centrations in all cases differ considerably from those found by surface tension measurements on aqueous solutions of the sulfonates.[1a] This change is considerably greater with the saturated than with the unsaturated solutions. With the latter the shift is probably caused by a partial saturation at the interface during the time that elapsed between the formation of the drop and the exposure of the photographic film.

The critical concentrations of the sulfonate solutions as shown by the equilibrium interfacial tension together with the values found by surface tension measurements on the sulfonate solutions[1a] are recorded in Table III, the percentage change in concentration being included. There is a marked relationship between this percentage and the carbon chain length of the sulfonate. The findings of Powney and Addison[4] are similar to the non-equilibrium values.

TABLE III

CHANGE OF CRITICAL CONCENTRATION UPON SATURATING AQUEOUS SOLUTIONS OF LONG-CHAIN SODIUM SULFONATES WITH BENZENE

Length of chain	Critical concentration Surf. ten.	Interfac. ten.	Change, %
10	0.0370	0.0317	14
12	.0100	.0073	27
14	.0027	.0017	37

The primary factor causing the shift in the critical concentration when the solution is saturated with benzene is not clearly understood. Most likely it is due mainly to the well-known solvent action of the micelles.[13] Many organic substances, which are normally insoluble in water, dissolve appreciably in solutions of paraffin-chain colloidal electrolytes with concentrations above the critical values; solution evidently occurs in the hydrocarbon interior of the micelle. The data presented above indicate that the benzene not only dissolves in the micelles but actually aids in their formation.

Some portion of the difference between the interfacial tension values for equilibrium and non-equilibrium conditions might possibly be due to solution of some sodium alkane sulfonate in the benzene,[14] although this would seem unlikely because of the low solubility of the sodium salt in benzene.[4] Further work is being done in an attempt to answer this question.

Summary

1. The equilibrium surface tensions of solutions of dodecane sulfonic acid and of magnesium octane sulfonate have been determined at 40°. The data, considered with others, indicate the marked role the gegen ion plays in micelle formation.

2. Both equilibrium and non-equilibrium interfacial tensions have been measured for solutions of sodium decane, dodecane and tetradecane sulfonate against benzene. The data show that the critical concentration for micelle formation with benzene-saturated solutions is lower than that for aqueous solutions of the corresponding sulfonates not containing benzene; the decrease is a function of the carbon chain length. Benzene appears to aid in micelle formation.

SEATTLE, WASHINGTON RECEIVED[15] APRIL 9, 1946

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[13] Smith, *J. Phys. Chem.*, **36**, 1401, 1672 (1932); Lawrence, *Trans. Faraday Soc.*, **33**, 325, 815 (1937); McBain and co-workers, THIS JOURNAL, **58**, 2610 (1936); **60**, 223 (1938); **63**, 670 (1941); *Ind. Eng. Chem.*, **34**, 915 (1942); "Recent Advances in Colloid Science," Interscience Publishers, New York, N. Y., 1942, p. 99; Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie, Paris, 1936.

[14] Davis and Bartell, *J. Phys. Chem.*, **47**, 40 (1943).

[15] Original manuscript received October 8, 1943.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA AND THE DEPARTMENT OF RESEARCH IN CHEMICAL PHYSICS OF MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

A Redetermination of the Lattice Constant of Lead

BY HAROLD P. KLUG

The lattice constants of the elements are of such fundamental importance in both theoretical and applied chemistry that it is desirable to know them with the highest precision possible. One of the problems of precise lattice constant determination is the acquisition of a sample of sufficient purity to warrant such a study. Recently a sample of lead of very exceptional purity became available, so it seemed desirable to make a redetermination of the lattice constant.[1] The results of the investigation are reported in this communication.

Spectrographic analysis indicated the sample to have a purity of $99.999^{+}\%$ lead. The only metallic impurity lines observed were a very weak bismuth line and a very weak copper line. The best sample of lead to have a diffraction study up to the present is apparently that used for a determination of its thermal expansion by Stokes and Wilson,[2] which they report to have a purity of 99.997%, the impurities observed being silver, copper, antimony and bismuth.

The details of the X-ray technique used in the precision lattice constant determination have been described earlier.[3] CuK radiation was used

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[1] The author wishes to express his appreciation to H. R. Harner, chief chemist, Eagle-Picher Lead Company, Joplin, Mo., for generously providing this sample.

[2] Stokes and Wilson, *Proc. Phys. Soc.* London, **53**, 658 (1941).

[3] Klug and Alexander, THIS JOURNAL, **62**, 1492 (1940).

TABLE I

DIFFRACTION AND LATTICE CONSTANT DATA FOR LEAD AT 25 ± 0.1°

Film no. →	Specimen A				Specimen B	
Indices	M395 Sin θ	M397 Sin θ	M398 Sin θ	M399 Sin θ	M411 Sin θ	M412 Sin θ
$(531)_{\alpha_1}$	0.92092	0.92086	0.92105	0.92110	0.92087	0.92093
$(531)_{\alpha_2}$	.92336	.92339	.92335	.92351	.92331	.92330
$(600)_{\alpha_1}$	.93400	.93398	.93397	.93395	.93389	.93396
$(600)_{\alpha_2}$	.93642	.93639	.93647	.93652	.93630	.93641
$(620)_{\alpha_1}$	.98405	.98422	.98418	.98422	.98416	.98421
$(620)_{\alpha_2}$	.98658	.98660	.98657	.98656	.98656	.98654
Lattice constant, a_0, in kX units	4.9409_5	4.9403_6	4.9406_4	4.9408_7	4.9406_0	4.9405_4

in this study. The specimen consisted of fine filings sealed inside a thin-walled ethyl cellulose tube of 0.6 mm. internal diameter.

A summary of the results from six separate determinations using two different specimens is given in Table I.

These findings show an average value of a_0 = 4.94066 ± 0.00006 kX units at 25°, in which the error indicated is the probable error of the mean. This value must be corrected for refraction[4] by the addition of the calculated correction 0.00014. Accordingly, the final value for a_0 is 4.9408 ± 0.0001 kX units. The density of lead at 25° calculated from this new value for the lattice constant is 11.341. The experimentally determined value is reported by the "I. C. T." as 11.348 at 16.34° and 11.337 at 19.94°.

In Table II the present value for the lattice constant of lead is compared with earlier data. Still earlier values are in the literature, but they cannot be considered to be precision values in any sense of the word. Where the observer did not determine his value precisely at 25°, it has been calculated at 25°, using Stokes and Wilson's[2] value of the coefficient of expansion, for inclusion in Table II. In addition to the present value, only that of Owen and Yates has been corrected for refraction.

The present value is slightly larger than previous values, being in line with its higher purity than other samples. Lead atoms are larger than other atoms commonly found as impurities. The atomic radii[5] for lead and the impurities reported by Stokes and Wilson are as follows: Pb, 1.746; Ag, 1.441; Cu, 1.275; Sb, 1.439; Bi, 1.55 kX units. Such impurities in substitutional solid solution would decrease the lattice constant from its value for pure lead. Accordingly successively purer samples should yield increasingly larger values of a_0.

TABLE II

COMPARISON WITH EARLIER LATTICE CONSTANT DATA FOR LEAD

Observer	a_0 at 25° in kX units	Sample purity reported
Klug (this study)	4.9408	99.999+%
Owen and Yates[a]	4.9406	99.9
Owen and Iball[b]	4.9405	99.9
Stokes and Wilson[c]	4.9404	99.997
Lu and Chang[d]	4.9400	? (Hilger H.S.)
Jette and Gebert[e]	4.9385 (room temp.)	99.9
Obinata and Schmidt[f]	4.938	99.99

[a] Ref. 4. [b] Owen and Iball, *Phil. Mag.* [VII] **13**, 1020 (1932). [c] Ref. 2. [d] Lu and Chang, *Proc. Phys. Soc.* (London), **53**, 517 (1941). [e] Jette and Gebert, *J. Chem. Phys.*, **1**, 753 (1933). [f] Obinata and Schmidt, *Metallwirtschaft*, **12**, 101 (1933).

Summary

The best value for the lattice constant of lead at 25 ± 0.1° is 4.9408 ± 0.0001 kX units.

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(4) Owen and Yates, *Phil. Mag.*, [VII] **15**, 472 (1933); Wilson, *Proc. Cambridge Phil. Soc.*, **36**, 485 (1940).

(5) Stillwell, "Crystal Chemistry," McGraw-Hill Book Co., New York, N. Y., 1938, p. 417.