Monolayers of Adipate Polyesters at Air-Liquid Interfaces [1]

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The surface pressure-area isotherms at 24.5 °C are reported for poly(ethylene adipate), poly(trimethylene adipate), and poly(propylene adipate), spread as monolayers at air-aqueous interfaces. The monolayers were spread on distilled water and 0.01 N HCl, using benzene, chloroform, and acetone as spreading solvents. Poly(propylene adiptate) was the least compressible of the three, and poly(ethylene adipate) the most. Poly(propylene adipate) did not collapse at the highest pressures studied. The spreading characteristics of both poly(ethylene adipate) and poly(propylene adipate) were independent of the amount of material used. The spreading of poly(trimethylene adipate) appeared to depend upon the spreading solvent. The effect of structure on the surface pressure—area isotherms and the specific areas for each polymer are discussed.

1. Introduction

The monolayer properties of a series of linear succinate polyesters, with a number-average molecular weight ($\bar{M}_n$) of the order of 4,500, at air-aqueous interfaces were recently reported [1]. It was shown that the monolayer of poly(ethylene succinate) was highly expanded but that it collapsed at very low surface pressures. Poly(pentamethylene succinate) monolayers were also expanded. They did not collapse with increasing pressure, but the surface compressibility went through a maximum and continued to decrease as the pressure increased. An isomer of this polymer, poly(neopentyl succinate), produced a much less expanded film which collapsed at a surface pressure higher than that observed for collapse or pressure decrease for the other two polymers. It also gave the smallest extrapolated specific area per repeating unit. Other work has been reported on polyesters by Harkins, Carmen, and Ries [2] and Moss [3].

The work reported in this paper is concerned with a surface film balance study of three linear saturated polyesters of adipic acid at the liquid-air interface.

2. Experimental Procedure

The polyesters used in this investigation were: poly(ethylene adipate) $[-O(CH_2)_2OCO(CH_2)_4CO-]_n$, poly(trimethylene adipate) $[-O(CH_2)_3OCO(CH_2)_4CO-]_n$, and poly(propylene adipate) $[-OCH(CH_3)CH_2OCO(CH_2)_4CO-]_n$. These polymers were prepared by Dr. James Farr, Jr., of the Thiokol Chemical Company and were synthesized from the melt without catalyst. They were purified by reprecipitation from chloroform solution with ethyl ether and dried in vacuum. Some of the bulk properties of these polymers are given in table 1.

The film balance used to study the monolayers of the spread films has been described previously [1]. The water used as a subphase was redistilled from an all-quartz system. The spreading solvents were twice distilled and tested for active impurities by measurements of the surface pressure of the solvent alone. The polymer solutions were spread from micropipets and 10 min usually allowed for solvent evaporation. The average time of an experiment was 1 hr. All measurements were made at 24.5 ±0.5 °C.

TABLE 1. *Bulk properties*

Polymer	Softening point	Molecular weight M_n [a]	Bulk density at 27 °C	Physical state at 23 °C [b]
	°C		g/cm^3	
Poly(ethylene adipate)_____	51	3800	1.3	Crystalline
Poly(trimethylene adipate)____	40	4000	1.3	Crystalline
Poly(propylene adipate)_____	_____	5400	1.2	Viscous liquid

[a] M_n, number average molecular weight determined from supplied end group analysis.
[b] Crystallinity detected by X-ray diffraction.

3. Results

The monolayer properties of poly(ethylene adipate) spread from benzene and chloroform on the two substrates are given in figures 1 and 2. The surface pressure in dynes per centimeter is shown as a function of the specific area of the polymer (area per unit weight). All of the runs shown in figure 1 were obtained using benzene as the spreading solvent. Extrapolation of the linear portion of the curve drawn gives a limiting specific area of 2.6 m²/mg. In order to obtain the entire isotherm 30.36×10^{-3} mg of polymer was used for the region of high surface pressure and 5.50×10^{-3} mg for the region of low surface pressure and large area. Both regions were reproducible as shown by duplicated experiments. The two regions overlapped and a smooth continuous isotherm was obtained.

The available area of the balance for initial spreading of the film was of the order of 800 cm². Using the specific surface area, the larger quantity of polymer corresponds to an area of approximately 790 cm² and the smaller to an area of approximately 145 cm². The isotherm was, therefore, independent of the quantity of material used over this relatively
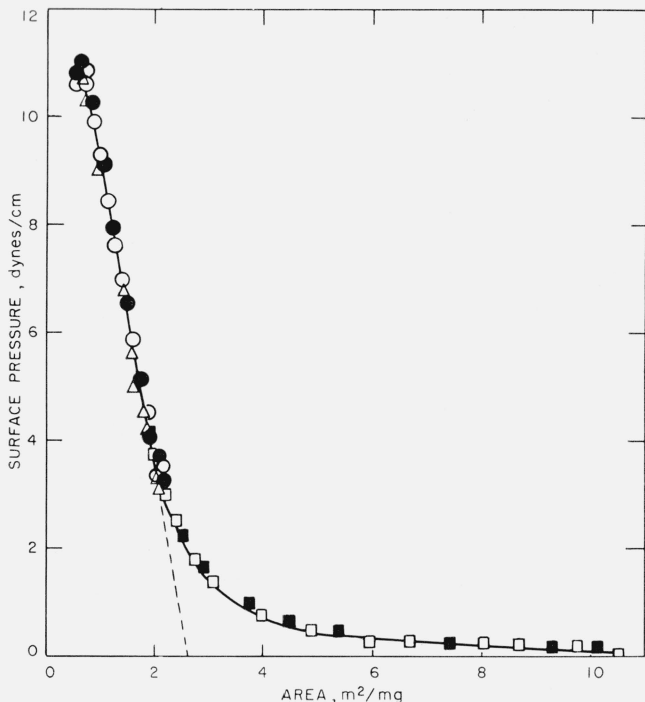
FIGURE 1. *Surface pressure-area isotherm of poly(ethylene adipate) spread from benzene at 24±0.5 °C.*

Distilled water subphase ◯, ● 30.36×10⁻³ mg.
□, ■ 5.50×10⁻³ mg.
0.01 N HCl subphase △ 30.36×10⁻³ mg.

wide range, which included a quantity near the maximum capacity of the balance. The absence of any change in the isotherm with quantity of material spread suggests that the films were completely spread and existed as monolayers. The use of 0.01 N HCl with a pH of 2 resulted in the same isotherm as the use of distilled water with a pH of 6.5. The collapse pressure of the films spread from benzene was 11.1 dynes per cm, as shown by figure 1. A quantity of polymer intermediate between the two amounts described above also resulted in the same isotherm as those spread from benzene, as shown in figure 2. Films spread from chloroform on distilled water also yielded the identical isotherm, but the collapse pressure was slightly higher, 12 dynes per cm.

The isotherm of poly(propylene adipate) spread from chloroform on distilled water is shown in figure 3. The properties for very dilute surface concentration were not studied for this film. The extrapolated specific area at zero surface pressure was 2.2 m²/mg. Films of this polymer did not collapse. Two quantities were again used to obtain different portions of the isotherm. These two sections overlapped and a smooth isotherm resulted. The spreading characteristics were, therefore, not dependent on the quantity of material deposited, within this range. The larger quantity, 29.94×10⁻³ mg, corresponded to an area of approximately 660 cm² at zero surface pressure, while the smaller quantity corresponded to one-half this amount.

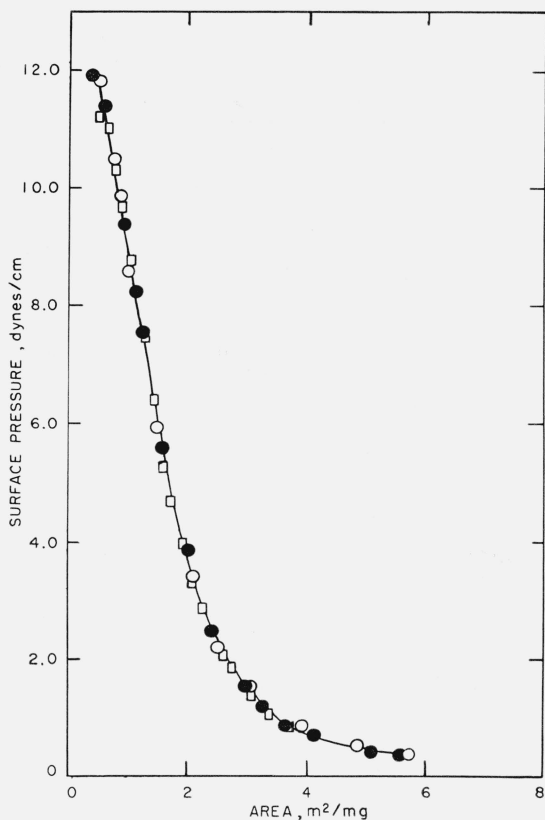FIGURE 2. *Surface pressure-area isotherm of poly(ethylene adipate) on distilled water at 24±0.5 °C.*
Spread from benzene □ 17.51×10⁻³ mg.
Spread from chloroform ◯, ● 12.12×10⁻³ mg.

This independence on the amount of polymer suggests that the films were monolayers.

Poly(trimethylene adipate) was sensitive to the spreading solvent. Films spread from benzene on 0.01 N HCl subphase exhibited the surface characteristics shown by curve A in figure 4. A limiting area of 3.1 m²/mg was obtained from this isotherm. The quantity of polymer spread, 5.47×10⁻³ mg, corresponds to an area of approximately 170 cm², and because of the small quantity should represent a completely spread film.

The effect of the spreading solvent on the characteristics of the film is shown by isotherm B in figure 4. Polymer was spread from acetone solution in two different quantities onto a distilled water subphase. In one case 50λ (λ=10⁻³ cm³) and in the other, 100λ were spread, using the same concentration of solution. Within the experimental error, both quantities resulted in the same isotherm, with a smaller specific area. The isotherm showed no signs of expansion to higher specific areas for the smaller quantity of solution spread. Repeat runs for both quantities resulted in the reproducible isotherm shown in figure 4. The fact that the maximum spreading area for the isotherm with the smaller amount of polymer was twice as large as that for the larger amount of polymer appears to indicate the spreading of the polymer with this solvent was complete.
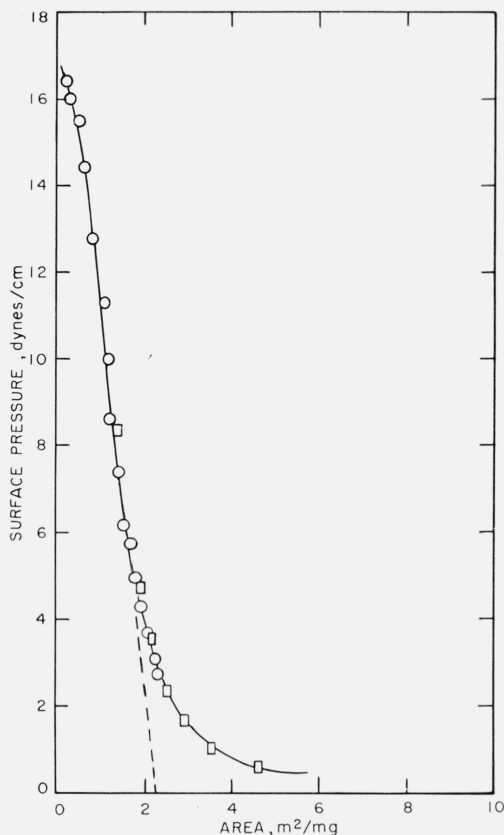
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FIGURE 3. *Surface pressure-area isotherm of poly(propylene adipate) on distilled water spread from chloroform at 24.5 ±0.5 °C.*

○, 29.94×10⁻³ mg.
□, 14.95×10⁻³ mg.

4. Discussion

4.1. Physical Properties

In table 2 are given values for the thickness of the monolayers, the energies of compressing the films to collapse or the point of inflection, and compressibilities. The approximate thicknesses of the films were calculated from the bulk density and the limiting specific area of the completely spread film. As seen in table 2 they are within the range of 3 to 4 Å and are of a reasonable thickness for monolayers. They fall in approximately the same range as did the succinate polyesters [1], and indicate that these polyesters lie relatively flat on the surface. Integra-
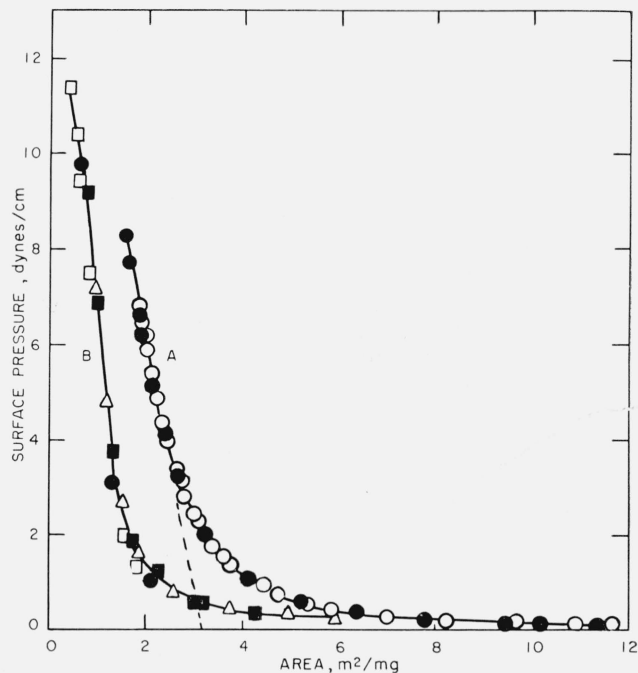

FIGURE 4. *Surface pressure-area isotherm of poly(trimethylene adipate) at 24±0.5°C.*

Curve A Spread from benzene on 0.01 N HCl subphase
○, ● 5.47×10⁻³ mg.
Curve B Spread from acetone solution on to distilled water subphase
□, ● 23.39×10⁻³ mg.
■, △ 11.70×10⁻³ mg.

tion of the area under the isotherms from very large segment areas to the point of collapse for poly-(ethylene adipate) and to the point of inflection for poly(propylene adipate) gives the energy to compress the film to a position of unstability. The energies shown in table 2 are rather high, one being of the order of 700 and the other 800 cal/mole/segment. For the succinate polyesters studied previously [1], only poly(neopentyl succinate) gave an energy above 700, as shown in table 2. Poly(ethylene succinate) gave an energy of 349, and poly(pentamethylene succinate) an energy of 568 cal/mole/segment. The compressibilities given in table 2 were calculated from the equation:

$$K = \frac{A_0 - A_1}{A_0 \pi_1}$$

where K is the compressibility, A_0 the extrapolated specific area at zero surface pressure, and A_1 the specific area at surface pressure π_1.

TABLE 2

Polymer	Extrapolated specific area	Area per segment		Energy to compress film to collapse, cal mole⁻¹ segment⁻¹	Compressibility	Thickness at $\pi=0$
		Calculated	Observed			
	m^2/mg	A^2	A^2		$cm/dyne$	A
Poly(ethylene adipate)	2.6	67	75	716	0.067	3.0
Poly(propylene adipate)	2.2	67	68	807	.048	3.8
Poly(trimethylene adipate)	3.1	74	98		.058	2.7
Poly(ethylene succinate)[a]	2.3	55	60 to 70	349	.11	3.1
Poly(pentamethylene succinate)[a]	2.9	74	90	568	.056	2.9
Poly(neopentyl succinate)[a]	2.0	60	63	734	.028	3.9

[a] Reference [1].

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4.2. Compressibility

The compressibility values for all the polyesters studied, except for poly(ethylene succinate) [1], are in the range observed for linear polyesters, such as the self ester of the hydroxydecanoic acid studied by Harkins, Carmen, and Ries [2], and poly(vinyl acetate) films studied by Ries, Ahlbeck, and Gabor [4]. The latter polymer contains the ester groups as side chains.

The compressibility data for the adipate monolayers and the succinate monolayers, as reported previously, point to the general observation that the compressibility of the monolayer decreases with the number of carbon atoms in the glycol and acid groups and also with the arrangement of these groups.

Second, it is to be observed that the polyesters with the lower number of carbon atoms between the carboxylic groups have greater compressibilities than those with large numbers, as evidenced by comparison of the compressibilities of poly(ethylene succinate) with poly(ethylene adipate). Similarly the compressibilities of polyesters containing the ethylene glycol grouping have greater compressibilities than those having segments of longer glycols. This is evidenced by a comparison of poly(ethylene adipate) with poly(trimethylene adipate) as well as a comparison of poly(ethylene succinate) with poly(pentamethylene succinate).

Third, it appears that differences in the arrangement of the carbon atoms in the glycol chain also affects the compressibility. Thus, poly(propylene adipate) and poly(trimethylene adipate) differ in their compressibilities in that the branched three carbon group has a lower compressibility than the straight chain arrangement. Similar behavior is observed in a comparison of poly(neopentyl succinate) with poly(pentamethylene succinate).

The spreading of polymer films has been shown by others [2, 5] to be independent of molecular weight. Crisp [5] has shown that polymer films are completely spread when the specific areas are reproducible and independent of the solvent or solution concentration over a moderate concentration range. The spreading of both poly(ethylene adipate) and poly(propylene adipate) were independent of the quantity of material spread, over the concentration range studied, as shown in figures 1 to 3. As completely spread films are assumed to be independent of molecular weight, the surface pressure was plotted as a function of the area of the repeating structural unit. Such isotherms for the three polyesters are given in figure 5. Experimental points from different runs are given on each curve, except those of poly(trimethylene adipate) spread from acetone.

There is a large difference in the isotherm of poly(ethylene adipate), as shown in curve C, figure 5, and that of poly(ethylene succinate) (fig. 5, ref. 1). The increase in the length of the repeating unit by the addition of two methylene groups in the acid changed the collapse pressure from approximately 4 dynes/cm for the succinate to approximately 12 dynes/cm for the adipate polymer. This is very likely due to the greater freedom of orientation of
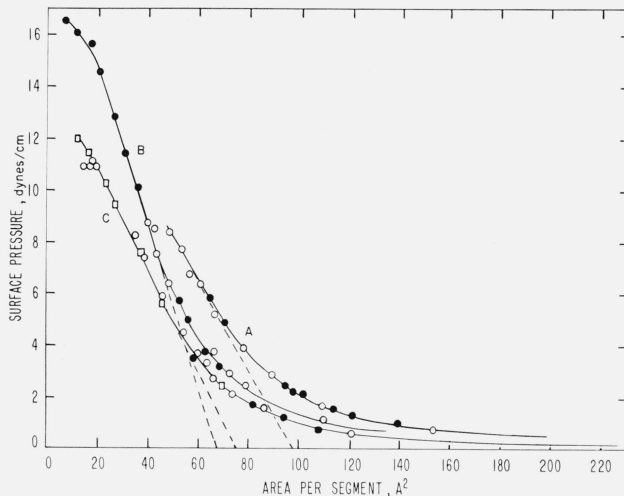

FIGURE 5. *Surface pressure-area isotherms of linear saturated polyesters on aqueous subphases at 24.5 ± 0.5 °C.*

Curve A Poly(trimethylene adipate)
Curve B Poly(propylene adipate)
Curve C Poly(ethylene adipate)

the carbonyls in the interface, resulting in a higher vertical component of the dipole. The extrapolated segment area for the adipate polymer is 75 A^2 and 60 to 70 A^2 for the succinate polymer. These values are somewhat larger than the minimum calculated from molecular models.

The monolayer properties of poly(trimethylene adipate) spread from benzene, curve A, are similar to those of poly(ethylene adipate), curve C, at moderate surface pressures. At all surface pressures studied the segment areas are larger for the poly(trimethylene adipate) than for the poly(ethylene adipate). The extrapolated segment area of 98 A^2 is 23 A^2 larger than the value obtained for the poly(ethylene adipate) which is in good agreement with the cross-sectional area of a long chain hydrocarbon, as established by monolayer measurements.

5. Summary

Differences in the surface pressure—area isotherms of the three adipate polyesters studied were found to be related to differences in the chemical structure. Large differences were also observed between these polyesters and succinate polyesters studied previously. A large difference was observed between the observed and the calculated specific area for the repeating unit of poly(trimethylene adipate). As in the case of the succinate polyesters, one of the adipate polyesters studied did not collapse at high pressures.

6. References

[1] W. M. Lee, J. L. Shereshefsky, and R. R. Stromberg, J. Research NBS **65A** (Phys. and Chem.) No. 1, 51 (1961).
[2] W. D. Harkins, E. F. Carmen, and H. E. Ries, Jr., J. Chem. Phys. **3**, 692 (1935).
[3] S. A. Moss, Jr., J. Am. Chem. Soc. **56**, 41 (1934).
[4] H. E. Ries, Jr., R. A. Ahlbeck, and J. Gabor, J. Colloid Sci. **14**, 354 (1959).
[5] D. J. Crisp, J. Colloid Sci. **1**, 49 (1946).

(Paper 66A5–178)

Publications of the National Bureau of Standards*

Correction

In the July–August 1962 issue of this Section, the abstract for the paper **Low Temperature Thermometry**, R. P. Hudson, *Book, Experimental Cryophysics, pp. 214–253 (Butterworth & Co., London, England, 1961)*, was presented incorrectly. The following abstract refers to this paper:

The principal methods for thermometry in the range 1°K to 90°K are critically reviewed, the discussion covering the physical principles involved, types of apparatus, and factors determining the attainable precision and accuracy. Supplementary data are provided in tables, some within the body of the article and others in appendices to the volume of which the article constitutes a chapter.

Selected Abstracts

Spark-gap flashover measurements for steeply rising voltage impulses, J. H. Park and H. N. Cones, *NBS J. Research* **66C** *(Eng. & Instr.) No. 3, 197 (July–Sept. 1962)*.
Dividers made up of special thin ribbon resistors with very low time constants were used for measuring linearly rising chopped impulses with peak voltages up to 300 kv and times to sparkover from 0.03 to 50 microseconds. Total errors were deduced by a combination of computation and experimentation to be probably not greater than 1.5 percent for times to sparkover greater than 0.1 microsecond.

From a large number of oscillograph records data were derived giving a relation between rate of rise (or rise time) and flashover voltage for (1) 12.5 cm diameter spheres spaced 6 cm apart, (2) 25 cm diameter spheres spaced 6 cm, and (3) uniform field electrodes spaced 5 cm. It is recommended that the volt-time curve showing these relations for the 25 cm diameter spheres be used as a reference standard for interlaboratory comparison of measurement methods.

A furnace for thermocouple calibrations to 2,200° C, D. B. Thomas, *NBS J. Research* **66C** *(Eng. & Instr.) No. 3, 255 (July–Sept. 1962)*.

A tantalum tube furnace has been constructed to calibrate and investigate the thermoelectric behavior of high temperature thermocouples. The furnace and its associated equipment were designed with emphasis on features that would assure a high degree of accuracy in measurements that are made at high temperatures and also with emphasis on trouble-free performance. Data that were obtained during furnace operation showed that thermocouple depth of immersion into a properly designed blackbody is of considerable importance if a good agreement is to be realized between a calibrated optical pyrometer and a calibrated thermocouple that has been placed in the hot zone of the furnace. High purity helium gas can be used in the furnace to keep thermocouple contamination to a minimum.

Method of measuring emissivities of metals in the infrared, A. G. Maki and E. K. Plyler, *NBS J. Research* **66C** *(Eng. & Instr.) No. 3, 283 (July–Sept. 1962)*.

A method of measuring normal spectral emissivities in the infrared region from 1 to 13 μ is described. It consists of comparing the rate of emission of radiant energy from a blackbody with that from the specimen. The two observed radiances are made equal by adjusting the temperatures. An equation is derived for use in calculating the emissivity for the observed temperatures. The main sources of error arise in the measurement of the temperature of the specimen and the temperature of the blackbody. As an example of the method, the normal spectral emissivity of gold has been measured in the spectral range from 4 to 13 μ with temperatures from 550 to 1,000 °K. The emissivity was found to range from 0.014 at 4 μ and 550 °K to 0.0256 at 9 μ and 1,000 °K. A table is included which lists the values of emissivity from 4 to 13 μ and from 550 to 1,000 °K at intervals of 50 °K.

Tables of spectra-line intensities. Part I. Arranged by elements, W. F. Meggers, C. H. Corliss, and B. F. Scribner, *NBS Mono. 32, Pt. I (Dec. 29, 1961) $4.00*.
The relative intensities, or radiant powers, of 39,000 spectral lines with wavelengths between 2000 and 9000 Angstroms have been determined on a uniform energy scale for seventy chemical elements. This was done by mixing 0.1 atomic percent of each element in powdered copper, pressing the powder-mixture to form solid electrodes which were burned in a 10 ampere 220 volt direct-current arc, and photographing the spectra with a stigmatic concave grating while a step sector was rotating in front of the slit. The sectored spectrograms facilitated the estimation of intensities of all element lines relative to copper lines which were then calibrated on an energy scale provided by standardized lamps and all estimated line intensities were finally adjusted to fit this calibration. Comparisons with other intensity measurements in individual spectra indicate that the National Bureau of Standards spectral-line intensities may have average errors of 20 percent, but first of all they provide uniform quantitative values for the seventy chemical elements commonly determined by spectrochemists. These data are presented by element in part I and all 39,000 observed lines are given in order of wavelength in part II.

Analysis of coaxial two-terminal conical capacitor, M. C. Selby, *NBS Mono. 46 (Apr. 6, 1962) 20 cents*.
Adjustable capacitors having electrodes in the form of coaxial cones or frustums have been used on rare occasions in the past; but their potential superiority to other types of capacitors for some important applications have been overlooked. The advantage of this geometry over cylindrical or disk forms is that the practical capacitance range is several times larger. An example cites the capacitance ranges of a disk, cylindrical, and conical type to be 10, 40, and 168 to one, respectively. An approximate equation was derived for this conical capacitor and close agreement is shown between computed and measured values of capacitance versus electrode displacement. Multiple cone and different shape electrodes are suggested to obtain large values of capacitance with an appreciable saving of space and further increased range of capacitance. The electric field is plotted and its construction steps for axial symmetry are given.

Dissociation constant of 2-ammonium-2-methyl-1, 3-propanediol in water from 0 to 50° and related thermodynamic quantities, H. B. Hetzer and R. G. Bates, *J. Phys. Chem.* **66**, *308–311 (1962)*.

The base 2-amino-2-methyl-1,3-propanediol, like the closely related compound tris-(hydroxymethyl)-aminomethane, is a solid substance of considerable use as a biological buffer material. The acidic dissociation constant, K_{bh}, of the substituted ammonium ion conjugate to the free base now has been determined at 11 termperatures from 0 to 50° by measurement of the electromotive force of hydrogen-silver chloride cells without liquid junction. The results are given as a function of the temperature (T) in °K. by the equation—log K_{bh} = $2952.00/T - 2.2652 + 0.0039092T$. The standard changes of free energy, enthalpy, entropy and heat capacity for the dissociation process have been calculated from the temperature coefficient of the dissociation constant. For the acidic dissociation of 2-ammonium-2-methyl-1,3-propanediol at 25°, the following results were obtained: $\triangle G^0 = 50,238$ j. mole⁻¹, $\triangle H^0 = 49,860$ j. mole⁻¹, $\triangle S^0 = -1.3$ j. deg.⁻¹ mole⁻¹, and $\triangle C_p^0 = -45$ j. deg.⁻¹ mole⁻¹. For the basic dissociation of 2-amino-2-methyl-1,3-propanediol at 25°, the corresponding quantities are $\triangle G^0 = 29,656$ j. mole⁻¹, $\triangle H^0 = 6720$ j. mole⁻¹, $\triangle S^0 = -76.9$ j. deg.⁻¹ mole⁻¹, and $\triangle C_p^0 = -150$ j. deg.⁻¹ mole⁻¹.

Study of electronically excited hydroxyl radicals in the H+O₃ **atomic flame**, H. P. Broida, *J. Chem. Phys.* **36**, *No. 2, 444–448 (Jan. 1962)*.

Ultraviolet emission of the $A^2\Sigma^+ \to X^2\Pi_i$ transition of OH has been observed in low-pressure flames of hydrogen atoms and ozone. In these flames, at pressures near 1 mm Hg, the intensity of this uv emission was found to be directly proportional to the square of the intensity of the rotation-vibration bands in the electronic ground state, $^2\Pi_i$. Under similar conditions, reactions of hydrogen atoms with oxygen atoms or with hydroxyl radicals were found to give too little emission to account for the observed radiation. It is concluded that collisions of two vibrationally excited OH radicals, $^2\Pi_i$, lead to the electronically excited radicals, $^2\Sigma^+$. Approximately 500 photons are emitted by all the vibrationally excited radicals ($\nu = 1$ to 9, $^2\Pi_i$) for each photon emitted in the electronic transition $A\ ^2\Sigma^+ \to X\ ^2\Pi_i$. Steady state partial pressures of vibrationally excited OH, $^2\Pi_i$, are estimated to be 10^{-7} mm Hg for a total flame pressure of 1 mm.

Theory of thermal diffusion in dilute alloys, R. E. Howard and J. R. Manning, *J. Chem. Phys.* **36,** *No. 4, 910–916 (Feb. 1962).*
A kinetic analysis is made of the thermal diffusion of a dilute impurity in an f.c.c. metal. Expressions are derived for the impurity current, the steady-state Soret gradient, and the mean atom displacement. It is shown how the "heats of transport" appearing in these expressions can be studied experimentally. An extension of the analysis to cases of nonthermal type gradients, in particular, a chemical concentration gradient, is briefly considered.

Hydrogen formation in the gamma-radiolysis of ethylene, P. Ausloos and R. Gorden, Jr., *J. Chem. Phys.* **36,** *No. 1, 5–9 (Jan. 1962).*
The radiolysis of ethylene-d_2 and C_2H_4-C_2D_4 mixtures has been investigated in the gas, liquid, and solid phases. The data indicate that hydrogen may be formed by two distinct molecular-elimination processes: $CH_2CH_2 \to CH_2C + H_2$ and $CH_2CH_2 \to CH \equiv CH + H_2$. The effect of xenon and pressure on the yields of H_2, HD, and D_2 in the gas-phase radiolysis of CH_2CD_2 has been investigated. The results for the $(^2P_1)$ Hg-sensitized and the 1237 A-photochemical decomposition have been compared with those for radiolysis.

Impurity effects in high purity metal, L. L. Wyman and G. A. Moore, **(Symp. Major Effects of Minor Constituents on the Properties of Materials. Sixty-fourth Annual Meeting ASTM, Atlantic City, N.J. June 26, 1962),** *ASTM Spec. Tech. Publ. No. 304—ASTM Materials Sci. Series 2, 3–16 (June 26, 1961).*
Obtaining metals of the highest possible degree of purity is a problem of major concern in both science and engineering. The determination of impurities, their effects, and control, demand extreme efforts in processing and analysis. Impurities in metals are characterized by the nature of their occurrence and their effects on host metals. Specific examples illustrate impurity effects in a number of currently important applications.

Vibration-rotation interactions in cyanamide; the question of planarity of amides, D. R. Lide, Jr., *J. Mol. Spectroscopy* **8,** *No. 2, 142–152 (Feb. 1962).*
The cyanamide molecule is approximated by a simple model which allows for a large-amplitude out-of-plane vibration of the NH_2 group. The kinetic energy of this model is derived, and the quantum-mechanical problem is formulated. Perturbation expressions suitable for the case where there is a potential hump in the planar configuration are given. Some of the consequences of the vibration-rotation interactions are discussed.

Vacuum ultraviolet photochemistry. III. Primary processes in the vacuum ultraviolet photolysis of water and ammonia, J. R. McNesby, I. Tanaka, and H. Okabe, *J. Chem. Phys.* **36,** *No. 3, 605–607 (Feb. 1962).*
Water and ammonia have each been photolyzed in the absence and presence of C_2D_4 which served to scavenge H atoms. Wavelengths used were: for ammonia, 1849 and 1236 A; for water, 1236 A. Under conditions where H atoms are efficiently scavenged by C_2D_4, the production of H_2 signifies a primary photochemical process giving molecular

H_2 directly. It is found that at 1849 A, ammonia decomposes almost entirely to $H + NH_2$. At 1236 A, two primary processes are observed.

$$NH_3 \to H_2 + NH, \tag{a}$$
$$NH_3 \to H + NH_2. \tag{b}$$
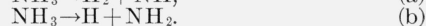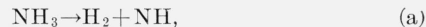
Process (a) is about $\frac{1}{6}$ as probable as process (b). At 1236 A, the photolysis of water proceeds via two primary processes.

$$H_2O \to H + OH, \tag{c}$$
$$H_2O \to H_2 + O. \tag{d}$$
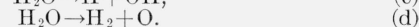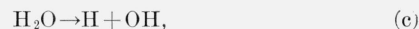
The probability of process (c) being three times that of process (d). It is suggested that primary process (d) constitutes a reasonable photochemical mechanism for hydrogen formation in the earth's upper atmosphere.

Accuracy of analytical procedures, W. J. Youden, *J. Assoc. Official Agricultural Chemists* **45,** *No. 1, 160–173 (Feb. 1962).*
Most analytical chemistry procedures are expected to give correctly, except for random analytical errors, the amount present. This means that if the amounts found are plotted against the amounts present, the points should lie closely along the line $y = x$ where y is the amount found for a material containing amount x. Some procedures may recover only a constant percentage of the amount present and the best fitting line would be of the form $y = bx$. Other procedures may be subject to a constant error and the appropriate line would correspond to the equation $y = a + x$. A simple statistical technique is described that may be used to ascertain whether the data constitute evidence that the theoretical line, $y = x$, does not adequately represent the relationship between the amount taken and the amount found. Some remarks on round robins are included.

Other NBS Publications

Journal of Research 66B (Math. & Math. Phys.) No. 2 (Apr.–June 1962) 75 cents.
Hindsight technique in machine translation of natural languages. I. Rhodes and F. L. Alt.
An extension of Jensen's theorem for the derivative of a polynomial and for infrapolynomials. O. Shisha.
Two matrix eigenvalue inequalities. S. Haber.
Graphs for determining the power of Student's t-test. M. C. Croarkin.

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