

method. The conversion factor is therefore not so precisely known as are the relative wave-lengths on the Siegbahn scale, and a general recalculation of wave-lengths is inadvisable before a sufficiently accurate value of the conversion factor has been established. Crystal measurements may be normally expressed in X-units, which should be recognised as differing from  $10^{-11}$  cm by about 0.2%; on the few occasions when values in cm or A.U. are required the conversion factor of  $1.00201 \times 10^{-8}$  should be used to obtain these from the values in X.U.

III.—In the third letter, Lipson and Riley mention a decision reached at the second X-ray Conference of the Institute of Physics, *viz.*, that the matter of the adoption of the new wave-lengths should be raised with the interested groups in America. They repeat their opinion that the change to an absolute scale is immediately desirable, particularly as they think it unlikely that the accuracy of the conversion factor will increase with time. They suggest in the meantime a convention whereby crystal measurements are given in A.U. if an accuracy not better than 0.1 % is claimed, but X-units should be utilised for measurements of greater precision. For example the lattice parameter of iron could be given as 2.86 A.U. or 2860.4 X.U., but not as 2.8604 A.U.

IV.—Wilson objects to the Lipson and Riley convention, first because it gives a wrong impression of the potential accuracy of X-ray measurements, and secondly because it is generally agreed that a unit about the size of the Ångström is more convenient for expressing results than the X-unit. He suggests that determinations based on the Siegbahn scale should be denoted by "kX" (thousands of X-units); this symbol is short and no changes in the unit are required merely for order of accuracy.  
H. P. R.

## Physical Methods, Apparatus, etc.

**Absolute X-ray Wave-lengths as Fundamental Units of Measurements.** I: H. Lipson and D. P. Riley. II: M. Siegbahn. III: H. Lipson and D. P. Riley. IV: A. J. C. Wilson. (*Nature*, 1943, 151, 250; 502; 502; 562.)—I.—There is a discrepancy between the values of X-ray wave-lengths as measured on the Siegbahn scale and absolute X-ray wave-lengths. At present lattice spacings of crystals are based on the Siegbahn X-unit, which is obtained from the calculated value 3029.04 X-units for the  $d_1$  lattice constant of calcite at 18°C. The X-unit was therefore as near as possible  $10^{-3}$  Ångström units, or  $10^{-11}$  cm, in the light of the accepted value of Avogadro's number,  $N_0$ , at the time of the original wave-length measurements.

Absolute wave-lengths, more recently determined by means of ruled gratings, do not agree exactly with the Siegbahn scale. A discrepancy is found which makes the X-unit differ from  $10^{-3}$  A.U. by 0.2%. The differences can be ascribed to an error of a few tenths % in the earlier value of the electronic charge,  $e$ , from which  $N_0$  was derived. Lipson and Riley suggest that the continued use of the Siegbahn scale is undesirable and that some endeavour should be made to adopt the new values. They instance errors that would be involved in the determination of molecular weights from X-ray measurements if the Siegbahn scale were combined with the most recent value of  $N_0$ ; the use of an arbitrary value of  $N_0$  is deprecated. The errors may be quite substantial when substances of high molecular weight are being studied.

II—Siegbahn points out that the ruled-grating method of determining X-ray wave-lengths does not give the same degree of accuracy as the crystal

**Spectroscopic Method for the Analysis of Hydrocarbon Mixtures.** R. B. Barnes, U. Liddel and V. Z. Williams. (*Ind. Eng. Chem., Anal. Ed.*, 1943, 15, 83-90.)—Infra-red absorption spectroscopy can be applied to the identification, analysis and control of hydrocarbon mixtures. Advantages over the ordinary methods of physical separation by fractional distillation are: (1) considerable saving of time; (2) the spectroscopic method works equally well with gases or liquids and requires only a small sample; (3) the spectroscopic method is readily adapted for use in the production plant, since the absorption cell can be arranged so that a portion of the product can be by-passed through it and, (4) the addition of a relay device permits automatic process control. Details are given of a compact, optically powerful, infra-red spectrometer designed for such analyses. This has been applied particularly to the investigation of materials used in the synthetic rubber industry. For example, mixtures of normal butane and isobutane can be analysed for each component with an accuracy within  $\pm 1\%$ . The time taken is about 3 hr. to establish the calibration curve and 10 min. for each subsequent sample. The necessary spectral requirements for the analysis of binary and more complicated mixtures are discussed. Spectra are illustrated of butanes, butenes, isobutylene, butadiene, styrene, polystyrene, acrylonitrile, 2,3-butylene glycol, natural rubber and seven types of synthetic rubber. The wavelength range  $5\mu$  to  $13\mu$  was found to be the most useful for the problems considered.  
B. S. C.

**Spectrographic Detection and Determination of the Halogens.** W. W. A. Johnson and D. P. Norman. (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 119.)—By the use of a normal high voltage spectrographic spark method the halogens can be detected. With chlorine and bromine, the most sensitive lines are masked by air lines, which cannot be quenched by the usual method of having a large self inductance in the circuit, as under these conditions the lines of the halogens also become exceedingly faint. For chlorine and bromine it is therefore necessary to run the spark inside a small Pyrex tube through which specially pure carbon dioxide is passed; carbon dioxide generated from solid  $\text{CO}_2$  was found to be contaminated with chlorine, and ordinary commercial carbon dioxide contained traces of nitrogen and chlorine. All spectrograms were taken in the first order of a 3-metre grating instrument having a dispersion of 5.6Å per mm. Pure graphite electrodes, 6 mm diam., were used, the powdered sample being placed in a suitable crater in the lower electrode and flattened off level with the rim of the crater. The upper electrode was pointed and placed 2 mm above the sample surface. The electrical conditions of the condensed spark were as follows:—25,000 volts, 17 to 21 milliamps., capacity 0.004μF, no added inductance, all leads as short as possible. The following lines are the most satisfactory:

Fluorine	6856.02Å	Chlorine	4794.54
	6902.46		4810.06
			4819.46
Bromine	4678.69		
	4704.86	Iodine	5161.19
	4785.50		5464.61
	4816.71		

The spectroscopic sensitivity of the halogens varies with the matrix in which they occur and the cations to which they are attached. In general, amounts of the following order of magnitude can be detected with certainty:

Element	Identification limit (μg)	Sensitivity limit (%)
Bromine (in $\text{CO}_2$ )	500	0.3
Chlorine (in $\text{CO}_2$ )	900	0.5
Fluorine (in air)	200	0.1
Iodine (in air)	100	0.07

B. S. C.

**Preparation of High-Temperature Stopcock Greases.** I. E. Puddington. (*J. Amer. Chem. Soc.*, 1943, **65**, 990–991.)—Solns. of metallic soaps, particularly lithium or aluminium stearate, in good quality lubricating oils form stable stopcock greases which resist high temperatures. Prepare a cold dispersion containing 15–20% of soap in the oil, and heat until solution occurs. If a hard gel forms on cooling, work it mechanically to a smooth paste, either by using a spatula and a glass plate or by forcing the gel through a small orifice several times. The vapour pressure of the resulting grease is due almost entirely to the oil; except where very high vacua are required, stripping the oil by vacuum distillation will probably render it sufficiently non-volatile. The vapour pressure of commercial aluminium stearate appears to be about  $10^{-5}$  mm at  $170^\circ\text{C}$ ., and that of lithium stearate less than  $10^{-8}$  mm, the difference possibly being due to free stearic acid in aluminium stearate. A lump of grease containing 20% of lithium stearate in a number 50 S.A.E. mineral oil retained its shape after 2 hr. at  $175^\circ\text{C}$ ., whilst a similar grease containing 20% of commercial aluminium distearate

melted to a viscous liquid in less than 20 min.; the viscosity of the melted material was sufficient to give a good seal. A small volume vacuum system containing a 14/35 ground-glass joint lubricated with these greases showed at  $170^\circ\text{C}$ . a pressure increase of non-condensable gases from  $10^{-5}$  mm to  $10^{-2}$  mm in 18 hrs. The consistence of these greases does not increase greatly until they are cooled below the pour-point of the oil. The greases resist halogenation. E. M. P.

**New Method for Measuring Specific Surfaces of Fibres.** J. d'A. Clark. (*Paper Maker*, 1942, **104**, TS 62–64, 65–67.)—The principle of the method is the deposition of a continuous film of metallic silver, about  $0.1\mu$  thick, on the fibres by reason of their reducing properties, and the subsequent measurement of the unknown area of exposed silver in terms of the amount of hydrogen peroxide it will decompose catalytically under standardised conditions. The method is calibrated against the results obtained with measurable surfaces, e.g., silvered cellophane. Heat for 10–30 min. (according to the reducing properties of the fibres) ca. 100 mg of the fibres in ca. 150 ml of a soln. prepared by adding ammonia carefully to a 4% soln. of silver nitrate until the colour of the brown ppt. lightens and almost completely disappears. To a measured vol. of the suspension containing a known wt. (ca. 20 mg) of fibres, add 5 ml of a buffer soln. (containing 25 g of hydrated sodium borate and 20 ml of  $N$  sodium hydroxide in 500 ml), and dilute to 100 ml. Pour the mixture into a reaction-flask fitted with a glass stirrer, a thermometer and 2 inlet tubes connected to a tap-funnel and to the jet of a burette, respectively. Place 25 ml of 0.5  $N$  hydrogen peroxide soln. (standardised against 0.5  $N$  potassium permanganate) in the funnel, the outlet tap of which is closed, start the stirrer, open the tap-funnel suddenly and start a stop-watch. The degree of catalytic decomposition of the hydrogen peroxide is directly proportional to the area of the silvered surface; the silver coating remains intact, so that the reaction is independent of either the wt. or thickness of the deposit. After ca. 50 sec. read the thermometer, close the tap of the funnel, and place 15 ml of 2  $N$  sulphuric acid in the latter. After exactly 100 sec. from the beginning of the reaction open the tap quickly, when the entry of the acid will stop the reaction. Titrate the unused hydrogen peroxide with the 0.5  $N$  potassium permanganate to a faint pink end-point. Cut sheets of cellophane of known area (not less than 5 sq. cm.) into fine strips, and repeat the experiment under exactly the same conditions; it is thus possible to construct a calibration chart relating the ml of 0.5  $N$  potassium permanganate used and the surface of the sample at various temperatures between  $16^\circ$  and  $40^\circ\text{C}$ . This corresponds with the formula  $A = 176 (1.398 - \log n) / [1.398 - \log (11.55 - 0.273 (t^\circ - 20)]$ , where  $A$  is the area of the sample in sq.cm;  $n$ , the vol. of unused peroxide in ml;  $t^\circ$ , the average reaction temp. in  $^\circ\text{C}$ . Thence, calculate the specific surface by dividing the area found by the wt. of sample. Care must be paid to the cleanliness of the apparatus, because of the danger of poisoning the catalyst. When the experiment has been completed add conc. nitric acid to the reaction-mixture to dissolve the silver, and then determine the amount of this metal present by titration with 0.1  $N$  potassium thiocyanate (ferric ammonium sulphate as indicator); the result enables the thickness of the silver coat to

be calculated from the area. Data are presented showing the effects of temperature, time, thickness and area of the silver coating, and concn. of the hydrogen peroxide on the reaction. Viscose is preferable to acetate transparent film or to silver foil for the standardisation. The method is more rapid and simpler than existing methods, and has an error of

*ca.* 5%; it also takes into account sub-microscopic irregularities, and for this reason there are indications that results obtained by the usual methods for rayon fibres are *ca.* 100% low. Applications to the study of the changes which occur during the beating of fibres for paper manufacture are described  
J. G.