

structure is essentially of discontinuous type.

On heating the low-temperature phase the transitional state is not observed, indicating that this phase does not have a stability field. It is considered that the formation of the transitional state represents an alternative continuous process in a situation where hysteresis occurs in the formation of the equilibrium low-temperature structure. Such a metastable transitional phase would be subject to symmetry constraints such that its structural state is compatible with the symmetry of the parent state. The definition of the operative constraints on behavior of this kind is discussed by McConnell (5).

The nature of the α -transformation can be considered according to Landau's general theory of phase transformations (6) in which the conditions for second-order transformations are derived from group theory. The transitional phase can be characterized in reciprocal space by the vector $\mathbf{k} = (\frac{1}{2} \frac{1}{2} 0)$ for which the proper symmetry group (the group of rotations and reflections that leave \mathbf{k} invariant) contains symmetry planes and axes intersecting at a point. Thus $(\frac{1}{2} \frac{1}{2} 0)$ is a "singular point" and a second-order transformation is possible from the high to the transitional phase. For the low structure the reciprocal lattice is characterized by the vectors $\mathbf{k}_1 = (\frac{1}{3} \frac{2}{3} \frac{1}{2})$ and $\mathbf{k}_2 = (\frac{1}{3} \frac{2}{3} 0)$, and hence the structure can be described only by a linear combination of functions corresponding to at least two irreducible representations. This precludes the possibility of a second-order transformation from the high to the low structure. The experimental observations outlined above are in accord with the predictions of Landau's theory, which provides a theoretical basis for the operative symmetry constraints on continuous transformations.

The transformation in troilite illustrates the general principles of behavior in a system in which the nucleation of a true equilibrium phase may be impeded. In stoichiometric FeS the barrier to nucleation of the low-temperature phase is small, although on increasing the iron deficiency in Fe_{1-x}S the transformation becomes more sluggish (7).

A. PUTNIS

Department of Mineralogy and Petrology, University of Cambridge, Cambridge CB2 3EW, England

References and Notes

1. H. Haraldsen, *Z. Anorg. Allg. Chem.* **231**, 78 (1937).
2. G. Hagg and I. Sucksdorf, *Z. Physik. Chem. Abt. B* **22**, 444 (1933).
3. E. F. Betraut, *Bull. Soc. Fr. Mineral. Cristallogr.* **79**, 276 (1956).
4. L. A. Taylor, *Carnegie Inst. Wash. Year* **68**, 259 (1970).
5. J. D. C. McConnell, *Mineral. Mag.* **38**, 1 (1971).
6. L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon, London, 1962), chap. 14.
7. F. Gronvold and H. Haraldsen, *Acta Chem. Scand.* **6**, 1452 (1952).
8. I thank Dr. J. D. C. McConnell for much helpful advice and criticism, and I acknowledge the receipt of a grant from the Natural Environment Research Council. The troilite is from the iron meteorite Odessa, for which I thank Dr. S. D. Agrell.

13 June 1974

The Temperature Gradient in the Solar Nebula

Abstract. *The available compositional data on planets and satellites can be used to place stringent limits on the thermal environment in the solar nebula. The densities of the terrestrial planets, Ceres and Vesta, the Galilean satellites, and Titan; the atmospheric compositions of several of these bodies; and geochemical and geophysical data on the earth combine to define a strong dependence of formation temperature on heliocentric distance. The pressure and temperature dependences of the condensation process are separable in the sense that the variation of the deduced formation temperatures with heliocentric distance is insensitive to even very diverse assumptions regarding the pressure profile in the nebula. It is impossible to reconcile the available compositional data with any model in which the formation temperatures of these bodies are determined by radiative equilibrium with the sun, regardless of the sun's luminosity. Rather, the data support Cameron's hypothesis of a dense, convective solar nebula, opaque to solar radiation, with an adiabatic temperature-pressure profile.*

Theoretical studies have been made of the chemistry of solar material in order to elucidate conditions in the solar nebula at the time of condensation of meteoritic and planetary material (1-3). With this knowledge of the stability fields of condensed minerals and ices and some basic information on the bulk chemical composition of solar system bodies, it is possible to constrain the temperature and pressure conditions present in the nebula at the time of condensation.

Figure 1 contains the results of calculations of the condensation temperatures of a variety of compounds of abundant elements from a gas having the same composition as the sun. Also given are several radically different types of temperature-pressure profiles through the nebula, including isobaric (constant pressure), isopycnic (constant density), and isentropic (adiabatic) sections. It can be seen that the sequence of chemical reactions going from high temperatures to low temperatures is insensitive to very widely divergent assumptions regarding the pressure. Note that all temperature-pressure plots with slopes less steep than that of an adiabat are unstable against convective overturn.

I will place limits on the bulk compositions of a number of solar system bodies whose densities are reasonably well determined, then use this information in conjunction with Fig. 1 to

constrain the conditions under which the dominant materials of these bodies condensed.

1) Mercury has a zero-pressure density of 5.3 g cm^{-3} , which requires that it be made of material very rich in metal. Iron-nickel alloy must make up at least 60 to 65 percent of the planet. No atmosphere has been detected. The density of Mercury is directly explained if it formed at a temperature so high that MgSiO_3 was not fully condensed (2). This is radically different from the proposal by Ringwood (3), who attributed the high density of Mercury to secondary volatilization of silicates from the planet by a putative highly luminous phase of the sun.

2) Venus has a zero-pressure density slightly less than that of the earth. Despite very high surface temperatures of 750°K , no sulfur-bearing gases have been detected in its dense and very dry atmosphere (4). Venera 8 has measured the potassium abundance in a small sample of the surface of Venus and found it to be ~ 4 percent (5). This requires formation within the stability field of alkali feldspar, but probably above the formation temperatures of FeS and hydrous silicates.

3) The earth has a mantle FeO content of ~ 10 percent and a liquid outer core significantly less dense than pure iron, presumably containing ~ 15 percent sulfur (2, 6). The earth's hydro-

sphere and crust contain a mass of water equal to about 0.05 percent of the mass of the planet. The average heat flow through the oceanic and continental crust is virtually identical to that expected for a planet with potassium, uranium, and thorium abundances equal to those found in chondritic meteorites. Thus, the earth appears to have formed below the FeS formation temperature, above the FeO end point for oxidation of metallic iron, and on the edge of the tremolite stability field (2).

4) Mars has a density so low that all metal may be oxidized to FeO in ferromagnesian minerals, but it is far too dense to contain an appreciable amount of talc or serpentine. Thus, it very likely lies between the tremolite and serpentine stability thresholds. Estimates of the rotational moment of inertia of Mars derived from observations of the motions of its satellites suggest that its core is less dense and its mantle more dense than those of the earth, suggesting an FeS rather than an Fe core, and an FeO-rich mantle.

5) Ceres and Vesta are the only asteroids whose masses are known (7). A number of asteroid radii have been determined recently by the polarimetric and infrared emission techniques, which permit estimates of their albedos as well (8). Ceres and Vesta are found to have the densities of the most volatile-rich meteorites, the carbonaceous chondrites. A density near 2.4 g cm^{-3} requires serpentinization of the ferromagnesian minerals. Spectral reflectivity studies of asteroids for comparison with laboratory reflection spectra of known meteorite classes strongly suggest that carbonaceous chondrite material is abundant throughout the asteroid belt, while ordinary chondrites are rare or absent (9).

6) Ganymede and Callisto, with observed densities of 1.8 and 1.6 g cm^{-3} , respectively, are both largely composed of ices (10). These satellites have extensive deposits of H_2O ice on their surfaces, but no methane has been detected on either (11). We conclude that both were formed below the condensation temperature of H_2O ice, but above the formation temperature of CH_4 clathrate hydrate. If the apparent density difference is real, then Callisto may well contain solid ammonia hydrate as well as H_2O ice (10).

7) Titan has an observed density of 2.1 g cm^{-3} , giving a zero-pressure density close to that of Ganymede or Callisto. However, Titan has a massive

methane atmosphere, which makes it very likely that its material originally condensed inside the stability field of methane clathrate hydrate (12).

There are no condensed bodies beyond Saturn's orbit whose densities are known with sufficient precision to be useful in the present effort. Much is known regarding the composition of the earth's moon, but its place of origin in the solar system remains a matter of debate.

With the above constraints on the composition of solar system bodies from Mercury to Titan, we now can use the theoretical results in Fig. 1 to place a limit on the formation temperature of each body for each of a variety of models for pressure variation in the nebula.

Figure 2 shows the dependence of

formation temperature on heliocentric distance for the seven compositional classes discussed above. The isobaric and isopycnic models are so similar to each other (as can be seen from Fig. 1) that only two isobaric cases are given, while two adiabatic models are given for comparison. The crucial result is that the variation of formation temperature (T) with distance from the sun (R) in every case gives a slope near -1.1 . For the adiabatic models, $T \propto R^{-1.13 \pm 0.17}$, while the isobaric models give $T \propto R^{-1.04 \pm 0.13}$. The dependence of temperature on distance for a radiative equilibrium model is $T \propto R^{-0.5}$, which is incompatible with the observations discussed above. The only model for the origin of the solar system which seems to lead to a slope near -1.1 is that of Cameron and

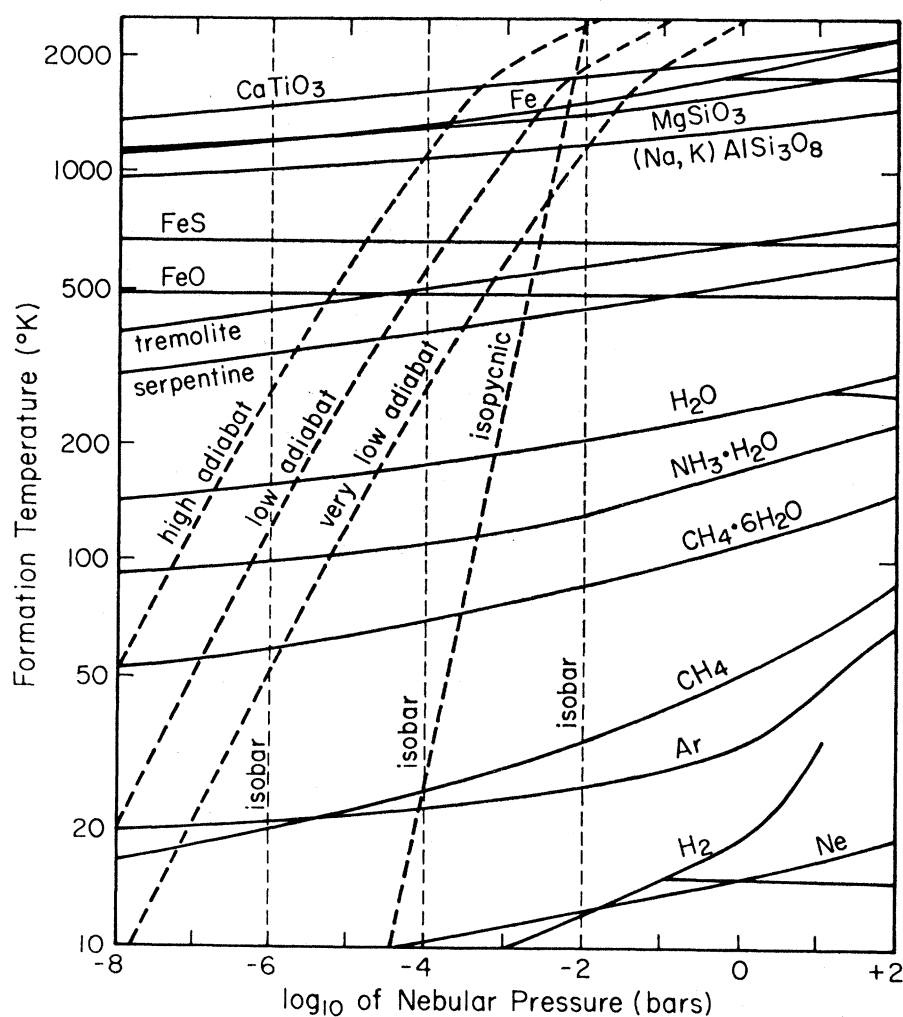


Fig. 1. Formation temperatures for condensates in the solar nebula. The condensation temperatures for a number of compounds of the most abundant elements are given as solid lines. The line labeled "FeO" is the end point for the progressive oxidation of metallic iron to ferrous oxide in olivine and pyroxene. Tremolite and serpentine are important water-bearing silicates. There is no present evidence for temperatures below $\sim 40^\circ\text{K}$ in the solar nebula. Dashed lines represent several grossly different types of pressure-temperature sections through the diagram. Notice that Cameron and Pine's (13) "high adiabat" and the 10^{-6} -bar isobar require complete oxidation of iron before retention of water, and hence do not explain the earth.

Pine (13). Many other models explicitly or implicitly assume radiative regulation of temperatures by the sun, or argue that opacity must have been negligible in the solar nebula (14). However, radiative control of the temperature gradient cannot be reconciled with present data on the composition of condensates formed in the nebula.

It is important to realize that the present method of estimating formation temperatures of planets represents an intentional gross oversimplification of the chemical history of planetary material. Temperature histories in the solar nebula were undoubtedly complex, and planets obviously did not accrete out of material formed at only one specific heliocentric distance. It would be wholly unwarranted to conclude that, for example, 100 percent of the mass of Venus originally condensed at $900^\circ \pm 150^\circ\text{K}$, as might mistakenly be deduced from Fig. 2. Rather, it can only be claimed that the bulk composition of Venus is dominated by material formed in this temperature range. The relative contributions of higher- and lower-temperature condensates can only be assessed from ele-

mental abundance data for Venus. On the other hand, the obvious ease with which the density trend is explained by this very simple model, and the strong disagreement of observational data with thermal models involving radiative control, are wholly unaffected by these considerations.

Hoyle and Wickramasinghe (15) have described a model for condensation of the planets in which the nebular density ρ is assumed to vary as R^{-3} , but the temperature is assumed to be radiatively controlled, $T \propto R^{-0.5}$. Cameron and Pine (13) assumed the temperature dependence on pressure (P) to be adiabatic, $P \propto T^{\gamma/(\gamma-1)}$, where γ is the ratio of specific heats. If we take $\rho \propto R^{-3}$ and the assumption of adiabatic structure, then

$$\rho \propto R^{-3} \propto \frac{P}{T} \quad (1)$$

$$P \propto T^{\gamma/(\gamma-1)} \quad (2)$$

$$R^{-3} \propto T^{\gamma/(\gamma-1)-1} = T^{1/(\gamma-1)} \quad (3)$$

At temperatures near 200°K , γ for a gas of solar composition is ~ 1.5 , and thus $R^{-3} \propto T^2$, or $d\log T/d\log R = 1.5$. At the temperature of condensation of the terrestrial planets, γ varies from

~ 1.42 to ~ 1.33 , and $d\log T/d\log R = -1.26$ to -1.00 . Figure 2 displays some evidence of just such a change in slope for the two adiabatic models.

It is of considerable interest to examine the role of chondritic meteorites in such a scheme. Miyashiro (16) has suggested that the gaps in the sequence of iron oxidation observed in chondrites correspond to the regions in the nebula in which the earth and Mars accreted. This was slightly modified by the suggestion of Lewis (2) that both H (high-iron) and L (low-iron) chondrites formed between the orbits of the earth and Mars, and that the primitive material throughout the asteroid belt was dominantly volatile-rich, suggestive of carbonaceous (C) chondrites. Recent observations of extremely low albedos, low densities, and reflection spectra similar to those of C chondrites for numerous belt asteroids bear out the plausibility of this idea (7-9). The chondritic meteorites seem to be debris left over after the formation of the planets, which swept up all the material close to their orbits. The earth is similar to H chondrites (17) because they originated nearby in the nebula, but the earth is not identical to them or to any other class of meteorites. Finally, metal-silicate fractionation processes, as observed in chondritic meteorites, seem to be artifacts of accretion of small parent bodies by selective intergrain forces. Gravitationally accreted bodies may show no such effects.

JOHN S. LEWIS*

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena 91109, and Department of Chemistry and Planetary Astronomy Laboratory, Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge 02139

References and Notes

1. H. C. Urey, *Geochim. Cosmochim. Acta* **1**, 209 (1952); *ibid.* **2**, 263 (1952); H. C. Lord, *Icarus* **4**, 279 (1965); J. W. Larimer, *Geochim. Cosmochim. Acta* **31**, 1215 (1967); *ibid.* **37**, 1603 (1973); — and E. Anders, *ibid.* **31**, 1239 (1967); *ibid.* **34**, 367 (1970); L. Grossman, thesis, Yale University (1971); *Geochim. Cosmochim. Acta* **36**, 597 (1972); J. S. Lewis, *Icarus* **16**, 241 (1972); *Space Sci. Rev.* **14**, 401 (1973); L. Grossman and J. W. Larimer, *Rev. Geophys. Space Phys.* **12**, 71 (1973).
2. J. S. Lewis, *Earth Planet. Sci. Lett.* **15**, 286 (1972).
3. A. E. Ringwood, *Geochim. Cosmochim. Acta* **30**, 41 (1966).
4. J. S. Lewis, *Earth Planet. Sci. Lett.* **10**, 73 (1970); *ibid.* **22**, 239 (1974).
5. A. P. Vinogradov, Yu. A. Surkov, F. F. Kirnozov, *Icarus* **20**, 253 (1973).
6. V. R. Murthy and H. T. Hall, *Phys. Earth Planet. Interiors* **2**, 276 (1970).

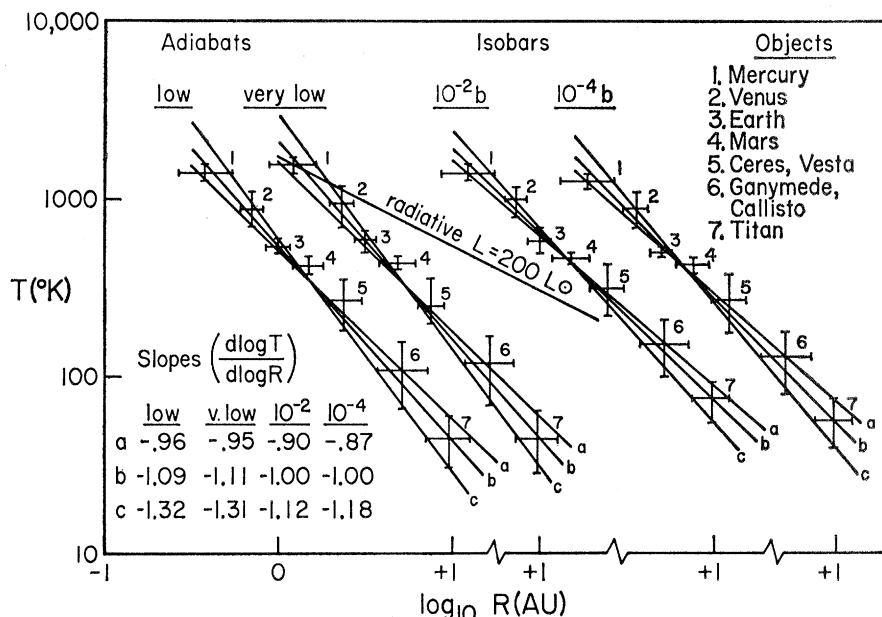


Fig. 2. Temperature variation with heliocentric distance in the solar nebula. Several radically different pressure variations are assumed. In every case, $T \propto R^{-1.1}$ within $\sim \pm 15$ percent. The vertical bars on each point are intended to enclose the entire range of acceptable formation temperatures, and the horizontal bars enclose the range of heliocentric distances over which each body may be able to draw condensed material. Line a for each model has the shallowest possible temperature gradient reconcilable with bulk composition data, while c has the steepest. Line b is a "best fit" estimated by eye. Lines drawn through all the vertical bars can be constructed for the adiabatic models, and have slopes of -1.00 ± 0.03 . A radiative equilibrium profile (for a solar luminosity 200 times the present value) is shown to demonstrate a radiative temperature profile, with $T \propto R^{-0.5}$. This slope is independent of luminosity, being purely geometrical in nature.

7. H. G. Hertz, *Science* **160**, 299 (1968); J. Schubart, *NASA SP-267* (1971), p. 33; *Astron. Astrophys.* **30**, 289 (1974).
8. D. Allen, *NASA SP-267* (1971), p. 41; D. L. Matson, thesis, California Institute of Technology (1971); D. P. Cruikshank and D. Morrison, *Icarus* **20**, 477 (1973); J. Veverka, *ibid.* **19**, 114 (1973); D. Morrison, *Comments Astrophys. Space Phys.* **5**, 51 (1973).
9. C. R. Chapman and D. Morrison, *Sky Telesc.* **47**, 92 (1974); T. V. Johnson and F. P. Fanale, *J. Geophys. Res.* **78**, 8507 (1973); M. Gaffey, thesis, Massachusetts Institute of Technology (1973); C. A. Chapman and J. W. Salisbury, *Icarus* **19**, 507 (1973); C. R. Chapman *et al.*, *Astron. J.* **78**, 126 (1973).
10. J. S. Lewis, *Science* **172**, 1127 (1971); *Icarus* **15**, 174 (1971).
11. C. B. Pilcher, S. T. Ridgway, T. B. McCord, *Science* **178**, 1087 (1972); U. Fink, N. H. Dekkers, H. P. Larson, *Astrophys. J.* **179**, L155 (1973).
12. J. S. Lewis and R. G. Prinn, *Comments Astrophys. Space Phys.* **5**, 1 (1973).
13. A. G. W. Cameron and M. R. Pine, *Icarus* **18**, 377 (1973).
14. G. Arrhenius and H. Alfvén, *Earth Planet. Sci. Lett.* **10**, 253 (1971); G. Arrhenius and B. R. De, *Meteoritics* **8**, 297 (1973).
15. F. Hoyle and N. C. Wickramasinghe, *Nature (Lond.)* **217**, 415 (1968).
16. A. Miyashiro, *Chem. Erde* **27**, 252 (1968).
17. J. S. Lewis, *Earth Planet. Sci. Lett.* **11**, 130 (1971).
18. I thank the National Aeronautics and Space Administration for support of the work reported here through grant NGL-22-009-521, and Prof. Barclay Kamb for providing me with a quiet place to write this report, free from the help and encouragement of my students. I am also indebted to Prof. E. Anders for his careful and helpful criticisms of the manuscript. This is Contribution No. 99 of the M.I.T. Planetary Astronomy Laboratory.

* Address correspondence to the author at the Massachusetts Institute of Technology.

29 March 1974; revised 2 July 1974

Isobaric Bubble Growth: A Consequence of Altering Atmospheric Gas

Abstract. During certain treatments of decompression sickness following dives made with compressed air, the U.S. Navy advocates breathing helium-oxygen mixtures. However, stable nitrogen bubbles created within gelatin by decompression have been found to enlarge when the atmosphere was switched from nitrogen to helium without changing ambient pressure. This suggests that decompression sickness would be worsened by switching from nitrogen to helium in the breathing gas mixture.

Decompression sickness affects divers whose tissues have become supersaturated with gas. The primary cause is generally thought to be the formation and growth of bubbles within tissues and blood (1). The treatment of decompression sickness involves (i) increasing the ambient pressure in order to reduce bubble size and (ii) breathing oxygen in order to increase the gradient for inert gas loss from the body and to increase tissue oxygena-

tion. Under certain conditions, such as very high ambient pressures, inert gas as well as oxygen must be breathed in order to avoid oxygen toxicity. The *U.S. Navy Diving Manual* (2) advocates that the inert gas breathed be helium, even when decompression sickness has occurred after diving with air or other nitrogen-oxygen mixtures. The rationale appears to be to increase the net rate of loss of nitrogen from the body (3). However, switching to heli-

um may be the wrong thing to do. There is considerable evidence that the body is saturated more rapidly by helium than it is desaturated by nitrogen (3, 4). During this transition period, bubbles within the body are expected to grow, since helium would diffuse into them faster than nitrogen would diffuse out. We have demonstrated this in a model in which stable bubbles were created in gelatin by decompression. The model simulates the body since diffusion calculations show that the gelatin is saturated by helium more rapidly than it is desaturated by nitrogen.

Experiments were performed in a small pressure chamber having a window in one end through which gelatin and bubbles could be seen and photographed by microscope at any pressure. Gelatin was prepared in a single batch by dissolving 127 g of Knox gelatin crystals in 5 liters of water. Portions were frozen and subsequently thawed at 40°C for each experiment. Thawed gelatin was pipetted into three rectangular glass chambers of horizontal cross section 6 mm by 27 mm, the gelatin depth at the meniscus being 4 mm. Before compression, the gelatin was converted from sol to gel by partly immersing the glass chambers in ice water for 10 minutes. The glass chambers were then placed in a water bath at 21°C inside the pressure chamber, which was pressurized at 13.6 atm/min by adding N₂. The chamber pressure was held at 21.4 atm absolute for 5.25 hours for the gelatin to become saturated with N₂. Pressure was then decreased to 11.2 atm absolute in 10 seconds, following which bubbles ap-

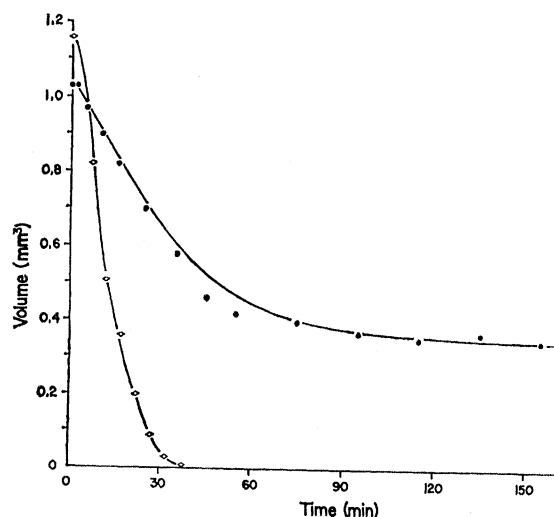
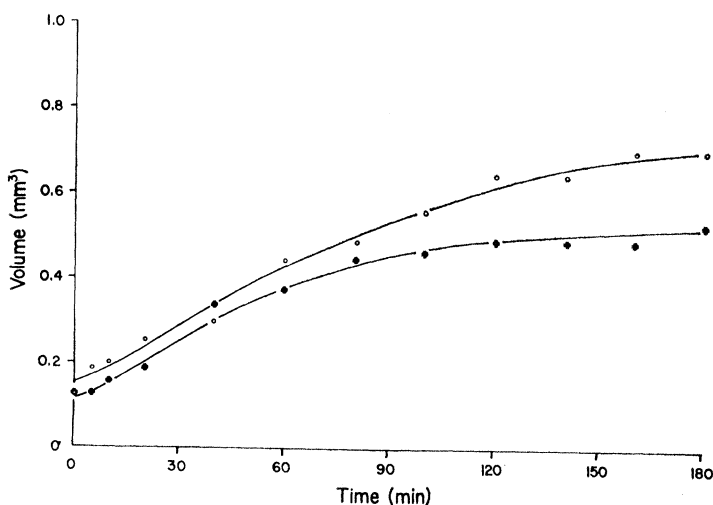


Fig. 1 (left). Switching atmospheric gas from N₂ to He causes bubbles in gelatin to grow. Ambient pressure is unchanged. Fig. 2 (right). Switching atmospheric gas from He to N₂ causes bubbles to shrink or disappear.