sec$^{-1}$ and states that the error in analyzed heat flow is, generally speaking, about ± 10 percent (*2*). It is unlikely that the difference between the two determinations at Barnstable is due to a difference in the actual heat flow at the two positions separated by as small a distance as 1.1 km. It may be attributed rather to errors inherent in the method, namely the effects of long-term trends in the climate, such as an unusually cool year followed by an unusually warm one, to possible disturbances due to the movement of ground water in the depths of the peat and to actual errors in the temperature measurement. The measurement of terrestrial heat flow through marsh peat appears to be sufficiently precise to give useful information on its regional value. The procedures might also be usefully employed in freshwater peat bogs, but in such situations the movement of ground water may be found to invalidate the results.

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22 March 1965

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## Sulfur: A New High-Pressure Form

Abstract. *Under high pressures and elevated temperatures, rhombic sulfur is converted to a new cubic form; this form was quenched at room temperature and pressure and studied by x-ray diffraction. Phase boundaries for this new form have been established.*

Elementary sulfur exists in many reasonably well defined forms (*1*). The temperature-pressure relation of sulfur up to 280°C and 20 kb has been established (*2*), and shows only the solid form of sulfur, rhombic sulfur. Bridgman (*3*) applied pressures up to 100 kb at and below room temperature without indications of a new phase of sulfur; he had anticipated the possibility of a metallic form analogous to black phosphorus. David and Hamann (*4*) subjected sulfur to shock pressures of about 250 kb, at which pressure the electric resistivity decreased to 0.03 ohm cm; this drastic reduction was attributed to a possibly metallic form of sulfur. Another interpretation (*5*) attributes this increase in conductivity to impurities as the sulfur is melting along the shock front.

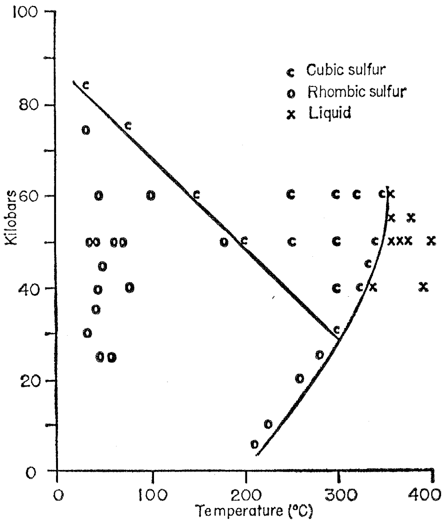

Fig. 1. High-pressure region of the phase diagram of sulfur.

The region above room temperature and at pressures greater than 20 kb is virtually unexplored for sulfur. Therefore, 20- to 30-mg samples of rhombic sulfur in powder form were subjected to pressures between 25 and 83 kb at temperatures at intervals between 25° and 400°C. An opposed-anvil, high-pressure apparatus (Tem-Pres model SJ-100) was used in the experiments. The samples were contained between 0.005-inch (0.13-mm) platinum sheets separated by a ring of the same material; under the conditions of the experiments, there was no indication of reaction between platinum and sulfur. An electric furnace surrounded the anvils and the sample. Occasionally in his experiments Bridgman experienced violent explosions, which he explained by the presence of oxygen adsorbed onto the sulfur. Zubova and Korotaeva (*6*) reached the same conclusion. In my investigation, explosions occurred only when the pressure seal between the platinum sheets and the ring became contaminated by sulfur and thus developed a leak; at elevated temperatures the sulfur burned when it contacted the atmosphere.

In the first of two types of experiment, after heating under pressure to a given temperature, the sample was slowly cooled to 50°C under the same pressure. In the other type of experiment, instead of cooling slowly, the sample was quenched in air. The quenching occurred the moment the pressure was released; the sample was withdrawn, at a given temperature, with a platinum wire that was welded to one of the platinum sheets. In both instances, x-ray diffraction patterns of the samples were obtained immediately.

The results were surprising. In the first series of experiments, when the sample was cooled under pressure, two different types of samples were obtained. One was a thin, solid wafer of rhombic sulfur, as shown by the x-ray pattern. Higher pressure and temperature caused a slight shift toward a more compressed lattice. The behavior of the other type of sample resembled that of plastic sulfur, indicating that it had been melted. The x-ray pattern showed only one single, very strong peak at about 4.04 Å. On exposure to the atmosphere, the plastic sulfur soon hardened and began to convert into rhombic sulfur. The time of conversion varied, depending on the applied pressure: samples prepared at the higher pressures converted at a lower rate. It is felt that the 4.04-Å peak corresponds to the 220 reflection (4.06 Å) of rhombic sulfur and that the crystal-

Table 1. Spacing and indexing of a new cubic form of sulfur.

| *d*Å | Intensities | *hkl* |
|---|---|---|
| 8.93 | vw | 110 |
| 6.55 | w | 200 |
| 6.07 | vw | 210 |
| 5.37 | vw | 211 |
| 4.89 | w | 220 |
| 4.50 | m | 300 |
| 4.31 | m | 310 |
| 4.16 | vvw | 311 |
| 3.91 | vw | 222 |
| 3.79 | w-m | 320 |
| 3.66 | s | 321 |
| 3.42 | m | 400 |
| 3.31 | w-m | 410 |
| 3.22 | w | 411 |
| 3.14 | w | 331 |
| 3.04 | w | 420 |
| 2.98 | vw | 421 |
| 2.93 | w | 332 |
| 2.83 | w | 422 |
| 2.73 | w | 500 |
| 2.68 | m | 510 |
| 2.66 | vw | 511 |
| 2.55 | w | 520 |
| 2.49 | w | 521 |
| 2.42 | vw | 440 |

lization from the liquid state under high pressure is oriented along this plane.

By this method it was possible to follow the liquidus line of sulfur up to 60 kb (Fig. 1). The slope of the liquidus curve shows that the slope of the line changes from positive to vertical with increasing temperature and pressure. According to the Clausius-Clapeyron expression, vertical behavior means that the difference in specific volume between the solid and liquid sulfur disappears, that is to say, their densities are equal.

The quenching experiments were conducted in the area of the temperature-pressure diagram in which the solid sulfur is the stable phase. The x-ray diffraction patterns showed two crystalline forms. One form was the conventional rhombic sulfur and the other was a new cubic form, $a$ = 13.66 Å (Table 1). The data plotted in Fig. 1 show that the triple point of cubic, rhombic, and liquid sulfur is at a pressure of 28 ± 4 kb and a temperature of 300° ± 5°C. The slope of the boundary line between cubic and rhombic sulfur is negative, which, according to the Clausius-Clapeyron expression, occurs because the density of cubic sulfur is higher than that of rhombic sulfur. The density of quenched samples of cubic sulfur was determined by the sink-float method in two experiments: the results were 2.18 and 2.19 g $cm^{-3}$ at 30°C, respectively. The normal density of rhombic sulfur is 2.04 g $cm^{-3}$. The heat of transformation from rhombic to cubic sulfur was calculated as 49 ± 5 cal $g^{-1}$, based on a temperature of 30°C and a pressure of 1 atm. The heat of transformation would be different if the density difference changed significantly with increase in pressure. The cubic form is light yellow and insoluble in carbon disulfide; the unit cell contains 104 sulfur atoms.

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## Nucleotide Synthesis under Possible Primitive Earth Conditions

Abstract. *The nucleosides adenosine, guanosine, cytidine, uridine, and thymidine were each heated with inorganic phosphate. Nucleoside monophosphates were formed in appreciable yield. This result has a bearing on the hypothesis of chemical evolution.*

In our study of chemical evolution the main endeavor has been to reconstruct the path by which the constituents of the nucleic acid molecule could have arisen on the primordial earth before the appearance of life. The synthesis of the bases, adenine and guanine, and the sugars, ribose and deoxyribose, under simulated primitive earth conditions has been demonstrated earlier (*1*). Recent experiments have also shown that the nucleosides, adenosine and deoxyadenosine, could be formed in such an environment (*2*). Several attempts have already been made to synthesize nucleotides abiotically (*3*). Previously, we found that, when a dilute solution of adenine and ribose was irradiated with ultraviolet light in the presence of ethyl metaphosphate, the nucleotides AMP, ADP, ATP, and A4P (mono-, di-, tri-, and tetraphosphates of adenosine) were formed. Although the source of phosphorus used in this experiment was not one most likely to be found on the primitive earth, the result clearly established that the process could occur abiotically. We now find that the simple expedient of heating a nucleoside with a source of inorganic phosphate gives rise to the nucleoside monophosphates in appreciable yield.

In a series of experiments, the nucleosides adenosine, guanosine, cytidine, uridine, and thymidine were heated with sodium dihydrogen orthophosphate, $NaH_2PO_4$. Two sets of experiments were performed. In the first, the nucleosides were labeled with $^{14}C$ (specific activity of 1 mc/mmole). In the second, the phosphate was also labeled with $^{32}P$. An aqueous solution, 100 μl, containing 2 μmole of a nucleoside and 2 μmole of the phosphate was placed in a 5-ml pyrex tube and lyophilized. By this method a film of solid material containing an intimate mixture of the nucleoside and the phosphate was deposited on the walls of the tube. The tube was then sealed and heated to 160°C for 2 hours. After the tube was cooled to room temperature the seal was broken, and the contents were dissolved in 200 μl of water. This solution containing the reaction products was then analyzed.

The analytical techniques used were electrophoresis, paper chromatography, electrophoresis combined with paper chromatography, and ion-exchange chromatography. In each one of these methods the identification of individual products was made with the coincidence technique of chromatography (*4*). This method, which had earlier been used by us for paper chromatography alone, was now extended to electrophoresis and ion-exchange chromatography.

The electrophoresis was performed at 1500 volts with a Pherograph (*5*). With a $p$H 3.5 buffer and Whatman 3MM paper, a satisfactory separation was effected in 1 hour (*6*). A 50-μl sample containing approximately 0.5 μc of the material to be analyzed was streaked at the origin with 10 μg of each of the 2′-, 3′-, and 5′-monophosphates and cyclic 2′,3′-phosphate as nonradioactive carriers. The radioactive spots were located as dark areas on an autoradiograph, and the nonradioactive carriers appeared on a shadowgram as bright spots on a dark background. There was coincidence between the light area on the shadowgram and a dark area on the autoradiograph. This indicated that material having the same electrophoretic mobility as the carriers at $p$H 3.5 had been synthesized in the experiment. Figure 1 illustrates such an analysis for five different experiments starting with adenosine, guanosine, cytidine, uridine,

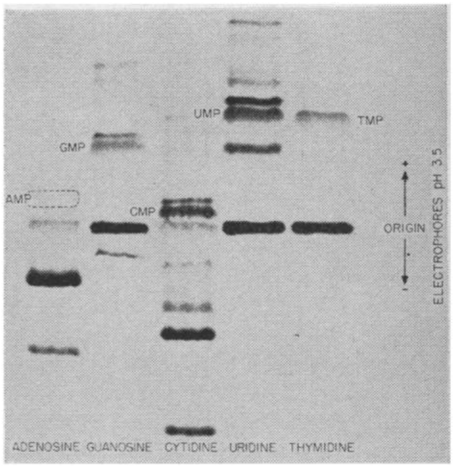

Fig. 1. Reaction between $^{14}C$-nucleosides and $NaH_2PO_4$; autoradiograph shows electrophoretic separation of products at $p$H 3.5. The monophosphates were indentified by the coincidence technique. Several unidentified bands are present.