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History and nature of the gel method

1.1 Introduction

It has long been appreciated that advances in solid state science depend critically on the availability of single crystal specimens. As a result, an enormous amount of labor and care has been lavished on the development of growth techniques. In terms of crystal size, purity, and perfection, the achievements of the modern crystal grower are remarkable indeed, and vast sections of industry now depend on his products. So do the research workers whose preoccupation is with new materials, no matter whether these are under investigation for practical reasons or because a knowledge of their properties might throw new light on our understanding of solids in general.

In one way or another, a very large number of materials has already been grown as single crystals, some with relative ease and others only after long and painstaking research. Nevertheless, there are still many substances which have defied the whole array of modern techniques and which, accordingly, have never been seen in single crystal form. Others, though grown by conventional methods, have never been obtained in the required size or degree of perfection. All these constitute a challenge and an opportunity, not only for the professional crystal grower but, as it happens, also for the talented amateur. New and unusual methods of growing crystals are therefore of wide interest; and if the crystals are by themselves beautiful, as they often are, there is no reason why this interest should be confined to professional scientists.

The art and science of growing crystals in gels enjoyed a long period of vogue close to the end of the last century and lasting well into the 1920s. It remained largely dormant during the 1930–60 period and then experienced a mini-renaissance which held great promise for the future. It would now be pleasing to be able to report on rapid and sustained

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progress ever since, but for a variety of reasons, developments have in fact been slow, especially as far as the more fundamental implications of the growth process are concerned. On the positive side, the astute reader will note that this leaves the research opportunities as great as and as open as they have ever been.

During most of the early period, the center of interest was held by the phenomenon of Liesegang Rings. Liesegang was a colloid chemist, a photographer, and an altogether remarkable man (see Section 5.1), who experimented with chemical reactions in gels (e.g. see Liesegang, 1896, 1898, 1924, 1926).[†] He covered a glass plate with a layer of gelatin impregnated with potassium chromate, and added a small drop of silver nitrate. As a result, silver chromate was precipitated in the form of a series of concentric rings, well developed and with regularly varying spacings. Such structures had actually been reported in the earlier literature, but Liesegang was the first to take them seriously. Runge (1855) had observed them in the course of experiments on the precipitation of reagents in blotting paper! Towards the end of the nineteenth century interest was regenerated in the context of photographic gelatin emulsions (e.g. see Lüppo-Cramer, 1912), and the discontinuous nature of the precipitation, its geometrical features, and the conditions of its occurrence, soon became objects of intense, if not altogether successful, investigations. The matter immediately attracted the attention of the great German chemist Ostwald (1897a, b) and, in due course, need one mention it, that of Lord Rayleigh (1919), thereby receiving what must have appeared as the ultimate seal of respectability. According to a report by Bradford (1926), J. J. Thomson, whose principal interests were in very different fields, likewise concerned himself with the problem of periodic precipitation (but the Royal Institution appears to have no record of the 1912 lecture to which Bradford refers). Oddly enough, all the intense turn-of-the-century activity in the field did not prevent Janek (1923) from reporting periodic precipitation as a new phenomenon. See Deiss (1939) for an extensive overview of phenomena leading to ‘Runge Bilder’, some reproduced in color.

Liesegang’s structures were (quite properly) called rings, because they were first observed in that form, i.e. as concentric deposits in a plane. Later they were more often grown in test tubes, and were therefore disks, but the ‘ring’ designation was by then firmly implanted in the literature, and has prevailed to this day. Rings were considered interesting partly

[†] See bibliography at the end of the book.

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because their origin was obscure and partly because they were reminiscent of certain structures found in nature, e.g. the striations of agate. Often they consisted of apparently amorphous material but, in due course, the achievement of microcrystalline reaction products came to be seen as desirable, because of the ease with which they could be identified by means of x-ray photographs. Larger crystals, several millimetres in size, were occasionally obtained, but not systematically looked for. In contrast, the growth of such crystals is the principal objective of most modern work in this field. This endeavor has, over the years, succeeded to a remarkable extent, but not (possibly not yet) sufficiently to make crystal growth in gels an industrial process. It remains a laboratory process, each specific substance grown being associated with problems of its own. An early claim by Fisher and Simons (1926a) to the effect that 'gels form excellent media for the growth of crystals of almost any substance under absolutely controllable conditions' survives as a shining example of faith, but is, even so, no more than a little tarnished by the sporadic nature of its fulfilment to date.

Surprisingly, in view of the history of the subject, the Liesegang Ring phenomenon itself is even now only partially understood. It has largely been displaced from the center of practical interests, but has in recent years achieved a new intellectual status in the context of fundamental 'order out of chaos' discussions (shades of Prigogine, 1984). It also awaits the talents of a modern Ostwald, with an appreciation of its beauties and more versatile resources than Ostwald was ever able to command. There is no basic mystery, in the sense that periodic solutions of the diffusion equations (with proper allowance for precipitation, resolution and boundary conditions) are known to exist, but little is known about the detailed parameters involved. Even so, a substantial beginning has been made, and recent work, partly with the aid of the computer, makes it possible to relate theory to practice in a general and consistent way. Chapter 5 of the present volume is devoted specifically to Liesegang Ring problems.

Of course, periodic ring and layer formations *found in nature* offer only the most limited opportunities for research into their origin. Indeed, many are due to quite different mechanisms, e.g. changes of overall environment, even though they bear the superficial appearance of Liesegang Rings. As one critical analyst has put it when faced with the suggestion that the stripes of tigers and zebras may be glorified Liesegang phenomena: 'enthusiasm has been carried beyond the bounds of prudence' (Hedges, 1931), a verdict with which the present writer is inclined to concur. In the same spirit of caution, we may want to reject

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the notion that Liesegang phenomena are responsible for the stripes on butterfly wings (Gebhardt, 1912).

Though geology-at-large does not permit experimentation, work during the early period derived a good deal of impetus from the interests of geologists, who believed that all quartz on earth was at one time a silica hydrogel. A vein of gelatinous silica, as yet unhardened by dehydration, was indeed reported to have been found in the course of deep excavations for the Simplon tunnel (Spezie, 1899). Von Hahn (1925) described a similar find on the Lüneburger Heide. (He asked a cardinal question, designed to quicken our interest: Can you eat it?, and remarked that the substance had a ‘cool, refreshing, slightly astringent taste’, and a smell reminiscent of fruit bonbons!) Moreover, some early experiments were on record, quoted by Eitel (1954), according to which microscopic silica crystals had been obtained from silica gels in the presence of various ‘crystallizing agents’ when heated in water vapor under pressure. Despite the exotic character of some of these findings, it is entirely plausible that crystalline foreign deposits which are so often found in quartz may be examples of crystal growth in gel. In this way, the gel method appeared to offer systems and opportunities for experiments in ‘instant geology’ (e.g. see Holmes, 1917), and indeed it does so.

Fig. 1.1.1 shows typical examples of natural growth, needles of tourmaline and rutile in a single crystal of quartz. The needles must have grown first, and it is tempting to believe that they did so when the medium was a gel, though current opinion among geologists and mineralogists leaves room for other interpretations, e.g. that the growth may have been hydrothermal in character, with convection playing a crucial role. On the other hand, little is known about the viscosity of the hydrothermal medium under the original growth conditions, and it may well be that the tourmaline and rutile crystals grew when the fluid was viscous. In such a case, the distinction between hydrothermal growth and growth in a gel would be blurred. This view is supported by the knowledge that a gel as such, though generally beneficial, is not absolutely required for the mode of crystal growth under discussion here (see below). On the role of gels in geology, there is an extensive early literature (e.g. Cornu, 1909 and Krusch, 1907, 1910). In the last analysis, the problem of consistency has not yet been unequivocally settled as far as quartz is concerned, but there are many examples of crystal growth in other viscous media, natural (Koide and Nakamura, 1943) and artificial. Among the unwelcome manifestations of the process are the occasional growth of ice crystals in ice cream, the growth of tartrate crystals in cheese, the crystallization of sulfur in rubber (Endres, 1926), the growth of zinc

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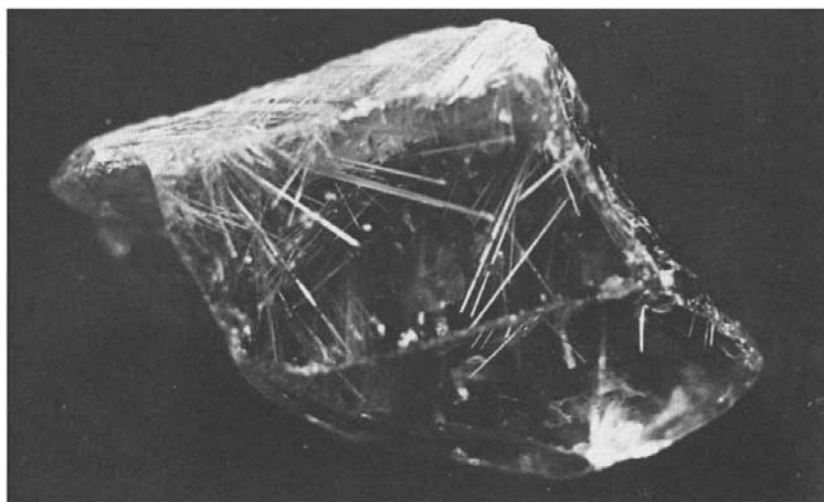
salts in dry batteries and, in rapidly descending order of desirability, the growth of uric acid crystals in joints (Knöll, 1938a, b) and of stones in human organs (Aschoff, 1939). The subject thus has much wider implications than is generally believed. Thus it is also related to our understanding of the processes which take place in photographic emulsions.

Fig. 1.1.1. Natural growths: needles of (a) tourmaline, and (b) rutile, in quartz.

(a)



(b)



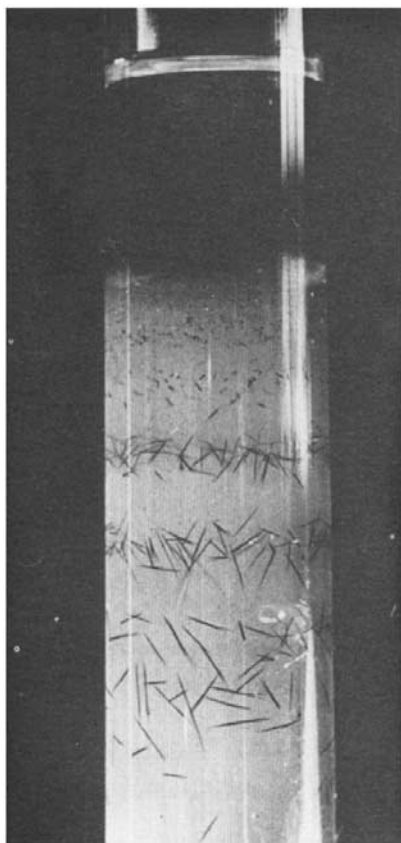
6 1 *History and nature of the gel method*1.2 **Early work**

In the course of early work a mass of empirical data was assembled, much of it too imprecise and unsystematic to lead to any real insight into the mechanism of the phenomena involved. However, some of these investigations remain interesting because they have the character of 'existence theorems', illustrating at least some of the things that can be done and suggesting new lines of approach.

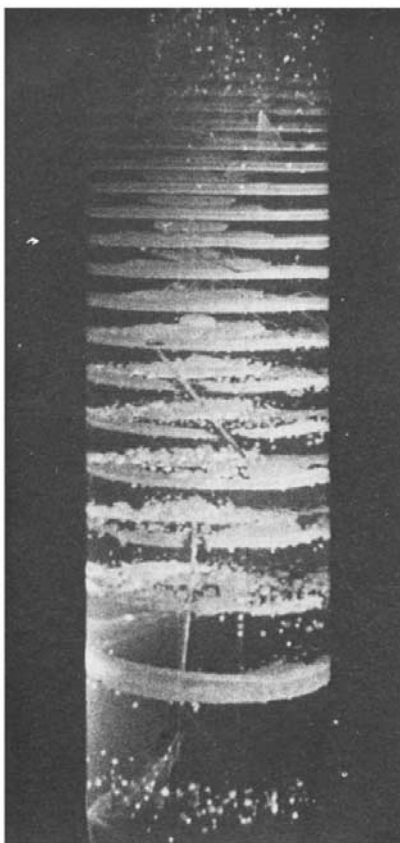
Among the indefatigable enthusiasts was Hatschek (1911), working primarily with (5–20%) gelatin and (1–5%) agar gels. He was the first to make a study of particle size distribution in a great variety of Liesegang Rings. Among other things, he also noted that even when good rings are formed, they are not necessarily the only reaction product. When a ring

Fig. 1.2.1. Liesegang Rings: (a) silver chromate system. (b) calcium phosphate system.

(a)



(b)



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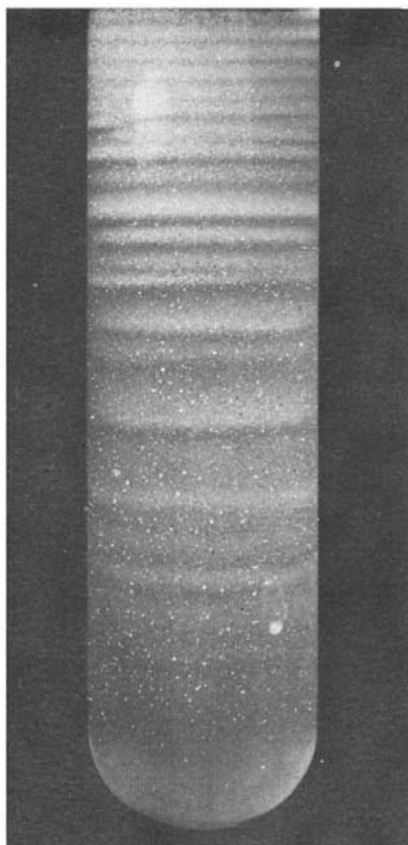
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system is prepared by allowing sodium carbonate to diffuse in a gel charged with barium chloride, distinct and well-formed barium carbonate crystals up to 1.5 mm in length are occasionally found in the otherwise clear space between adjacent rings. The observations must have been the first hint, if one was needed, that Liesegang Ring information is indeed a complicated process, especially since Ostwald and Morse and Pierce (1903) had earlier placed great emphasis on the sharpness with which the rings are often defined. The work of these researchers will be more extensively discussed in other parts of this book. In any event, it has since been amply demonstrated that the rings themselves may consist of substantial crystals (Fig. 1.2.1(a)).

Silver chromate, and the dichromate, chromate, chloride, iodide, and sulfate of lead, as well as calcium sulfate and barium silicofluoride

Fig. 1.2.1 (continued). Liesegang Rings: (c) gold system.

(c)



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were included in Hatschek's crystal-growing repertoire. Hatschek was also the first to point out that crystals often grow better in silicic acid gels than in gelatin or agar, but it is not actually possible to generalize such a rule; there is no such thing as a universal 'best' growth medium. In one of the most truly interdisciplinary experiments on record, Marriage (1891) had earlier grown lead iodide crystals in fruit jellies and jams.

A description of the basic procedures will be found in the next section. It was always realized that agents could be diffused into a gel, and conversely, that gels could be dialyzed to free them from excess reagents or unwanted reaction products. Such experiments were conducted by Holmes (1926), who used the dialyzing process for the treatment of gels in U-tubes, in order to eliminate excess reagents that could have interfered with the two principal components of the formation process diffusing in from the two sides. Holmes also grew single crystals of copper and gold by diffusing a reducing agent into a gel charged with appropriate metal salts. Hatschek had done so before, but Holmes claimed 'better results than any yet recorded', without actually mentioning crystal sizes. Both experimenters concerned themselves to some extent with the effect of non-reagent additives, such as glucose, urea, and gum tragacanth. Holmes and also Davies (1923) noted that reactions in gels can occasionally be influenced by light and, in particular, by short wavelength, ultraviolet radiation; see Section 5.2. Holmes used alkaline gels to promote the formation of cuprous oxide layers, but though he aimed at cuprous oxide crystals (perhaps because of their interesting electrical and photoelectric properties) the product was always amorphous.

One of the most important early experiments was performed by Dreaper (1913), who wanted to elucidate the role played by the capillarity of the gel structure. For this purpose, he substituted fine sand and even a single capillary tube for the usual gels and found that crystalline growth products would indeed be obtained with such systems. Many crystals do, in fact, grow under such conditions in nature, e.g. ice in soil and pure gypsum crystals in clay. Holmes later used barium sulfate and alundum powders for the same type of demonstration. Of course, these experiments prove nothing in particular about the nature of gels, but they provide a valuable hint of the circumstances which favor single crystal formation; see Section 4.4.

A comprehensive survey of early work on gel structures has been given by Lloyd (1926). Structure and classification problems were hotly debated by scientific workers in the 1920s and earlier, often with

1.3 Basic growth procedures

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enviable self-confidence and just occasionally with a trace of venom (e.g. see von Weimarn, 1926). During the next 30 years or so, the subject of crystal growth in gels fell into virtual oblivion, until it was revived by the modern interest in outlandish materials and, more generally, in room-temperature growth methods. In comparison, an enormously higher level of interest was sustained throughout this period in Liesegang Ring phenomena, a fact for which bibliographies by Hedges (1932) and Stern (1967) comprising many hundreds of publications bear eloquent testimony. Some beautiful color photographs of Liesegang Ring formations have been published by Kurz (1965).

1.3 Basic growth procedures

To all outward appearances, the gel method is exceedingly simple, but it is now abundantly clear that the physical and chemical processes which determine its outcome are in fact highly complex. One procedure, much used for demonstration purposes (e.g. see Henisch *et al.*, 1965), involves the preparation of a hydrogel from commercial waterglass, adjusted to a specific gravity of about 1.06 g/cm. This is mixed with an equal volume of approximately 1 molar (1 M) acid solution. One's natural inclination is to pour the acid into the waterglass (or metasilicate, see below) solution, but that leads to disaster. Instead, the waterglass should be added drop by drop to the acid, with constant stirring. The purpose of this procedure is to avoid excessive ion concentrations which otherwise cause premature local gelling and make the final medium inhomogeneous; see also Madeley and Sing (1962). The mixture is then allowed to gel, a process which depends in a complicated manner on the silicate concentration and on the degree of acidity (see below and also Chapter 2). In the circumstances specified, it generally takes between 24 and 36 hours, after which the gel is left for another 12 hours or so to allow it to set firmly. Once a firm gel is formed, some other solution can be placed on top of it without damaging its surface, as shown in Fig. 1.3.1(a). This solution supplies one of the components of the reaction and also prevents the gel from drying out. In order to avoid damage, the supernatant solution should be added dropwise with a pipette, the drops being allowed to fall on to the side of the test tube. If the reagent in the gel is tartaric acid and the supernatant reagent is an approximately 1 M solution of calcium chloride, then, in due course, crystals of calcium tartrate tetrahydrate are formed in the gel, the result of an exchange reaction, which yields hydrochloric acid as a by-product. The crystals are only sparingly soluble in water. They can usually be seen near the

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gel surface within an hour or so. Good crystals appear further down the column within about a week, and grow to about 8 mm average size. Occasionally they are larger, but then usually less perfect. The speed of formation depends on the concentrations involved, and the time taken before crystals are seen with the naked eye may vary from very few hours to a few days. When much higher acid concentrations are used, sodium tartrate crystals also tend to grow, in the form of long clear needles. Calcium tartrate crystals are beautiful, and the fact that they appear to be totally useless has always been a matter of profound regret within the crystal-growing community. Along these lines a ray of hope has recently appeared, in the form of a reported anomaly of the electrical conductivity (Gon, 1985), but these observations remain to be consolidated. There

Fig. 1.3.1. Basic growth procedures. During gel preparation the waterglass or sodium metasilicate solution should be added drop by drop to the acid with constant stirring. (a), (b) Simple test tube systems; (c) test tube system with tubular insert for easy gel removal; (d) U-tube system.

