nated. In addition, with an attached barometer and a system for evacuation and supplying gas, an experiment can be conducted at either a standard pressure or at a pressure which may be chosen in order to simplify calculations.

Manometers constructed of glass are necessarily fragile, and are likely to be somewhat variable. More important, it is not convenient to provide definite stops for the valves at the off and on positions, nor is it convenient to provide strong spring-loading of the valves to prevent leakage. It appeared that Lexan, a clear and extremely tough plastic, would be a good choice for the body of a manometer, and that Delrin would be a good material for the stopcock inserts. The manometer shown was machined from block Lexan, but will be injection-molded in the future. The valves are spring-loaded, and have definite stops. An additional valve is provided to disconnect individual manometers from the manifold (Fig. 2).

In the operation of a respirometer, simultaneous opening and closing of the operating valves offers a great convenience. The construction mentioned above makes it possible to perform this function simply. Pressure on one lever will close all of these valves, and pressure on another will open all of them. The valves may also be operated individually.

In order to utilize more fully the possibilities inherent in a constant pressure system, a respirometer was constructed with stationary micrometric manometers (volumometers) (Fig. 3). These volumometers are each connected by means of a flexible plastic tube to a Warburg-type flask of whatever variety is needed for the experiment in progress. Shaking of the flasks is continuously variable in rate from 75 to 150 per minute, and in extent from 0 to 5 cm.

The respirometer constructed has a number of advantages for nondifferential as well as for differential respirometry: (i) a digital reading is obtained directly in microliters; (ii) calibration of the glassware is not necessary; (iii) the manometers are stationary, and easily read; (iv) all manometers are simultaneously visible; (v) spring-loaded valves have definite stops for off and on positions; (vi) valves may be simultaneously operated by levers for opening and closing; and (vii) a very solid construction can readily be employed.

The most significant improvement in technology in this apparatus is provided by a combination of the above-named advantages, with the immunity to changes in temperature and barometric pressure inherent in the differential connection. In comparison with the conventional nondifferential Warburg apparatus, the several-fold increase in accuracy and reproducibility of results of a differential system is achieved without the added bulk or complexity of multiple reference flasks.

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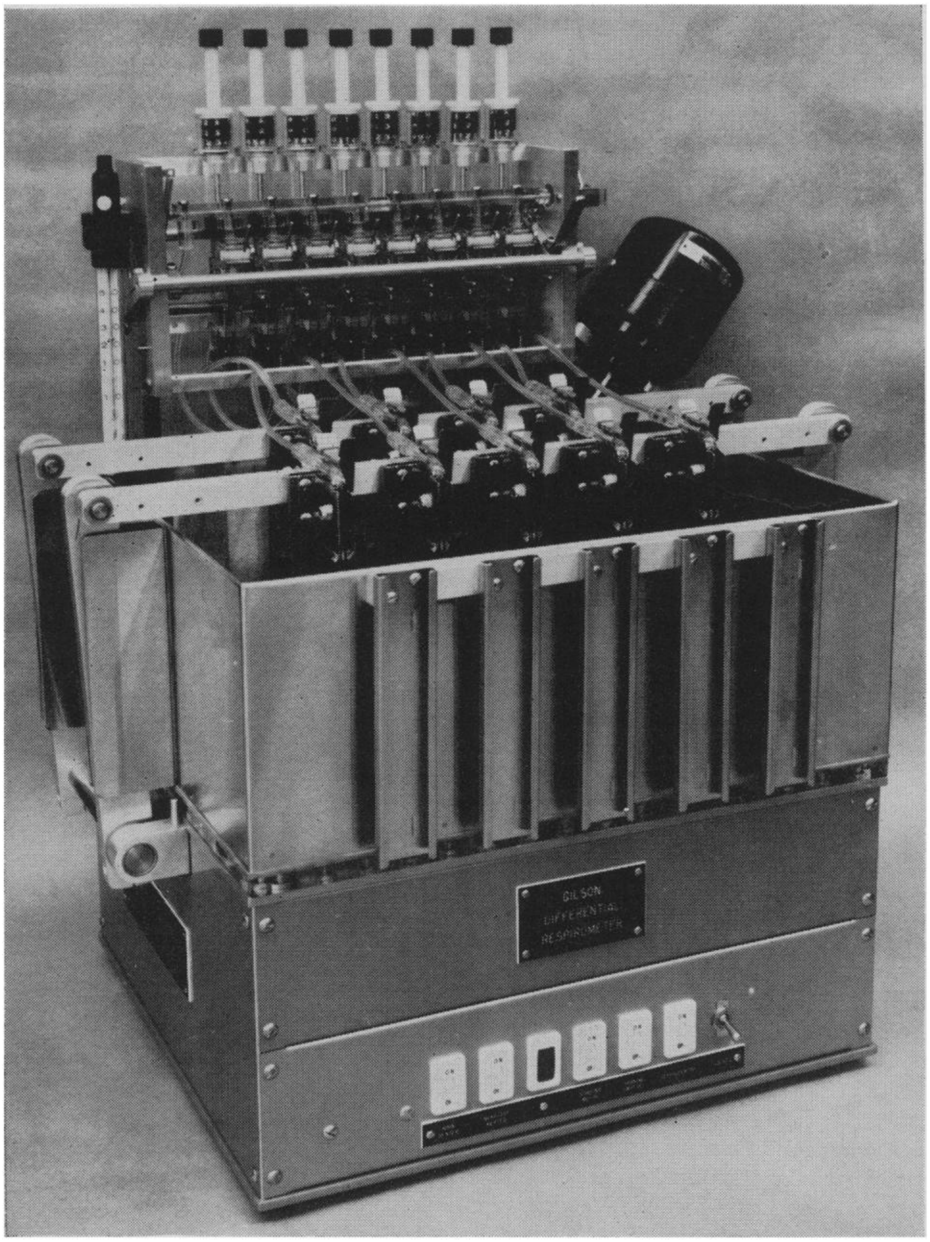

Fig. 3. Differential respirometer.

Geometry of the Perxenate Ion

Abstract. *A three-dimensional x-ray analysis of a crystalline solid of* Xe^{+8} *formed by the reaction of* XeF_6 *with sodium hydroxide solution indicates that it is sodium perxenate octahydrate,* $Na_4XeO_6 \cdot 8H_2O$*. The perxenate ion,* XeO_6^{-4}*, has approximately a regular octahedral configuration with a mean xenon-oxygen bond length of 1.875 Å.*

The reaction of XeF_6 with sodium hydroxide has been shown by Malm *et al.* (*1*) to produce compounds which contain octavalent xenon and which, on the basis of chemical analyses, prob-

Table 1. Parameters for the $Na_4XeO_6 \cdot 8H_2O$ structure. B is the isotropic thermal parameter.

Atom	x	y	z	B (Å^2)
Xenon	0	0.2020 ± 0.0002	¼	0.81 ± 0.06
O_1	0	.385 ± .002	¼	1.8 ± 0.4
O_2	0	.022 ± .003	¼	
O_3	0.104 ± 0.002	.204 ± .003	0.378 ± 0.003	
O_4	.118 ± .002	.206 ± .002	.130 ± .002	
Na_1	.119 ± .001	.430 ± .001	.438 ± .001	1.9 ± 0.2
Na_2	.281 ± .002	.214 ± .001	.264 ± .001	
$Water_1$	.316 ± .002	.418 ± .002	.410 ± .002	1.9 ± 0.2
$Water_2$	.436 ± .002	.144 ± .002	.428 ± .002	
$Water_3$	.326 ± .002	.018 ± .002	.157 ± .002	
$Water_4$	.380 ± .002	.349 ± .002	.123 ± .002	

ably contain the XeO_6^{-4} ion. These salts were described as relatively stable, with a tendency to change hydration number. The formula $Na_4XeO_6 \cdot 5H_2O$ was given to the product which first separates from NaOH solution. Siegel (*2*) ascribes to this compound an orthorhombic unit cell, with constants $a = 10.36$, $b = 10.45$, $c = 11.87$ Å.

Because of the paucity of information concerning the geometry of xenon coordination in the higher valence states, we decided to investigate the crystal structure of one of these salts. In addition to providing information about the geometry of this unique ion, the crystal-structure determination provides a powerful method of determining the formula of the compound.

Our material was prepared by adding about 1 ml of 1*M* NaOH to several milligrams of XeF_6 containing some XeF_4 at 77°K. A yellow color which appeared in the frozen mixture disappeared as the mixture melted. After several minutes, colorless well-developed crystals with dimensions ranging up to several tenths of a millimeter began to separate out on the walls of the test tube. Several of these crystals were selected for x-ray photography and mounted in thin-walled glass capillaries to reduce dehydration or possible decomposition to a minimum.

All photographs were taken with MoKα x-rays on plate-like crystals measuring approximately $0.2 \times 0.2 \times 0.05$ mm. The linear absorption coefficient calculated for the formula $Na_4XeO_6 \cdot 8H_2O$ is 29 cm^{-1}, so that absorption errors should not seriously affect the intensity measurements.

The crystals investigated are orthorhombic with cell constants $a = 11.87$, $b = 10.47$, $c = 10.39$ Å (all ± 0.02 Å). On the basis of the agreement between these cell constants and those of Siegel (*2*) (after a redefinition of axes), it is clear that the same material was prepared here as was analyzed for Xe oxidation number and ratio of Na to Xe by the Argonne workers. The observed extinctions (*hk*0, $h + k$ odd; *h*0*l*, *l* odd; 0*kl*, *k* odd) indicate that the space group is D_{2h}^{14} – *Pbcn* (*3*). The density, as measured by flotation in mixtures of methylene dibromide and carbon tetrachloride, is 2.33 ± 0.05 g cm^{-3}.

Although this is in poor agreement with four formula weights of the pentahydrate in the unit cell ($\rho_{calc} = 2.10$ g cm^{-3}), it is in excellent agreement with the formula $Na_4XeO_6 \cdot 8H_2O$ ($\rho_{calc} = 2.38$ g cm^{-3}) which was deduced from the structure determination.

Data suitable for structure analysis were collected at room temperature by multiple-film Weissenberg photography of the reciprocal lattice nets *hkl*, with $h = 0, 1, \ldots, 13$. All independent intensities strong enough to be observed that were accessible within the scattering angle of 26° for the MoKα source were estimated visually. The 718 observed intensities were corrected for Lorentz and polarization effects and converted to structure amplitudes. A final set of photographs of the (0*kl*) nets was taken at the end of the experiment. These were identical with the initial photographs and thus they provide good evidence for the stability of the material during the 72 hours of photography.

As the multiplicity of the general positions in *Pbcn* is 8, the four Xe atoms must lie in special positions. It was clear from the examination of the intensities of several reflections that Xe must be placed on the twofold axis in the special positions (*3*)

$$c) \pm (0, y, \tfrac{1}{4}; \tfrac{1}{2}, \tfrac{1}{2} + y, \tfrac{1}{4})$$

with y approximately equal to 0.20. Examination of the Patterson function confirmed this assignment and indicated clearly the positions of the six atoms bonded to Xe. Two of these were placed in two sets of special positions on the twofold axis, and four were placed in two sets of general positions. Successive least-squares refinements and difference electron-density syntheses led to the placement of six more atoms in general positions in the asymmetric unit. From their coordination and peak heights in the electron-density maps, two of the atoms were identified as sodium, and the four remaining were assigned as oxygen, presumably in water molecules. A final series of least-squares refinements on the present data led to the parameters listed in Table 1. A final difference electron-density synthesis contains no peaks higher than 2.0 electrons Å^{-3}, while the peaks for the atoms identified in earlier difference syntheses have heights which range from 10 electrons Å^{-3} for water to 17 electrons Å^{-3} for sodium. The final agreement factor

$$R = \frac{\Sigma \left| \, |F_{obs}| - |F_{calc}| \, \right|}{\Sigma \, |F_{obs}|}$$

is 0.10 for all the 718 observed reflections and is 0.16 for the generally weaker 123 reflections with $h + k$ odd to which the Xe, O_1, and O_2 on the twofold axis do not contribute.

It would be impossible to distinguish between hydroxyl groups and water molecules by the x-ray diffraction experiment. The presence of hydroxyl groups would, however, be hard to explain in view of the clear stereochemical evidence that there are four sodium atoms per molecule and also the reported oxidation number of + 8 for Xe.

Chemical analyses on our sample confirm this oxidation number of Xe and indicate that the material is fluoride free. Furthermore, there are a number of O . . . O distances in the range 2.65 to 3.0 Å which can be interpreted in terms of a very reasonable overall hydrogen-bonding scheme for water molecules and XeO_6^{-4} ions. From these arguments, and from the reasonableness of the molecular packing, we conclude that the material studied here is $Na_4XeO_6 \cdot 8H_2O$. The volume per oxy-

Table 2. Geometry of the XeO_6^{-4} octahedron. The ± indicates estimated standard deviation.

Bond	*Distance* (Å)
Xe-O_1	1.92 ± 0.03
Xe-O_2	1.88 ± 0.03
Xe-O_3	1.82 ± 0.03
Xe-O_4	1.87 ± 0.02
Bond Angle	*Angles* (*degrees*)
O_1-Xe-O_3	89.4 ± 0.9
O_1-Xe-O_4	88.9 ± 0.6
O_3-Xe-O_4	88.7 ± 0.9

gen atom is thus 23.1 Å^3, a typical value for hydrates.

Some interatomic distances and angles are listed in Table 2. The perxenate ion, XeO$_6^{-4}$, has approximately the form of a regular octahedron of oxygen atoms surrounding the central Xe. The O-Xe-O bond angles do not differ significantly from 90°. Although the Xe-O bond lengths do differ slightly, and might be expected to because of the different ways in which the four independent oxygen atoms appear to hydrogen-bond, the hypothesis, "the four independent Xe-O bond lengths are equal," cannot be rejected at the 5 percent significance level by a χ^2 test. The ion is required by its position in the unit cell to have a twofold axis passing through Xe, O$_1$, and O$_2$, and our results indicate that the symmetry of the ion may not be significantly different from O_h. The mean bond length is 1.875 Å with a standard deviation of the mean of 0.021 Å. This is 0.12 Å longer than the average Xe-O distance of XeO$_3$ (*4*). This compares well with the increase of 0.11 Å in the I-O distances in the isoelectronic iodine-containing ions. The I-O bond length in a typical iodate ion is 1.82 Å (*5*), while in the IO$_6^{-5}$ ion in (NH$_4$)$_2$H$_3$IO$_6$ it is 1.93 Å (*6*).

Each of the two independent sodium ions is coordinated to six oxygen atoms in a distorted octahedral arrangement, with Na-O distances ranging from 2.39 to 2.70 Å. In the complex hydrogen-bonding scheme postulated for the structure, each of the oxygens of an XeO$_6^{-4}$ octahedron is involved in hydrogen bonding to water. This hydrogen bonding and the linking of the sodium octahedra by the sharing of edges and corners appear to determine the overall structure of the crystal (*7*).

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High Pressure X-ray Diffraction Studies on Barium

Abstract. *Simultaneous x-ray diffraction and electrical resistance measurements on barium establish, with certainty, that Bridgman's 78-kb resistance transition is identical with his 59-kb volume transition. During this transition, the body-centered cubic structure changes to hexagonal-close packed. Lattice parameters for the latter structure at 62 kb (volume scale) are:* $a = 3.90$ *Å,* $c = 6.15$ *Å, and* $c/a = 1.58$*. Compression* ($\Delta V/V_0$) *at 62 kb is 0.359* ± *0.005 compared to 0.345 previously reported by Bridgman. Below the transition, at 49 kb, compression is 0.300* ± *0.005 compared to Bridgman's 0.288. Bridgman's 17-kb volume transition was not detected by x-ray diffraction.*

In addition to the intrinsic interest of determining the crystallographic nature of pressure-induced phase changes previously reported to occur in barium (by displacement and electrical resistance measurements), x-ray measurements are important because the 59-kb transition is used as a fixed-pressure calibration point. In 1942, Bridgman published compressions of Ba to 100 kb and reported two volume discontinuities (*1*). The first of these was said to occur at 17 kb with compressions ($\Delta V/V_0$) of 0.135 and 0.141. The second was reported to occur at 59 kb with compressions of 0.318 and 0.337.

In 1952, Bridgman published a curve of the relative electrical resistance of Ba to 100 kb (*2*). There was a sharp resistance discontinuity occurring at 78 kb (which Bridgman suggested might be associated with the 59-kb volume discontinuity observed 10 years earlier). He also reported evidence of a small electrical resistance discontinuity related to the 17-kb volume change.

During the early development of ultra-high pressure, high-temperature apparatus, researchers assumed 78 kb to be the correct value for the Ba resistance transition and used it as a fixed-pressure reference point. This was comfortable because this value, along with Bridgman's values for electrical resistance transitions in Tl (44 kb) and Cs (54 kb), gave a straight-line relationship between applied load and chamber pressure. This "old" pressure scale was unquestioned until Kennedy (*3*) suggested that Bridgman's resistance transitions in Tl, Cs, and Ba were all too high and that these transitions were actually identical with Bridgman's volume transitions reported to occur at about 25-percent lower pressure. Very shortly thereafter, researchers generally accepted the identity of the resistance and volume transitions, and adopted a "new" pressure scale which accepted pressure values based on the volume transitions (37, 42, and 59 kb in Tl, Cs, and Ba, respectively).

We have now been able to establish with certainty the fact that Bridgman's 78-kb electrical resistance transition and his 59-kb volume transition occur at the same pressure. This has been made possible by the development of a tetrahedral, x-ray diffraction, high-pressure, high-temperature press at Brigham Young University. This apparatus is equipped with a modified x-ray diffractometer and both strip-chart and print-out recording devices. With this equipment, the electrical resistance of Ba foil was monitored (at room temperature) simultaneously with the monitoring of its Debye-Scherrer diffraction pattern as pressure was slowly increased. A new diffraction pattern appeared simultaneously with the crossing of the resistance discontinuity. This was observed in five separate and independent experiments. The new pattern indicates transformation to a hexagonal close-packed structure. Diffraction data at 62 kb (new scale) for the new structure are presented in Table 1. At 62 kb the values for the lattice parameters *a* and *c* are 3.90 Å and 6.15 Å, respectively. The *c*/*a* ratio is 1.58 which is within the normal range for hexagonal close-packed metals.

Table 1. Diffraction data for Ba with hexagonal close-packed structure at 62 kb.

hkl	$d_{\text{calc.}}$*	$d_{\text{exp.}}$	$I_{\text{calc.}}$	$I_{\text{exp.}}$†
100	3.379	3.376	24	32
002	3.077	3.074	25	38
101	2.962	2.963	100	100
102	2.275	2.264	17	14
110	1.950	1.954	22	23
103	1.754	1.748	23	17
200	1.688		4	
112	1.647	1.646	7	11‡
201	1.628	1.627	19	20‡
004	1.539	1.533	4	5
202	1.481		5	
104	1.400	1.395	4	2
203	1.305	1.305	9	3
210	1.277		3	
211	1.250	1.250	16	5

* Calculated for $a = 3.901$ Å and $c = 6.154$ Å; $c/a = 1.578$. † Integrated intensity. ‡ Incompletely resolved lines.