity: destructive and regenerative, both with advantages and disadvantages. A review of literature is presented covering the last two decades of Soviet and foreign publications on extractive regeneration of adsorbents: activated charcoal and synthetic polymers. Extractive regeneration methods may be divided into three groups: ionization, oxidation and

extraction methods. The most prevalent is the ionization method in which the material captured by the solvent is ionized and desorbed by excess of regenerating agent. This is especially useful for substances with low pH. Unfortunately, selection of reagents and conditions is rather empirical. Oxidation regeneration is less popular. This method is based on oxidation of adsorbed substances in which they decompose to some extent so that this method somewhat resembles the thermal destructive method. The greatest attention is being paid presently to extractive method of regeneration. The review concentrates on various methods of extraction, effects of the regenerating agents on the extraction process and the effect of adsorbate and adsorbent. The authors conclude that current state of knowledge is not adequate to develop an effective technology of extractive desorption of organic substances from the adsorbents. References 68; 23 Russian, 45 Western.

UDC 541.183.5

**Adsorption of Hydroxylated SAS on Porous Acetatecellulose Membrane From Aqueous Solutions**

18410048d Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 10 No 4, Jul-Aug 88 (manuscript received 21 Oct 86) pp 311-314*

[Article by N. A. Klimenko, N. A. Yaroshenko, T. B. Kondratova and D. I. Kuryland, Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] The degree of water purification of reverse osmosis or ultrafiltration in presence of an adsorptive layer of surfactant molecules called "liquid membrane" depends on the structure and nature of this modifying layer. Adsorption and structure of such an adsorbed layer of SAS on a porous acetatecellulose membrane MFA-MA No 3 with average pore diameter of 300 nm was studied. The following hydroxyethylated surfactant substances (HSAS) were investigated: triton X-100, OP-10, OS-20 differing by their structure of the hydrophobic radical and the number of hydroxyethyl groups in the hydrophilic portion of the molecule. It was shown that, depending on the structure of hydrophilic and hydrophobic groups of the SA molecules on the membrane, associates could form from mycellar solution with ellipsoid or semiellipsoid form which could hydrophilize the surface of the sorbent. The thickness and orientation of these surfactant films varied. This makes it possible to select the desired structure and thickness of the adsorbed layer and alter the structure of "liquid membranes". Figures 1; references 12: 10 Russian, 2 Western.

UDC 541.183:2

**Adsorption of Anionic Dyes on Carbon-Mineral Adsorbents**

18410048e Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 10 No 4, Jul-Aug 88 (manuscript received 29 Apr 87) pp 315-317*

[Article by Yu. I. Tarasevich, V. Ye. Doroshenko, V. M. Rudenko and Z. G. Ivanova, Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Activated carbon is normally used to purify effluent from cellulosepaper and textile plants to remove anionic dyes. However, even the most porous material is not quite adequate for this task. In trials of replacement adsorbents, spent aluminum silicate sorbents and catalysts are often used after a thin layer of carbon is deposited on their granules. Such materials are known as carbonmineral sorbents (CMS). Adsorption of anionic dyes from water solution by CMS was evaluated, the CMS being prepared from natural dispersive materials (a mixture of polygorskite and montmorillonite (Cherkassy source), attapulgite (American source) and askan montmorillonite (GSSR source). These sorbents were calcined in a reactor at 500°C for 1 hr in absence of oxygen. The best results were obtained with the attapulgite and askan montmorillonite, whose porous structure adsorbed not only individual dye ions but also their associated and mycellae. Figures 2; references: 11 (Russian) (1 by Western authors).

UDC 547.292:546.214

**Oxidation of EDTA With Oxone in Aqueous Solution**

18410048f Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 10 No 4, Jul-Aug 88 (manuscript received 13 Mar 87) pp 322-324*

[Article by M. A. Grachok, S. A. Prokudina, M. I. Shulyatyev and T. S. Gerasimova, Belorussian Institute of National Economy imeni V. V. Kuybyshev, Minsk; NPO "Energiya", Moscow]

[Abstract] Oxidation of EDTA with ozone was studied in temperature range 15-85° and pH 5-11 as a function of concentration of the starting materials, the rate of ozone-air mixture addition (OAM), pH and temperature. The process was affected by the starting concentration of the reacting components and by increased level of ozone in OAM. The temperature had a significant effect only at 65°C: below it, the effect was marginal and minimal above 65°C. Increase in pH intensified the process. Optimal conditions for ozonization of EDTA were 65°C and pH of 11. The oxidation products included:  $\text{NH}_4^+$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , acetic and oxalic acids. Figures 4; references 9: 5 Russian, 4 Western.

UDC 628.16-541.18.048

**Effective Use of Calcium Gamma-Orthosilicate as Component of Composition Coagulants**

18410048g Kiev *KHIMIYA I TEKHNLOGIYA VODY* in Russian Vol 10 No 4, Jul-Aug 88 (manuscript received 12 Nov 86) pp 324-327

[Article by L. A. Kul'skiy, A. A. Pashchenko, M. V. Znamenskaya, Yu. I. Tarasevich, B. B. Shmidt and L. P. Shapirova, Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] One of the more important tasks in technology of purification of effluents is improved effectiveness coupled with decreased cost of the coagulants and flocculants. An attempt was made to evaluate the potential use of powdered wastes from metallurgic plants as additives to inorganic coagulants with the goal of improving their technical quality. Specific additive studied came from ferroalloy-plant wastes and consisted of material containing: CaO: 53.9 percent; MgO: 6.0-9.1 percent;  $Al_2O_3$ : 7-8.7 percent;  $Cr_2O_3$ : 2.5-4.5 percent;  $SiO_2$ : 24.96 percent; FeO: 0.5-0.8 percent and  $P_2O_5$ : 0.02 percent. It was shown that in presence of such additive and calcium gamma-orthosilicate, technological properties of the mineral coagulants improved and the content of organic

materials in purified water dropped significantly. Presence of ferrochromium slag improved coagulating action of the reagents forming coagulated structures with better adsorption properties. Figures 4; references 6 (Russian).

UDC 628.16

**Role of Electrokinetic Properties of Hydrolysis Products of Basic Aluminum Salts in Water Purification**

18410048h Kiev *KHIMIYA I TEKHNLOGIYA VODY* in Russian Vol 10 No 4, Jul-Aug 88 (manuscript received 8 Jul 87) pp 329-332

[Article by N. G. Gerasimenko, I. M. Solomentseva and A. K. Zapolskiy, Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Basic aluminum sulfates (BAS) exhibit greater coagulation properties than the traditional aluminum sulfate used in water purification processes. Effect of pH, ionic strength of the solution, concentration of the solution and the dose of coagulant of -potential of hydrolysis product particles of basic aluminum sulfates were investigated. It was shown that electrokinetic properties of the hydrolysis products of BAS differ from those of aluminum sulfate and are functions of various factors. This circumstance requires precise knowledge of factors involved in maintaining the coagulation purification process. At the same time it makes it possible to modify surface electric properties of the hydrolysis products of BAS and along with it the coagulation properties of BAS. Figure 1; references 14: 13 Russian, 1 Western.

UDC 631.811:633.15

**Corn for Grain in Crop Rotation and in Permanent Seeding Under Systematic Use of Fertilizers in Central Chernozem Zone**

18410050a Moscow GENETIKA in Russian  
No 9, Sep 88 (manuscript received 29 Jun 87) pp 41-49

[Article by A. F. Stulin, Voronezh Experimental Station  
Corn NPO "Dnepr"]

[Abstract] Effect of the types of mineral fertilizers, their dosage and ratio of individual components on the productivity of corn for grain was studied under conditions of crop rotation and permanent seeding. The fertilizers were applied annually. The work was done on the Voronezh experimental station; a ten-year crop rotation was studied in which the following grains were used: oats for hay, winter wheat, sugar beets, corn for silos, winter wheat, corn for grain, oats for hay, winter wheat, sunflower, barley. The work was carried out during the period 1983-1986. The yield of corn by either method of seeding was optimal with application of N120P60K60 fertilizer; with crop rotation it was 55.8, with permanent seeding—40.7 hundredweight per hectare (without the fertilizer it dropped to 40.2 and 23.4 respectively). The crop rotation method gave higher yield of corn for grain by 14.7-20.6 hundredweight per hectare. Systematic use of fertilizers improved the nutritional balance of the soil. Positive nitrogen and potassium balance can be achieved by adding 120 hundredweight per hectare in crop rotation and 60 in the permanent seeding system (phosphorus should be added at 60 and 30 hundredweight per hectare respectively). Crop rotation had a positive effect

on the content of lysine and tryptophan in grain protein and on the weight of 1000 kernels; it did not affect the content of starch or fat. References 18: 14 Russian, 4 Western.

UDC 631.811:546.15:631.893:633.2

**Iodine Content in Altai Plants**

18410050c Moscow GENETIKA in Russian  
No 9, Sep 88 (manuscript received 24 Jun 87) pp 88-94

[Article by M. A. Malgin, Institute of Soil Science and Agrochemistry, Siberian Department, USSR Academy of Sciences, Novosibirsk]

[Abstract] Considerable variation in iodine levels was noted in Altai vegetation ranging from trace amounts to 1.32 mg/kg. This seems to be related to variation of the iodine content in the soil and the phase of plant development. The lowest iodine content was noted in cereal grasses and the rosaceae plants. The highest—among the thistle family plants. Forest grasses grown on acid soil, regardless of their classification, showed higher iodine content than plants grown in arid steppes and in dry meadows. During early stages of development, plants have more iodine than in the later stages. A low iodine level was noted in stored fodder, especially in cereal grasses and fodder grain, the absolutely lowest contents were observed in greases from winter-early-spring crop. The iodine levels could be increased 4-7 fold by adding KI to mineral fertilizers (2-4 kg KI per hectare) or by spraying the growing vegetation (2 kg salt per hectare). References 30: 29 Russian (1 by Western authors), 1 Western.

UDC 669.017.11.28'293'295'181

**Reaction and Properties of Intermediate Phases in System Iron-Titanium-Molybdenum at 900°**

18410023c Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: *KHIMIYA in Russian* Vol 29 No 4, Jul-Aug 88 (manuscript received 9 Mar 87) pp 404-405

[Article by Ye. M. Sokolovskaya, Ye. F. Kazakova, V. I. Gryzunov, M. Duysebayev and B. K. Konysova, Department of General Chemistry]

[Abstract] Reactions and some properties of Fe-Ti-Mo alloys were studied along the section  $\text{Fe}_2\text{Ti}-\text{Fe}_2\text{Mo}$ , also determined were solubility limits of molybdenum in FeTi. The alloys were prepared from titanium iodide, powdered molybdenum and iron carbonate. It was shown that a continuous series of solid solution formed between  $\text{Fe}_2\text{Ti}$  and  $\text{Fe}_2\text{Mo}$ . All alloys along the  $\text{Fe}_2\text{Ti}-\text{Fe}_2\text{Mo}$  section were monophasic. Monophasic  $\text{Fe}_2\text{Ti}$  spread into a ternary system with about 13 percent Mo. Solid solution based on Loves phase and solid solution based on FeTi reacted with each other forming biphasic field  $\text{FeTi} + \lambda$ . In addition, four triphasic and eight diphasic regions were observed. Figures 2; references 5: 2 Russian, 3 Western.

UDC 666.112.9:546.289.534

**Velocity of Sound and Compressibility of Germanate Glasses Containing Lead and Bismuth Oxides**

18410278a Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: *KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian* Vol 30 No 12, Dec 87 (manuscript received 14 Aug 85) pp 22-25

[Article by A. I. Rabukhin and M. M. Smirnova, Chemical Technology Institute imeni D. I. Mendeleyev, Moscow]

[Abstract] The supersonic characteristics and compressibility of lead and bismuth germanate glasses, which are recommended for use as light and sound conductors in optical acoustic devices, have not been well studied. Only the sound velocity measurements (longitudinal wave) of four compositions of glass have been published, and the measurements were not correlated with composition. Photoelastic properties of glasses, however, depend greatly on their deformation, whereas the acousticoptical effect is a function of the velocity of sound in the material. In the present work, a study was made of the velocity of sound and the compressibility of 14 different compositions of lead and bismuth germanate glasses. Three series of glasses were synthesized (four compositions each) that have the general formula  $x\text{PbO} \cdot y\text{Bi}_2\text{O}_3 \cdot (1-x-y)\text{GeO}_2$  with a constant molecular

content of bismuth oxide (10, 20, and 27.5 percent), as were two compositions with equimolar concentrations of PbO and bismuth oxide equal to 15 and 25 percent. The maximum concentration of PbO in the above three series was selected in a manner to allow for glassification in the  $\text{PbO}-\text{Bi}_2\text{O}_3-\text{GeO}_2$  and comprised 50, 40, and 32 percent. The method of synthesis was described previously. Composition of the glasses was determined by an X-ray spectrographic method on a "Comebax" microanalyzer and was in satisfactory agreement with synthesis data. Up to 6 percent aluminum oxide was detected, evidently due to reaction of the glass mix with the corundum crucible during the preliminary fritting of the charge prior to sintering in a platinum crucible. The velocity of longitudinal supersonic sound waves was measured by using the optical heterodyne method at 30 MHz, glass density was determined hydrostatically in xylene, and adiabatic compression was calculated by a known formula from experimental data. Compressibility increases with PbO concentration independent of bismuth oxide concentration, whereas supersonic sound velocity diminishes with increasing PbO concentration. This was observed in all the glasses studied. Evidently, as the concentration of heavy metal oxides in the glass increases, the density and molecular weight also increase and cause the sound velocity to decrease. Figures 3; references 13: 10 Russian, 3 Western.

UDC 541.118-36:537.621.4

**Magnetic Properties of  $\text{MgCl}_2$  Alloys With Alkali Metal Chlorides**

18410025d Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 62 No 8, Aug 88 (manuscript received 4 Feb 87) pp 2158-2162

[Article by S. G. Bakhvalov, A. A. Cheremisin and P. M. Shurygin, Krasnoyarsk State University]

[Abstract] Thermodynamic and spectroscopic data show that with low concentrations of  $\text{MnCl}_2$  alloys with alkali metal chlorides, complex ions  $[\text{MnCl}_4]^{2-}$  are formed with correct tetrahedral structure. In previous work, magnetic properties of  $\text{MnCl}_2$  alloys with NaCl and KCl were studied; in this paper, results are reported for  $\text{MnCl}_2$  alloys with LiCl, RbCl and CsCl. Determinations of molar magnetic susceptibility were done by the relative Faraday method. Effective magnetic moments for  $\text{Mn}^{2+}$  are calculated and compared with models of complex formation in alloys. Areas of premelting and precrystallization are identified for congruently-melting substances. The polytherm characteristics are determined to a great extent by the magnetic system of the starting crystal. Structural aspects of the molten and solid phases are discussed; in some cases, the parent crystalline structure is retained, in others—in cases of precrystallization—structural rearrangements occur. Figures 4; references 13: 7 Russian, 6 Western.

UDC 621.373.826

**Effective Two-Frequency IR-Laser Synthesis of  $(CF_3)_3Cl$  Molecules**

18410014f Moscow *KHIMIYA VYSOKIKH ENERGIY* in Russian Vol 22 No 4, Jul-Aug 88 (manuscript received 13 Nov 86) pp 368-372

[Article by V. N. Bagratashvili, V. N. Burimov, L. Ye. Deyev, A. P. Sviridov, and I. M. Turovets, Scientific Research Center for Industrial Lasers, USSR Academy of Sciences]

[Abstract] A two-frequency, dual impulse photolysis of  $(CF_3)_3CBr$  in presence of  $I_2$  vapors was studied. The first impulse led to a multiphoton (MP) excitation of molecules at lower vibration levels, the second was used to perform MP-dissociation of excited molecules. Proper selection of optimal frequencies made it possible to tune out the absorption spectrum of intermediate radicals increasing the MP-dissociation yield of the starting molecules and the direction of  $(CF_3)_3Cl$  synthesis. It was shown that, in comparison to single frequency, the dual frequency laser-radical synthesis of  $(CF_3)_3Cl$  lowered the necessary radiation energy density and increased the process output; then the fragmentation of  $(CF_3)_3C$  radicals was diminished, increasing the overall yield of the final product. Whenever the spectra of starting molecules and of the intermediate radicals are similar, the dual frequency MP-excitation may be used as a universal method for highly effective laser radical synthesis. Figures 3; references 7: 3 Russian (1 by Western author), 4 Western (3 by Russian authors).

UDC 547.538.141:542.952.6

**Role of Adsorption in Surface Photopolymerization of Styrene Exposed to Laser UV-Radiation**

18410014g Moscow *KHIMIYA VYSOKIKH ENERGIY* in Russian Vol 22 No 4, Jul-Aug 88 (manuscript received 25 Sep 86) pp 373-376

[Article by A. V. Shaposhnik, G. A. Grigoryeva, V. A. Saksonskiy, and V. K. Potapov, Scientific Research Physical-Chemical Institute imeni L. Ya. Karpov]

[Abstract] The effect of experimental conditions on growth kinetics of polymer films was studied in previous work using the piezo-quartz microsuspension method. In the present work, the sensitivity of this method was increased making it possible to determine the principal physical-chemical parameters and to perform accurate adsorption determinations under the same conditions which, upon comparison with kinetic data, made it possible to establish the mechanism of surface growth of polymer films. Specifically, formation kinetics of styrene films on a metallic

surface was studied under exposure to a UV laser beam ( $\lambda = 266$  nm) and related to the monomer pressure and metal support temperature for both the surface and volume-based initiation process. The effect of the concentration of adsorbed molecules on the rate of surface photopolymerization was studied. Supplementary mass increase processes of the polymer film were noted after the radiation and desorption of substances from film surface were stopped. Figures 4; references 5: 2 Russian (1 by Western author), 3 Western.

UDC 533.6.011.8

**Effect of Critical Cross-Sectional Venturi Height on Gas Stream Characteristics of Reacting Mixture  $N_2O$  Plus CO Plus He**

18410288c Moscow *KHIMICHESKAYA FIZIKA* in Russian Vol 7 No 2, Feb 88 (manuscript received 20 Nov 86) pp 251-262

[Article by S. V. Kulikov and O. V. Skrebkov, Chemical Physics Institute, Chernogolovka Branch]

[Abstract] Reacting mixtures of nitrous oxide and carbon monoxide are used to create working media for a carbon dioxide gas dynamic laser. The possibility of obtaining supplemental energy pumping at the  $CO_2$  upper laser level by means of chemical reactions taking place in a nitrous oxide-carbon monoxide mix is being studied both experimentally and theoretically. It has been demonstrated that, as a result of "freezing" chemical reactions even in the transonic stream, practically the entire effect of super-equilibrium chemical pumping of fluctuating levels of nitrogen and carbon dioxide molecules is manifested in the presonic flow region where the characteristic fluctuating relaxation times and the effects of pumping on the characteristics of the active laser medium are low. By increasing the characteristic chemical reaction times it is possible to establish intense chemical reaction conditions in the transonic and even in the supersonic flow regions. It then becomes possible to expect a significant increase in inverse population density through chemical pumping energy. One way to increase chemical reaction time is to increase the Venturi height, which has a greater effect on reaction time than does the Venturi profile. In the present work a series of computations of the flow of a reacting mixture of nitrous oxide, carbon monoxide, and helium through a planar nozzle at various heights was made to check this hypothesis. The results indicate that increasing the reaction time cannot result in transition to the supersonic flow region of nonequilibrium chemical pumping and its effect is manifested in the presonic region at relatively small residence times of the gas in this region. The GDL-effect plays a determinant role in forming inverse population density. Figures 4; references 24: 19 Russian, 5 Western.

UDC 547.827

**Addition of Phosphoric Acid to  
1,4-Dihydronicotinamides**

18410016c Kiev UKRAINSKIY KHIMICHESKIY  
ZHURNAL in Russian Vol 54 No 8, Aug 88  
(manuscript received 22 Jan 87) pp 869-872

[Article by T. K. Nikolayenko, A. B. Uziyenko, V. A. Pokrovskiy, and A. A. Yasnikov, Institute of Organic Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] Studies of the addition of nucleophilic agents, especially phosphoric acid, to 1,4-dihydronicotinamides are important in connection with the problem of the so-called NADH-X conversion to NADH. Addition of phosphoric acid to N-propyl and N-benzyl-1,4-dihydronicotinamides was studied (PNAH and BuNAH respectively). The adducts were obtained by mixing phosphoric acid with PNAH or BuNAH in acetonitrile at 15°C, with intensive stirring. The product—a yellowish precipitate was analyzed by UV, IR, NMR and mass-spectroscopy. Both products have a tendency to dimerize. Possible mechanism for this is proposed. References 7: 1 Russian, 6 Western.

UDC 665.61.033.55

**Sulfides and Thiophenes From Diesel Fraction of Mordovo-Karmal Crude Oil Extracted by Different Methods From Bituminous Rock**

18410024a Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 4, Jul-Aug 88 (manuscript received  
16 Sep 87) pp 435-441

[Article by N. V. Yegorova, A. N. Sadykov, D. F. Fazliyev, I. N. Diyarov, N. K. Lyapina, A. D. Ulendeyeva and V. S. Shmakov, All-Union Scientific Research Institute of Crude Hydrocarbon, Kazan; Institute of Chemistry, Bashkir Branch, USSR Academy of Sciences, Ufa]

[Abstract] The goal of this study was to investigate the composition and properties of sulfur organic compounds (SOC) obtained by extraction with sulfuric acid of the diesel fraction (180-350°C) of the Mordovo-Karmal crude recovered from bituminous rock by natural flow and using intra-layer combustion. The diesel fraction obtained by intra-layer combustion showed lower density and viscosity than the natural flow material and the yield was 8 percent higher. About 70 percent of the originally contained sulfur could be extracted from the diesel fraction using sulfuric acid. Material obtained by either method consisted mostly of thiamono-, thiadi-, thiacycloalkanes and thiaindanes. The degree of cyclizability of sulfides and thiophene isolated from the distillate obtained by the intra-layer combustion was lower than that from the distillate obtained by natural flow. The structural and group composition of sulfides and thiophenes of the SOC concentrates of the Mordovo-Karmal, the Arlan and the West-Surgut crudes were similar. The distillate from the Mordovo-Karmal crude was shown to be a promising source for industrial production of sulfides. References 12 (Russian).

UDC [547.532+547.533]:542.952.537:621.892.28

**Some Characteristics of Synthetic Oils Obtained by Oligoalkylation of Benzene (Toluene) With Ethylene in Presence of Titanium Containing Systems Modified With Metal Dithiocarbamates**

18410024h Moscow NEFTEKHIMIYA in Russian  
Vol 28 No 4, Jul-Aug 88 (manuscript received 4 Dec 87)  
pp 557-562

[Article by A. G. Azizov, A. B. Aliyev and G. A. Mamedaliyev, Institute of Petrochemical Processes imeni Yu. G. Mamedaliyev, ArSSR Academy of Sciences]

[Abstract] In an earlier work it was shown that oligoalkylates are formed by oligoalkylation of aromatic hydrocarbons with ethylene in presence of  $TiCl_4 + C_2H_5AlCl_2$  modified by organic dithioderivatives of  $Ti/Zn/Al$ ,  $Ti/Pb/Al$  and  $Ti/Mg/Al$ . Effect of reaction conditions (nature of aromatic hydrocarbon, temperature, pressure, ratio of the components of the catalytic system) on

fractional composition and some properties of the oily fraction boiling above 350°C (viscosity index, solidification temperature, index of refraction) are investigated. The yield of the oily fraction does not depend on the pressure but temperature has a definite effect. A rise in temperature also elevates the viscosity index of the oily fraction and increases the yield of waxy products. The highest index of viscosity (151) was observed in the oil obtained over  $Ti/Pb/Al$  catalyst while the best combination of the index of viscosity (110-112) with the temperature of solidifications (-35 to -38°C) was achieved over  $Ti/Zn/Al$ . Figures 2; references 7 (Russian).

UDC 662.753.1:541.123.81

**Formation of Liquid-Phase Precipitates in Reactive Fuels**

18410030a Moscow KHIMIYA I TEKHOLOGIYA  
TOPLIV I MASEL in Russian No 8, Aug 88 pp 28-29

[Article by B. G. Bedrik, V. N. Golubushkin, N. M. Likhterova, A. F. Yakovleva, S. I. Uspenskiy and T. Ya. Vakulenko]

[Abstract] Hydrocarbon fuels contain certain levels of water, the concentration of which is proportional to air humidity and temperature. In practical terms, water in excess of an equilibrium level, does not necessarily evaporate into the gas phase; some of it forms a liquid layer: emulsion and residue, in which liquid phase and gel-like sediments are formed (LPS and GLS). The principal reason for the formation of LPS is the strong interaction among polar water molecules. This phenomenon has a very undesirable effect during utilization of such fuel in aviation technology. Mechanism of formation of LPS and GLS in fuels was therefore investigated. It was shown that formation of LPS and GLS in fuel may be averted by increasing its purity, by stabilization of the system: fuel-antiwater crystallization (AWC) liquids-water and by controlling the content of AWC in the fuel down to 0.1 percent. Figures 4; references 6 (Russian).

UDC 621.892.86:542.943.7:546.56-121

**Catalytic Effect of Copper on Oxidation of Petroleum Oil With Additives**

18410030b Moscow KHIMIYA I TEKHOLOGIYA  
TOPLIV I MASEL in Russian No 8, Aug 88 pp 30-31

[Article by A. B. Vipser, G. M. Balak, N. A. Ponomarenko and L. L. Kalinin]

[Abstract] The goal of this work was to compare effectiveness of copper oxidation inhibition additives and its passivator. The study covers determination of the accumulation of oil-soluble copper compounds during its oxidation, analysis of oil oxidation at moderate and high temperatures in presence and absence of copper and determination of a correlation between copper content in the oil and its oxidizability in presence of various additives. A direct correlation was observed between the

copper content and the quantity of carbonyl oxidation compounds accumulating in oil. A clear differentiation of the effect of the additives studied on catalytic action of copper was obtained: passivation effect of benzotriazole was related to its effect on the rate of copper

accumulation along with its oil soluble compounds in the oil. DF-II additive, which accelerated this process somewhat, interfered somewhat with the effect of copper on the accumulation of oxidation products in oil. Figures 3; references 7 (Russian).

UDC541.64:536.42

**Study of Reaction of para-Aminosalicylic Acid With Polyacrylic and Polymethacrylic Acids in Aqueous Solutions**

18410278d Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 1, Jan-Feb 88 (manuscript received 31 Oct 85) pp 43-47

[Article by V. A. Frolova, S. Ye. Kudaybergenov, and Ye. A. Bekhturov, Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata]

[Abstract] It has been shown previously that using electrolytes as polymer-carriers prolongs the therapeutic action of medications. As a rule, prolongation of the therapeutic action of a medication is closely related with its reactions with polymers. In the present work viscosimetry, conductivity, and IR-spectroscopy were used to demonstrate that para-aminosalicylic acid, a known anti-tubercular medication, does react with weak polymeric acids, i.e., polyacrylic and polymethacrylic acids. When para-aminosalicylic acid reacts with either of these compounds, macromolecular chains are formed as a result of the formation of hydrogen bonds between the functional groups of both components and hydrophobic reactions. Figures 3; references 13: 10 Russian, 3 Western.

UDC678.5:669.71:539.61

**Effects of Modification Method on Bonding Strength of Metal-Polymer Composite**

18410161b Riga IZVESTIYA AKADEMII NAUK LATVIYSKOY SSSR: SERIYA KHIMICHESKAYA in Russian No 5, Sep-Oct 87 (manuscript received 19 May 87) pp 575-580

[Article by A. V. Viksne, I. I. Tiltinya, I. N. Pavlova, Riga Polytechnical Institute imeni A. Ya. Pelshe]

[Abstract] Various methods of modifying aluminum substrates and high-molecular weight reinforcing fibers of laminated metal polymer composites were studied, and their effects on the adhesion stability of composites made using VK-41 adhesive were measured. Edge cohesion stability between the adhesive and the organic fibers was found to be lower than that between the adhesive and the aluminum substrate. These differences were more pronounced after treatment with boiling water. The amount of water absorbed depended on the surface state of the fibers and was significantly greater for those that had been subjected to preliminary thermal treatment at 523 K and that had no lubricant on their surfaces. Treatment with  $\gamma$ -aminopropyltriethoxysilane decreased adhesive swelling at the aluminum contact but increased adhesive swelling at the point of contact with the reinforcing fibers. This indicates that use of this silane does not increase initial adhesion stability. However, adhesion resistance to water was increased. UV irradiation had no effect on initial adhesion although it increased adhesion resistance to water. Figures 4; references 3: 2 Russian, 1 Western.

UDC 539.17

**Hydrogen Formation in Thermo-Radiation Processes During Hypothetical Coolant Escape Accidents at Nuclear Power Plant With Water Moderated Reactors**

18410014a Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 22 No 4, Jul-Aug 88 (manuscript received 4 Aug 87) pp 295-300

[Article by S. A. Kabakchi, M. A. Budayev, and O. M. Kovalevich]

[Abstract] Processes involved in the formation of hydrogen at various stages of an accident involving escape of the coolant in water-moderated reactors are analyzed. Hydrogen formation depends on temperature, amount of water and steam in the active zone etc. The scenario considered in this modelling attempt involved three stages: loss of hermetic seals of the first periphery with accompanied loss of pressure, escape of dissolved radiolytic hydrogen into the gas phase. During the next phase, water evaporates from the first periphery and produces more hydrogen due to its radiolysis. At the third stage, water evaporates from the active zone and hydrogen forms due to radiolysis of steam, boiling water, reactions on the exposed reactor, reactions of steel construction components with  $\text{UO}_2$ , with steam and thermal dissociation of water. The contribution from each source changes with the progress of the accident. Initially, water radiolysis plays the most important role, reaching a maximum and then dropping off (the zirconium- and steel-steam reactions show an analogous course). A mathematical model was proposed to handle the dynamics of the formation of hydrogen which is a linear combination of the calculations for the three stages noted above. Overall, the rate of hydrogen formation depends on the quantity of water in the active zone, the dose of radiation and the temperature. References 9: 6 Russian, 3 Western.

UDC 541.15+546.183

**Catalysis of Radiation-Induced Chain Decomposition of Hydrogen Peroxide and Its Reaction With Phosphonic Acid**

18410014b Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 22 No 4, Jul-Aug 88 (manuscript received 27 Nov 86) pp 317-321

[Article by M. B. Muratbekov and S. P. Nazarbekova, Kazakh State University imeni S. M. Kirov]

[Abstract] Possible catalysis of radiation-stimulated chain reactions was analyzed modelled by the breakdown of hydrogen peroxide and its reaction with phosphonic acid. The rate-determining step in this process is the reaction of hydroperoxide radical with hydrogen peroxide. Catalysis of this process depended on the formation of an intermediate structure  $[\text{TiO}_2(\text{SO}_4)_2]^{3-}$  from one of two reactions  $\text{HO}_2 + [\text{TiO}_2(\text{SO}_4)_2]^{2-}$  yielding

$\text{H}^+ + \text{O}_2 + [\text{TiO}_2(\text{SO}_4)_2]^{3-}$  in absence of phosphonic acid, or  $\text{H}_3\text{PO}_3 + [\text{TiO}_2(\text{SO}_4)_2]^{2-}$  yielding  $\text{H}_3\text{PO}_4 + \text{H}^+ + [\text{TiO}_2(\text{SO}_4)_2]^{3-}$  in presence of phosphonic acid. Kinetics equations for these processes were determined. Figures 2; references 16: 12 Russian (1 by Western author), 4 Western (1 by Russian authors).

UDC 541.15:666.192

**Effect of OH Groups on Optical Properties of Irradiated Quartz Glass**

18410014c Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 22 No 4, Jul-Aug 88 (manuscript received 5 Nov 86) pp 322-325

[Article by G. N. Pirogova, A. I. Ryabov, and V. Ye. Kritskaya, Institute of Physical Chemistry, USSR Academy of Sciences]

[Abstract] The goal of this work was to study the optical properties of quartz glass, containing various levels of OH groups, during electron impulse irradiation and stationary  $\gamma$ -radiation at 77 and 298 K. Stationary  $\gamma$ -radiation at room temperature increased optical density (OD) in UV and the visible spectral range; low doses gave two maxima at 215 and 305 nm and high doses produced a third maximum at 550 nm. The highest increase in OD occurred in glass with the lowest content of OH groups. An analogous situation was observed when the temperature was lowered to 77 K, except that the concentration of the OH group had no effect on the absorption maxima. Impulse irradiation with electrons showed no relationship to the content of OH groups in the glass and the spectra at 77 and 298 K had different patterns. Coloration of quartz glass is the result of various admixtures, principally aluminum which replaces silicon in the matrix; aluminum may exist in a tri- or tetra-coordinated configuration. Its contribution to this process under the above experimental conditions is discussed. Figures 3; references 9: 2 Russian, 7 Western.

UDC 543.422.27:541.515-171:547.412.732

**Formation and Stabilization of Free Radicals During Radiolysis of Hexafluoropropylene**

18410014d Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 22 No 4, Jul-Aug 88 (manuscript received 3 Mar 86) pp 333-337

[Article by S. R. Allayarov, I. M. Barkalov, S. I. Kuzina, N. N. Loginova, and A. I. Mikhaylov, Institute of Chemical Physics, USSR Academy of Sciences]

[Abstract] The goal of this work was to investigate the formation and photoreactivity of radicals obtained in radiolysis of hexafluoropropylene (perfluoro-2,4-dimethyl-3-ethylenepentene-2, HFP) in a wide range of temperatures. The radiolysis was carried out in vacuum with a  $^{60}\text{Co}$  source of  $\gamma$ -radiation and 8.4 V/kg dosage. Samples were illuminated in quartz ampoules with a

mercury lamp DRS-1000. It was shown that such irradiation led to the formation of an oligomeric perfluorocarbon radical, stable in liquid state. Formation of such dimer and trimer radicals occurs in stages: first, formation of a primary radical followed by its addition to molecules of HFP. Mechanism of the formation of such long lasting paramagnetic centers (LLPC) requires further studies. The fact that formation of stable radicals showed a minimum at 194 K cannot be explained as yet. Concentration of LLPC in liquid HFP at 300 K drops in time, reaching a low of 15 percent after 100 hrs. Figures 3; references 9: 8 Russian, 1 Western.

UDC 541.15

**Degradation of Methanol in Aqueous Solution in Microdischarge at Rectifier Anode**

18410014h Moscow *KHIMIYA VYSOKIKH ENERGIY* in Russian Vol 22 No 4, Jul-Aug 88 (manuscript received 16 Oct 87) pp 377-378

[Article by Ye. G. Volf, L. T. Bugayenko, G. V. Kovalev, A. M. Sizikov, and Ye. P. Kalyazin, Moscow State University imeni M. V. Lomonosov]

[Abstract] Methanol conversion products in microdischarge on aluminum were studied. The electrolyte consisted of an aqueous solution of  $\text{Na}_2\text{CO}_3$  (0.1 mole/dm<sup>3</sup>) and  $\text{CH}_3\text{OH}$  (3 mole/dm<sup>3</sup>); the anode was an aluminum bar and the cathode was made from graphite. The process was carried out in a hermetically-sealed vessel. Experimentally determined composition of the products agreed well with calculated data. It was found that the principal conversion occurred in the discharge volume where high temperatures are reached. Figure 1; references 9: 6 Russian, 3 Western.

UDC 621.039.325;541.183.12

**Uranium (VI) Adsorption by Cryogranulated Hydroxides of Divalent Metals**

18410042a Leningrad *RADIOKHIMIYA* in Russian Vol 30 No 4, Jul-Aug 88 (manuscript received 5 May 87; after final revision, 18 Feb 88) pp 513-518

[Article by V. S. Pakholkov and V. I. Zelenin]

[Abstract] Experimental results are reported of a study of principal patterns of ion exchange and adsorption of uranium (VI) by cryogranulated Cu, Zn, Cd, Mg, Co and Ni hydroxides. The effect of pH on this process varied and depended on the hydroxide and uranium salt used in the procedure: for  $\text{UO}_2\text{Cl}_2$  and  $\text{UO}_2(\text{NO}_3)_2$  the following order of adsorption was noted:  $\text{Zn}(\text{OH})_2$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ; for all of them the adsorption increased with the rise of pH. A much lower level of hydrolysis was noted during adsorption of uranium from  $\text{UO}_2\text{F}_2$  and  $\text{UO}_2\text{SO}_4$  solutions because of the formation of  $\text{UO}_2\text{F}^+$ ,  $\text{UO}_2\text{F}_2$ - $\text{UO}_2\text{SO}_4$  complexes and associates. Individual hydroxides exhibited an aging process; adsorbent was

prepared from mixed Ni-Cu hydroxides with greater stability, exceeding even that of titanium hydroxide. An ion exchange process coupled with formation of uranyl hydroxide and uronate compounds occurred during adsorption of uranium. A foreign electrolyte [ $\text{NH}_4\text{F}$  or  $(\text{NH}_4)_2\text{CO}_3$ ] decreased the amount of adsorbed uranium due to the formation of complex ions. Figures 4; references 4 (Russian).

UDC 669.822;621.039.325

**Synthesis and Ion Exchange Properties of Cryogranulated Hydroxides of Divalent Metals**

18410042b Leningrad *RADIOKHIMIYA* in Russian Vol 30 No 4, Jul-Aug 88 (manuscript received 7 May 87; after revision, 18 Feb 88) pp 508-512

[Article by V. S. Pakholkov and V. I. Zelenin]

[Abstract] Polyvalent metal oxides and hydroxides are widely used as inorganic ion-exchange resins in isolation, concentration and separation of various radionuclides. Experimental results are reported on synthesis of granulated Cu, Zn, Cd, Co, Ni and Mg hydroxides obtained by cryogranulation; their physical-chemical and ion exchange properties are discussed. The following variables were evaluated by regression analysis as to their effect on the final product: metal salt concentration in the starting solution (x-1), time of the addition of the precipitating solution (x-2), excess NaOH (x-3) and gel freezing temperature (x-4); only x-1 and x-2 were found to have a significant effect on end results. The optimal conditions were: x-1: 0.1 mole/l; x-2: -6°C; x-3: 50 percent and x-4: 2.0. Derivatographic and x-ray phase analysis data are reported for the products along with IR spectra and potentiometric titration data. It is shown that these hydroxides could be used effectively in isolation and concentration of uranium ions from electrolyte solutions. Figures 3; references 7 (Russian)

UDC 546.79.5:551.510.721

**Potential for Use of VPK and VP-IAP Ion Exchange Resins in Separation of Americium in Environmental Samples**

18410042c Leningrad *RADIOKHIMIYA* in Russian Vol 30 No 4, Jul-Aug 88 (manuscript received 7 Dec 87) pp 504-507

[Article by G. N. Romanov, T. A. Grigoryeva and Ye. A. Lomovtseva]

[Abstract] With increased production and application of plutonium and transplutonium elements, interest increases in determination and control of their contents in environment. Potential use of VP-IAP and VPK ion exchange resins in determination of americium in environmental specimens was studied along with its separation from plutonium, thorium and various macrosalts of iron, aluminum and calcium which are the principal elements interfering in such determinations. It was

shown that both of these resins could be used for isolation of americium from above admixtures. In this system, purified americium could contain up to 0.07 percent plutonium, 0.2 percent thorium and 0.001 percent iron of their starting levels in the analyzed samples. To obtain purer preparations, hydroxide purification of the specimens must be carried out prior to the ion exchange separation. The yield of americium obtained in this purification ranges from 84 to 96 percent. References 17: 4 Russian, 13 Western.

UDC 546.799.3.062

**Use of Ion Exchange Resin in Isolation and Separation of U, Np and Pu From Other Elements Out of Sulfuric and Phosphoric Acid Solutions**

18410042d Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 4, Jul-Aug 88 (manuscript received  
25 Dec 87) pp 499-504

[Article by L. I. Guseva, G. S. Tikhomirova and V. V. Stepukhina]

[Abstract] The possibility of using organic ion-exchange resins for isolation and concentration of U, Np, and Pu from other elements out of solutions of sulfuric and phosphoric acids was investigated as a function of the concentration of acids, presence or absence of organic solvent and various types of ion exchange resins. Distribution coefficients for these elements between the  $H_2SO_4$  and Dowex-1X8 (anionic) and Dowex-50 (cationic) resins was reported. It was shown that both of these exchange resins could be used to isolate the three elements in question from admixtures of transplutonium and other elements in the acids studied. Using this approach, isotopically-pure  $^{239}Np$  was obtained from its mother radionuclide  $^{243}Am$ . Figures 6; references 12: 4 Russian, 8 Western.

UDC 542.61

**Effect of Characteristics of Extraction System Component Used in Separation of Radionuclides Upon Interphase Tension. Part 12, Sodium Salts of Carboxylic and Organophosphorus Acids in Tributylphosphate Containing System**

18410042e Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 4, Jul-Aug 88 (manuscript received  
22 Aug 87) pp 475-481

[Article by S. D. Nikitin]

[Abstract] The goal of this work was to study interphase surface activity and emulsifying capability of a series of carboxylic, dialkylphosphoric, -phosphonic and -phosphinic acids in a system of 30 percent TBP in n-dodecane-5 percent aqueous sodium carbonate. In addition, an attempt was made to find patterns which could be used to prognosticate interphase properties of these compounds in TBP based extraction systems. Both the surface activity and emulsifying capability of these

organic acids increased with increasing values of dissociation constants of free acids in the series: dialkylphosphoric carboxylic acids. An equation was developed for calculating the effect of various acids on the phase separation rate in above systems based on the concentration and accumulation kinetics of hydrophobic acid compounds in the organic phase. Figures 6; references 15: 10 Russian, 5 Western.

UDC 546.799.7

**Study of  $Bk^{(III)}$  and  $Bk^{(IV)}$  Complex Formation and Stability of  $Bk^{(IV)}$  in Acetonitrile Solutions of Phosphoric Acid**

18410042f Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 4, Jul-Aug 88 (manuscript received 2 Mar 87;  
after final revision, 1 Feb 88) pp 452-457

[Article by S. A. Perevalov, I. A. Lebedev, Yu. M. Kulyako and B. F. Myasoyedov]

[Abstract] The use of acetonitrile instead of water as a solvent increased the stability of the 4+ oxidation state of transplutonium elements in phosphoric acid solutions. The stability constants in phosphate complexes are higher in acetonitrile solutions than in water. Therefore, the goal of this work was to study the composition and stability of  $Bk^{(IV)}$  and  $Bk^{(III)}$  phosphate complexes  $[BkH_2PO_4]^{2+}$  and  $[Bk(H_2PO_4)_2]^+$  along with the stability of tetravalent berkelium  $[Bk(H_2PO_4)_3]^+$  in acetonitrile solutions of phosphoric acid. In aqueous solutions,  $Bk^{(IV)}$  is unstable and gradually is reduced to  $Bk^{(III)}$  by water radiolysis products. The "selfreduction" is a zero-order reaction with respect to the concentration of  $Bk^{(IV)}$ . The same order was observed for selfreduction of  $Bk^{(IV)}$  in acetonitrile solution of phosphoric acid except that its stability was much higher than in water, probably because of lower concentration of the radiolysis products. The reduction rate constant decreased with increase of  $H_3PO_4$  concentration. Figures 4; references 16: 8 Russian, 8 Western (4 in Russian authors).

UDC 669.822;621.039.325

**Reaction of Uranium (VI) Ions With Cryogranulated Titanium, Zirconium and Niobium Hydroxides During Adsorption**

18410042g Leningrad RADIOKHIMIYA in Russian  
Vol 30 No 4, Jul-Aug 88 (manuscript received 8 Jun 87;  
after final revision, 18 Feb 88) pp 518-523

[Article by V. S. Pakholkov and V. I. Zelenin]

[Abstract] In continuation of a series of papers on cryogranulated metal hydroxides, properties of Ti, Zr and Ni hydroxides are described. The effect of pH, concentration of  $UO_2(NO_3)_2$  and of the electrolytes  $NH_4Cl$ ,  $NH_4NO_3$  and  $(NH_4)_2SO_4$  on uranium adsorption is discussed: uranium adsorption increased with pH rise, the electrolytes showed no effect on the process. Adsorption isotherms are recorded and kinetic characteristics of this adsorption calculated. All three hydroxides appeared to act as polyfunctional amphoteric ion exchange

resins with an activation energy ranging from 38-42 kJ/mole. For the  $\text{UO}_2(\text{NO}_3)_2$  solutions with pH greater than 3.5, the ion exchange process was complicated by coordination polymerization. The limiting step for the overall process was internal diffusion. Figures 5; references 11 (Russian).

UDC 547.514.48:546.110.23

**Synthesis of Tritium-Tagged Prostaglandins F and Their Methyl Ethers**

18410042h Leningrad *RADIOKHIMIYA* in Russian  
Vol 30 No 4, Jul-Aug 88 (manuscript received 2 Apr 87;  
after final revision, 9 Mar 88) pp 527-531

[Article by V. P. Shevchneko, T. Yu. Lazurkina and N. F. Myasoyedov]

[Abstract] The goal of this study was to develop preparatory conditions for conversion of radiolabelled prostaglandins E and their methyl ethers into respective prostaglandins F (PGF) and MEPGF using L-selectride reagent. Good yields were obtained using sodium borohydride and lithium trialkylborohydride, increasing the ratio of the reducing agent to prostaglandin proportionately to the decreasing concentration of the latter and increasing several-fold the reaction time. The reduction was effectively carried out at  $-78^\circ\text{C}$  as well as at  $0^\circ\text{C}$ , although the higher temperature gave somewhat lower yields. Figures 4; references 10: 8 Russian, 2 Western.

UDC 546.791 + 546.799.4

**Determination of Atomic Ratio of Oxygen to Metal in Uranium-Plutonium Mixed Oxide Fuel**

18410042i Leningrad *RADIOKHIMIYA* in Russian  
Vol 30 No 4, Jul-Aug 88 (manuscript received  
28 Jan 88) pp 542-546

[Article by A. Ya. Kuperman, S. I. Korolev, N. F. Mukhortov, Yu. A. Smirnov, T. L. Nikolskaya and N. S. Yefimova]

[Abstract] Oxygen coefficient: atomic ratio of oxygen to metal ( $\text{O/U} + \text{Pu}$ ) is an important characteristic of mixed fuels. One of the methods used in determining this coefficient is the combined method and it is based on dissolving the analyzed specimen in phosphoric acid followed by determination of the volume of liberated hydrogen. In this paper, results are reported of attempts to refine this method. The equipment for dissolving test samples was improved by substituting a quartz lamp as a heating unit. This accelerated the time needed for dissolving the specimens and had no effect on the oxidation of Pu or U. Instead of a vacuum pump for removal of oxygen, it was purged with argon from the system. The extrapolation method of Meites is suggested

for more precise coulombmetric determination of  $\text{Pu}^{(\text{III})}$  and  $\text{U}^{(\text{VI})}$ . Optimization of such steps shortened the time of this procedure significantly. Figures 1; references 5: 1 Russian, 4 Western.

UDC 541.28:547.579.1'3

**Nuclear-Chemical Synthesis of Tritiated Phenyl Onium Derivatives of Oxygen, Sulfur, Selenium and Tellurium**

18410042j Leningrad *RADIOKHIMIYA* in Russian  
Vol 30 No 4, Jul-Aug 88 (manuscript received  
14 Dec 87) pp 576-578

[Article by V. D. Nefedov, M. A. Toropova, N. Ye. Shchepina, V. V. Avronin, V. Ye. Zhuravlev, V. V. Shchepin and N. I. Trofimova]

[Abstract] In spite of intensive development of heteroorganic chemistry, production of radiolabelled compounds by classical methods is a complicated multifaceted process often failed to yield the desired product. A single phase nuclear-chemical synthetic method is described for production of tritiated phenyl onium derivatives of oxygen, sulfur, selenium, tellurium  $[\text{C}_6^3\text{H}_5(\text{C}_6\text{H}_5)\text{El}]^+\text{BF}_4^-$  and diphenyl compounds. The yield of onium cations increased in the order: OAdvantages of solid and liquid phase reactions are discussed (higher yield versus breakdown of the products). References 11: 6 Russian (1 by Western authors), 5 Western.

UDC 621.373.826

**Isotope-Selective Dissociation of  $\text{BCl}_3$  in Dual Frequency IR Laser Field**

18410288b Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 7 No 2, Feb 88 (manuscript received  
30 Apr 87) pp 165-171

[Article by V. B. Laptev and Ye. A. Ryabov, Spectroscopy Institute, Troitsk]

[Abstract] Isotope-selective dissociation of molecules during pulsed multiphoton  $\text{CO}_2$ -laser excitation is one of the most effective methods for laser separation of isotopes. For example, large-scale separation of sulfur and carbon isotopes has already proved feasible, while the laser separation of other elements, particularly  $^{10}\text{B}$  and  $^{11}\text{B}$  still remains to be achieved. The purpose of the present work was to identify those processes that affect the selectivity of separation. The use of multiphase excitation for  $\text{BCl}_3$  dissociation results in much lower energy consumption compared with single-frequency excitation. However, owing to this compound's high dissociation threshold and its small number of atoms, dual-frequency excitation may also be inadequate. Optimization of dissociation conditions improved selectivity and resulted in an 8 percent isotope yield at 3.7 and 3.0 joules per square centimeter energy density. Secondary chemical reactions of dissociation products such as  $\text{BCl}_2$  and  $\text{BCl}$  radicals with the  $\text{BCl}_3$  itself or with acceptor radicals have a marked effect on multiphoton dissociation. Experimental conditions for eliminating secondary chemical processes were determined. Figures 3; references 13: 10 Russian, 3 Western.

UDC 773.92

**Solid State Photolysis of Aromatic Azides**  
18410014e Moscow *KHIMIYA VYSOKIKH ENERGIY*  
in Russian Vol 22 No 4, Jul-Aug 88 (manuscript  
received 29 Oct 86) pp 343-346

[Article by L. N. Karyakina, V. V. Kurenkova, A. M. Yanin, and A. V. Oleynik, Gorki State University imeni N. I. Lobachevskiy]

[Abstract] Solid state photolysis of a number of aromatic mono- and di-azides was studied. A number of nitrene reactions occurring in solid state were postulated on the basis of the analysis of thin-layer-chromatographic and IR spectroscopic data. The type of observed reactions depended on the nature of the azide and the method of its layer formation, and included: a reaction with the neighboring nitrene or azide groups, break off of a hydrogen atom from C-H or O-H groups or insertion into a double bond. Recombination of radicals formed in this process leads to appearance of polymers which comprise the principal photolysis products (at a 70-80 percent azide conversion, 50-60 percent of the products are polymers). Figures 3; references 6: 5 Russian (1 by Western authors), 1 Western.

UDC 548.737

**Crystal Structure and Electrophysical Properties of Dimethylethylenedithiotetrathiafulvalene Perchlorate**

18410288a Moscow *KHIMICHESKAYA FIZIKA*  
in Russian Vol 7 No 2, Feb 88 (manuscript received  
3 Mar 87) pp 151-159

[Article by T. G. Takhirov, O. N. Krasochka (deceased), O. A. Dyachenko, L. O. Atovmyan, M. Z. Aldoshina, L.

M. Goldenberg, R. N. Lyubovskaya, V. A. Merzhanov, and R. B. Lyubovskiy, Chemical Physics Institute, USSR Academy of Sciences, Chernogolovka]

[Abstract] Several cation-radical salts containing asymmetric S- and S, Se-containing donors, i.e., dimethylethylenedithiotetrathiafulvalene (DMEDT-TTF) and dimethylethylenedithiodiselenadithiafulvalene (DMEDT- DSDTF), which were prepared in a previous work, manifested dielectric, semiconductor, and metallic properties. In organic metals based on the asymmetric donors, the cations are packed in the form of piles of central-symmetric dimers having pronounced electron cross-sectional interactions. The relationship between the structure of these cation- radical salts and their electrophysical properties is currently being studied intensively. In the present work a detailed x-ray study of the molecular and crystal structure of (DMEDT-TTG)<sub>2</sub> was made. Its conductivity and thermal-emf at 8-300 K were also measured. The crystal structure consists of two independent layers of DMEDT-TTF cations and an intermediate ClO<sub>4</sub> anion layer. The conductivity of the perchlorate at room temperature is 25-30 reciprocal ohms per centimeter. At lower temperatures it increases monotonically, reaching a maximum at 105 K, after which it starts dropping. At 80-100 K small jumps in resistance were observed. These evidently resulted from cooling stresses in the crystal. Thermal-emf is almost constant at 30 microvolts per K at high temperatures, but it decreases markedly at 100 K, reaching a minimum at 10 K. From the thermal-emf data and the existence of a maximum in the logarithmic derivative of conductivity in the same temperature zone, it may be concluded that a metal-dielectric phase transition takes place at 22 K. Figures 3; references 13: 8 Russian, 5 Western.

10

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