

THE USE OF EQUILIBRATED SILICA GEL FOR THE PROTECTION OF GLASS WITH INCIPIENT CRIZZLING

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IN A PREVIOUS PUBLICATION¹ we have discussed glasses showing incipient crizzling, that is, glasses in the earliest stages of crizzling. This condition threatens many pieces of European, East Asiatic, and American glasses manufactured between the seventeenth and nineteenth centuries. Examples exist in public and private collections throughout the world. These glasses have absorbed moisture during their lifetimes, becoming hydrated to a depth of approximately 50 microns (0.05 mm). For some reason, however, possibly because they have been stored more-or-less continuously in moist environments, they have not developed the same severe surface crazing as that which characterizes the more familiar condition described simply as "crizzling." On glasses showing incipient crizzling, the damage may often be overlooked, for only when the objects are viewed in just the right light do the silvery, crazed patterns of early crizzling become evident. Nonetheless, these glasses are very unstable, and if exposed to low relative humidities for extended periods of time (ranging, perhaps, from several months to a few years) the glasses slowly release their water of hydration. This drying-out is accompanied by shrinkage in the affected layer which leads to the opening of fissures within that layer. The glass is thus transformed into a fully-crizzled

state marked by a loss of transparency. If this degenerative process proceeds far enough, not only do the objects become unsightly, but a loss of surface material may also occur. The process is not unlike that which produces crackling when a layer of mud dries out in strong sunlight.

The chemical effects causing crizzling were discussed at length in the earlier publication, along with experiments in which the effects were reproduced in the laboratory. It was verified that the primary cause of crizzling is a deficiency in lime in the glass composition or an excess of alkali, two conditions which accelerate the hydration of glasses. Because it is believed that the degeneration of a glass with incipient crizzling into a severely crizzled state is the result of the loss of water of hydration, it seems reasonable to assume that in order to prevent degeneration, glasses with incipient crizzling should be stored or exhibited in relatively moist conditions, so as to inhibit loss of their water. With that aim in mind, storage at

1. Robert H. Brill, "Crizzling—A Problem in Glass Conservation," *Conservation in Archaeology and the Applied Arts*, London: The International Institute for Conservation of Historic and Artistic Works, 1975, pp. 112-134. The first stage of this research, that described in the above publication, was conducted in part under a grant from The National Endowment for the Arts.

constant and moderate levels of temperature and RH was recommended. Moreover, it was recommended that dramatic spotlighting and regular cycling of temperature (as might be brought about by turning on and off gallery lights according to a daily schedule) both be avoided. It was concluded that ambient temperatures comfortable to people were fully satisfactory and that an RH of 45–47% should be the target, although any RH within a range of 40–55% would probably be quite safe. Short-term excursions to about 35% or 65% were thought to cause little harm, although long-term storage outside those limits might be harmful. From what has been learned in the meantime, these guidelines still seem valid.

It must be emphasized that by storing glasses under these conditions one can only hope to forestall the degeneration of incipient crizzling into severe crizzling. Storage under these, or under any other conditions which we can presently imagine, is not going to undo the damage already inflicted upon the glass, nor is it going to correct the inherent chemical instability and susceptibility to future degeneration.

It is the author's opinion that the same target conditions of temperature and RH are probably also as safe as any other conditions for the storage or exhibition of already-crizzled glasses. We see no advantage, and indeed see distinct disadvantages, to unnecessarily subjecting already-crizzled glasses to markedly more moist or markedly drier conditions than those specified for glasses showing incipient crizzling.

After the requirements for safe storage had been established, a schematic plan for an exhibition case intended to attain these conditions was prepared. The second stage of our work was to construct such a case and monitor its temperature and RH through a full year's cycle. That stage has now been completed, and the results are presented here.

The next stage of our work will be to design cases for glass installations in the new galleries of The Corning Museum of Glass which will

open in 1980. It is hoped that the galleries themselves will be maintained between limits of about 35 and 65% RH as part of the architectural specifications, but there is no assurance that these will be met, and there are likely to be widely ranging short-term fluctuations. These conditions should probably suffice for the major parts of the glass collection which are not very susceptible to damage by RH changes. However, the crizzled glasses (especially those with incipient crizzling), certain glasses with painted or gilt decoration, and glasses with particularly fragile weathering crusts will require several individually controlled cases. Our present intention is that these cases will be controlled by equilibrated silica gel according to the guidelines listed below.

SUMMARY OF FINDINGS

The discussions which follow are likely to be of interest mostly to conservators and museum scientists. Therefore, so as to aid other readers, we present a summary of our findings here at the beginning of this article, along with some recommendations.

Although a great deal of useful information has been gathered, this stage of the project has been only partially successful.² We have demonstrated, to our own satisfaction, that storage in a case controlled by equilibrated silica gel is a valid, safe, and practical means for preventing glass with incipient crizzling from degenerating into a severely crizzled state. All the advantages anticipated for the system seem to have been realized. However, the experimental case used in the most important experiment, while it proved effective in isolating

2. We have certain reservations about publishing the results of only partially successful work, but the system seems as promising as ever, providing that proper corrections are applied, and the results complement nicely the findings of Thomson. Moreover, it will be another year before we can gather additional useful data, and we feel that others might benefit from knowing our experiences now.

the glass from high exterior ambient humidities prevailing during the summer months, showed a persistent drift downward in relative humidity during the dry winter months. Because the dry winter months are the time when protection is most needed, questions arose about the usefulness of the system.

The main point of concern was whether the drift was the result of simple leakage—as was expected—or whether there was some fundamental flaw in the principle of the system. The appearance of two fine articles related to the use of conditioned (equilibrated) silica gel systems as this manuscript was in its late stages of preparation have pretty well settled our doubts. These two articles are by Nathan Stolow of the National Museum of Canada in Ottawa³ and Garry Thomson of the National Gallery in London.⁴ Both emphasize the problems of case leakage and provide guidelines for the quantities of gel required to compensate for leakage. It is apparent to us now not only that our case was not well enough sealed, but that the reservoir of silica gel was too small to prevent the downward drift under the extremely dry conditions prevailing in our galleries.⁵

Our findings and recommendations (stated in the form of intentions for our own new installations) are summarized as follows:

1. The equilibrated silica gel system is a valid, safe, and practical means for controlling RH in cases used for the storage of glass and is recommended for preventing the degeneration of incipient crizzling into full crizzling.

2. Leakage is a major problem. In all but the most extraordinary conservation systems, where the expenditure of extraordinary amounts of money and effort are warranted, it is wise to consider leakage inevitable. Instead of attempting to stop leakage altogether, it is probably much more practical to minimize it and compensate for the leakage that does occur. (One difficulty is the lack of any straightforward way of measuring leakage and therein lies part of the value of Thomson's theoretical

treatment, which permits one to come to grips with the leakage problem.)

3. In our case designs for the Museum's new building, care must be taken to provide a sufficiently large quantity of equilibrating gel following the guidelines of Stolow and Thomson. The quantity of gel should be of the order of 20 kg per cubic meter of total case volume. (This is a four- to five-fold increase over what was used in our experimental case.)

4. It is probably more practical to use a few small exhibition cases than one large case. We will aim to have no controlled case larger than about 1.0–1.5 cubic meters in volume (including the equilibrating chamber).

5. The silica gel will be spread so as to present a large effective surface area to the air within the cases, and will be located, as much as possible, in close proximity to those objects it is intended to protect. Depending upon the nature of the individual cases, the gel will either be incorporated into fabric-covered panels or will be placed in open trays partially hidden by perforated surfaces. While we would like to minimize the presence of water-absorbent materials other than silica gel, on the basis that they introduce other variables into the system, those materials which are necessary will be selected with a view toward providing further beneficial buffering of the RH.

6. A separate conditioning apparatus will be constructed for the equilibration and reconditioning of the silica gel, and a back-up reserve of conditioned gel will be maintained.

7. A remote sensing RH and temperature probe system, similar to that described here,

3. Nathan Stolow, "The Microclimate: A Localized Solution," *Museum News*, 56, No. 2, November/December, 1977, pp. 52–63. This publication also serves as an excellent entry into the bibliography on this general subject.

4. Garry Thomson, "Stabilization of RH in Exhibition Cases: Hygrometric Half-Time," *Studies in Conservation*, 22, No. 3, August, 1977, pp. 85–102.

5. As these words are being written, during the Great Blizzard of February 1978, the RH in our Museum's main gallery is about 12%.

will be used to monitor case conditions and ambient conditions.

8. All lighting devices will be external and well-vented, with heat shields installed. No spotlighting will be used for dramatic effects unless it can be demonstrated that it produces no temperature increase in the objects.

9. We will consider the use of a "double-walled" barrier to attain longer hygrometric half-times. Thomson has shown that the hygrometric half-time depends upon the difference between the internal and average external RH. If an enclosed exhibition space is surrounded by another enclosed space containing silica gel equilibrated to the same target RH, then leakage from the inner chamber actually holding the glass objects should be much slower, because the gradient between that chamber and the surrounding chamber will be much smaller.

A few further remarks on the use of silica gel are worth repeating. Most readers already will be familiar with the use of silica gel as a desiccant, that is, as a material intended to absorb all the moisture from its surrounding air and leave the air as dry as possible. If the silica gel is itself dry to begin with, this is exactly how it behaves, because it has such a strong tendency to absorb water. In the present application, however, the silica gel used has already had water added to it in proportions of the order of 20–30 percent by weight. Hence, its tendency to absorb water has been much reduced. Silica gel containing this much water does not produce a near-zero RH in the surrounding air but instead, establishes an equilibrium RH of about 40–50 percent in the surrounding air. If the gel is the most abundant phase in a closed system and has a large surface area exposed, it will either remove moisture from the air or release moisture into the air until its own equilibrium RH has been established. Silica gel is well-suited for controlling exhibition cases because it is easy to handle, can be regenerated, does not become messy to handle in the hydrated state,

and is chemically inert. In addition, its equilibrium RH, for a given water content, is said to be relatively insensitive to temperature changes.⁶

As with all conservation treatments or procedures, however, the silica gel system must be employed judiciously. In this instance, *judiciously* takes on a very important meaning because there is one way that the system could go seriously wrong.

As was described above, the whole efficacy of this system centers around one particular property of silica gel, namely, that it will release or take up moisture to maintain some constant RH in the surrounding air. This property of the gel is characterized quantitatively by its equilibrium Rh *vs.* moisture content curve, which describes what surrounding RH corresponds to what water content of the gel. During the course of this work, we have come to appreciate that this curve is not necessarily the same for all lots of silica gel. In fact, buying silica gel might be much like buying vegetables. A basket of corn bought in Petunia Pump last year might be quite different from a basket of corn bought in Pathan next spring, even though both are quite properly called "corn." So, for the present at least, we feel each new lot of silica gel should be regarded as a unique entity, and unless the manufacturer has provided an EMC *vs.* RH curve (an adsorption isotherm) the user must determine one himself.

Our recommendation to those who might consider making use of silica gel is, by all means, to go ahead but to be certain that the installation is supervised by a conservator or someone else who has a general understanding of how silica gel behaves. It is important first that care be taken to prepare the gel properly and to be certain that it is equilibrated to the target RH desired. (This process might take as long as a few weeks.) Then it is crucial that

6. Nathan Stolow, "Fundamental Case Design for Humidity Sensitive Museum Collections," *Museum News*, 44, No. 11, February, 1966, pp. 45–52.

the RH of the system be reliably monitored. The danger is that if silica gel which is not sufficiently moist is used, or if the gel is allowed to dry out somehow, it could have the effect of drying out the glass and thereby cause harm. But this is not reason for alarm, for as long as the RH of the system is monitored, that should never happen. If the RH shows signs of drifting downward, the drift can be very simply corrected by adding water to the system; if it drifts upward, drier silica gel can be added. (In actual practice, this usually would be done by adding freshly-equilibrated silica gel.)

DESCRIPTION OF AN EXPERIMENTAL CASE

Because of budgetary limitations, we did not construct new cases for our experiments, but instead modified existing cases. At the outset it was realized that the results would not be ideal, and that the cases would not meet the optimum specifications. Nevertheless, the experiments served well to evaluate realistically a number of variables.

Our most important experiment made use of an aluminum-framed case with permanently-fixed glass walls on three sides and four large sliding glass doors on the front. The original top and bottom of the case were also of plate glass. The inside dimensions of the case are: height 1.66 m, width 2.87 m, and depth 40 cm. The volume of the exhibition case proper is approximately 1,900 l. It rests upon a steel base supported by six steel legs with a clearance of 45 cm beneath. The case contains three plate glass shelves mounted on adjustable steel racks.

The main advantage of this case for our experiment was that because it is made of plate glass and metal, it did not present surfaces which were highly absorbent to water vapor. The presence of fabrics or wood in a case is a complicating factor, as is demonstrated below in an experiment with a different case. The

main disadvantage of the case was its sliding glass doors which were notoriously loose-fitting. The doors were sealed during the experiment with lengths of plastic tubing, used as gaskets, and duct tape. While this afforded a seal of sorts, it proved inconvenient to remove and replace the tape on those occasions when the case had to be opened. The interior seams of the case were caulked with a silicone caulking which worked fine, because it remained pliable and, therefore, would not have cracked if the case had shifted. (No build-up of fumes released from the caulking was detected.) Despite the effort taken, however, we know now that the case was not sealed nearly as well as we would have liked.

The original glass bottom was removed for the experiment, and a tightly-fitting, brazed sheet-metal compartment was fastened permanently in place beneath the case to serve as the chamber for the silica gel. Access to this lower chamber is through two gasketed, metal faceplates, held in place with sheet-metal screws. The exterior of the metal chamber was painted, but the interior surfaces were not.

The lower chamber contains six sheet-metal racks, each of which supports four enamel trays measuring 39.0 cm by 17.5 cm by 5.0 cm. The trays hold the equilibrated silica gel. In the experiment described, the silica gel filled the trays to a depth of approximately 1.5 cm. The exposed surface area, not corrected for granularity, was about 1.2 m². The trays were easily removed whenever necessary by sliding the racks out through the opened faceplates. The lower chamber is separated from the case itself by a polyethylene grid which provides adequate support for objects to be placed upon it while also permitting a free exchange of air between the lower chamber and the case proper. The volume of the equilibrating chamber is approximately 400 l, so that the total volume of the system (exhibition chamber plus equilibrating chamber) is approximately 2,300 l.

During our experiments, it was found that no fan or circulating device was necessary, as there seemed to be sufficiently free exchange of air between the two compartments. This was helpful because it meant there was one less thing to go wrong and one less item in the system requiring maintenance. This case was not lit except by ambient room lighting, so no precautions were required against heat build-up from that source.

THE SILICA GEL

The silica gel used for our experiments had been prepared earlier by Dr. David Fischer, who worked at the Museum from January, 1973 to December, 1975 with the assistance of Mr. Joseph Maio, of the Museum's staff. In all, they equilibrated about 145 kg of silica gel. When purchased, the gel was nearly dry. De-ionized, distilled water was sprayed directly onto the gel to hasten its absorption because storage with liquid water in a closed compartment proved to be too slow a means for equilibrating the gel. (Caution must be exercised when adding water to silica gel because heat is evolved by the process.) The amount of water added was calculated from data published by Stolow.⁷ The curve reported in Dr. Stolow's publication gives relative humidity values for various equilibrium moisture contents of silica gel. (The equilibrium moisture content, or EMC, is the water content expressed as a percentage of the weight of the *dry* gel.) In Dr. Fischer's preparations, adjustments had to be made, which we assume resulted from differences between the silica gel we were using and that used by Dr. Stolow. The separate batches of moistened gel were then stored in double-thickness plastic bags inside galvanized metal cans which were then sealed with tape. Dr. Fischer measured equilibrium RH values for samples of the separate batches after the air above them in closed chambers had come to a constant RH. The results ranged from 43.5%

to 47.8% RH. Measurements made two years later on the batch of gel actually used in our case experiment⁸ agreed to within $\pm 0.5\%$ RH with Dr. Fischer's measurements.

Silica gel of 12–28 mesh was used. This was a compromise between two effects. The smaller the gel particles, the greater the exposed surface area and, consequently, the more rapid the equilibrium time. But it was thought that gel of too small a particle size might produce dust problems throughout the case. Actually, although we carried out tests specifically to detect dusting, none was found, and it was concluded that for the way we had introduced the gel (in horizontal trays), the 12–28 mesh size was fine. However, Dr. Stolow recommends using a larger size, 3–8 mesh, as mentioned below. (See A Final Note.)

A curve for equilibrium RH values *vs.* EMC for the gel used in this experiment was estimated by adding known weights of water to known weights of the gel, which had been dried previously at 190°C for seven hours. The water was added to the gel by evaporation transfer inside sealed 9.7-liter desiccator chambers. After the water had completely evaporated and the RH in the chambers had become constant—a process which required several weeks in some instances—the systems were assumed to have come to equilibrium. Samples of the gel were removed, and their water contents were determined by drying to constant weight at 180°C. The resulting EMC *vs.* RH curve is shown in Figure 1. Also plotted on this graph are data for three samples of silica gel removed from the Crizzling Case during an experiment described below.

The curve is displaced somewhat from the similar curve published by Stolow. Because we do not have a sufficient number of points for plotting both ascending and descending

7. Stolow, *loc. cit.*, p. 51. See also, A Final Note.

8. Davison, Code No. 408-08-72-201, Grade 408, Mesh 12–28, Package 9445.

branches reliably, we have elected not to indicate hysteresis. Some of the points on the curve drawn were probably crossing over from the ascending branch toward the descending branch, and the three points for the samples withdrawn from the case should be on the descending branch.

The rather sharp bend in the curve near EMC -25% is of special interest. One wonders if such a plateau might result from saturation with water of hydration corresponding, for example, to $\text{H}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$ ("EMC" -23%), $\text{H}_2\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ ("EMC" -26%), or some other stoichiometric composition. Unfortunately, because of a very tight publication deadline, we have not yet been able to verify these data by repeat runs—and we confess to not having made a thorough literature search on the subject.

TEMPERATURE AND RELATIVE HUMIDITY MONITORING

The temperature and relative humidity of the sealed experimental case were measured by two sensing probes placed inside the case at diagonally-opposed corners. The probes were attached by cables to a humidity-temperature reader manufactured by the Phys-Chemical Research Corporation.⁹ Although the system is designed to incorporate only one sensor probe, a special switch box was made which allows the system to accommodate twelve different sensors. These are attached by cables of various lengths (measuring up to 28 m) spread out in a network to various locations in the Museum where we chose to monitor the temperature and RH. The sensors were all individually calibrated by the manufacturer, and those used in the experiments described here were checked periodically against a sling psychrometer. The two probes in the experimental case check one another to within 2% of RH units.

It was decided not to record the data automatically, partly because it would have been very expensive, and partly because it would

have been difficult to do that simultaneously for several sensors. In any event, there was no need for recording data automatically. For routine monitoring, four readings of temperature and RH were taken between 9 a.m. and 5 p.m. daily on each of the probes in the experimental case. During the hours when the Museum offices were closed, and on weekends, readings were taken by the Museum security guards on their rounds. Normally, four readings were taken each night. As each reading was taken, a notation was made of the weather conditions. When experiments had just been started or at particularly important stages, more frequent readings were taken. It is such an easy matter to collect data—one simply presses a button and reads the temperature and RH off two dials—that it is quite convenient to obtain nearly continuous data, providing only that one is willing to stay near the read-out meter for the interval required. The temperature and RH of the ambient air immediately outside the test case were recorded continuously on a recording hygrothermograph¹⁰ which was in reasonably close calibration with the sensors, but which did not yield data of quite as high precision and accuracy.

In retrospect, the number of data taken during the course of the research described below—the Crizzling Case experiment, the monitoring of the Ravenscroft Case, the monitoring of three stations in the galleries, and the determination of the EMC *vs.* RH curve—is quite astounding. Some 20,000 individual readings of RH were recorded, along with an equal number of temperature measurements. This attests to the facility with which the readings

9. The instrument is a Humitemp-2 equipped with PCRC-11 HPT sensing probes. The address of the manufacturer is Phys-Chemical Research Corporation, 36 West 20th Street, New York, New York, 10011.

10. The instrument is a familiar one: model no. 5-594-2 manufactured by the Belfort Instrument Corporation of Baltimore, Maryland.

are taken, for it never seemed at all a bother, and also emphasizes our indebtedness to the security guards who collected half of these data.

THE "CRIZZLING CASE" EXPERIMENT

The case described above was closed on August 25, 1976, after 12 kg of equilibrated silica gel had been spread out in the enameled trays. It was monitored according to the schedule outlined above (about nine readings per day) until September 20, 1976, when the relative humidity had leveled off at 44%. Then, 120 objects of glass, 15 with incipient crizzling and 105 already-crizzled pieces, were placed in the case, and it was resealed. The presence of the objects in the case appeared to cause the RH of the enclosed air to drift downward over the course of three weeks to a level of 40%. Evidently, the crizzled glass absorbed moisture from the air more quickly than the silica gel could replenish it. At that point, liquid water was added to the system in order to elevate the RH. This had to be done five more times over the succeeding year to keep the RH from dropping below the 40% level. In most instances, the water was sprayed directly onto the surface of the gel (see A Final Note, below), but occasionally it was added as liquid water in small beakers distributed throughout the case. This latter procedure is definitely not recommended (see A Special Precaution, below). Whenever water was added, the gel was always lightly raked to expose a fresh surface. Sometimes a slight crustiness was found to have developed on the surface of the gel after it had been in the case for several weeks. This was accompanied by a faint yellowish coloration.

From the above it is clear that the presence of this large number of crizzled objects with their large effective surface area altered the RH within the case, and that this effect is not negligible. This is to be expected, because where two absorbent phases are present within

a closed system, the actual RH established should be intermediate between the individual equilibrium values for the two phases. If the equilibrium RH values of the two phases are very different, and if a much greater effective surface area of either phase is present, the net result would be that water would be "pumped" from one phase to the other, forcing the less abundant phase to absorb or desorb moisture until it could tolerate the equilibrium RH demanded by the more abundant phase. In this experiment the equilibrium RH values of the crizzled glass¹¹ and of the silica gel are quite close to begin with, and the effective surface areas seem well balanced against one another, so no extensive transfer of water from one phase to the other occurred.

The case was taken through more than a full year's cycle during which it became well stabilized for nearly six months from April until October at a level of 40–43% RH. During that interval, the ambient RH changed from 40% to 65% back to 40%. During the winter months, however, a gradual drift downward could be seen, and it was this which had to be compensated by the addition of liquid water to the system. From mid-October until mid-March, when the central heating was on, the RH just outside the case was rarely above 25% and frequently below 20%, sometimes remaining for more than a week at a time at 12–14%. We attribute the drying out of the case to exchange with this very dry air by leakage. The temperature and RH history of the experimental case is summarized and plotted in Figures, 2, 3, and 4.

Perhaps the most significant point is that the silica gel buffered the RH changes in precisely the way it was intended to do. Setting aside for the moment the drift caused by leakage, it is very satisfying to see that the short-term fluctuations are so small. It will be recalled that one of the advantages of using silica gel is

11. See Miscellaneous Notes.

that its equilibrium RH values are said to have but a small temperature dependence, so that when the temperature changes, the gel still tries to maintain virtually the same RH. This was borne out in several instances where after abrupt temperature changes occurred, the RH was restored to its starting value, lagging behind by only a few tens of minutes.

During the course of these experiments, no visible changes occurred in the objects in the cases—but then none were anticipated. (See the exception in the note below.) The changes which would occur in crizzled glasses or glasses with incipient crizzling over a year would not be expected to be noticeable at the RH level maintained. That, after all, was the point of the experiment. However, changes on a microscopic scale should be monitored in future experiments. Some such experiments were underway at The Corning Museum of Glass in 1971, wherein tapes were applied to make microscopic replications of crizzled surfaces, and the tapes were recorded by electron microscopy. However, the original tapes were destroyed in the 1972 flood, and the work has not been revived, because there is a certain danger in such experiments. To put a tape on the surface of a crizzled glass is to risk the removal of any loosely-attached material on the surface, and we have been hesitant to run that risk.

THE "RAVENSCROFT CASE"

As part of a special exhibition mounted at the Museum in 1976, a fine example of English glass, a goblet made by George Ravenscroft in 1676, was exhibited (CMG no. 50.2.2). This vessel bears a raven's head seal, which Ravenscroft used to mark his later glasses made with a corrected formula. These glasses, he supposed, would not be susceptible to crizzling, as had some of his earlier glasses.¹² Nevertheless, Ravenscroft's corrected formula did not produce really stable glasses, and this par-

ticular object shows clear signs of incipient crizzling. It is a prime example of the sort of glass which must be carefully protected. If it is not, it will surely deteriorate into a severely-crizzled condition.

The object was to be exhibited in a small case constructed of plywood. The exhibition compartment volume was 68 l. The case was designed originally to be lit from above with spotlights, since it was to be located in a darkened gallery. The interior of the case was lined with about one square meter of purple felt, which complicated control of the relative humidity, as the felt tended to absorb a great deal of moisture. The case was made reasonably air-tight by sealing it with duct tape around all seams. A sheet-metal trough covered with the same felt and lined with polyethylene bags was placed in the rear of the exhibition compartment. Then 1,500 g of equilibrated silica gel was placed in it. A sensor was suspended unobtrusively in the rear of the case, and the case was carefully tested before the Ravenscroft goblet was installed. A mock-up of a colorless glass laboratory beaker was placed where the goblet was to be and lit with a twelve-volt lamp of a sort which frequently has been used throughout the Museum. The temperature readings as measured by a thermistor thermometer—which accurately measures the temperature of the glass, and not just the surrounding air—showed that illumination with this light raised the temperature of even this colorless glass from 27.0 to 37.5°C. This was judged to be completely unacceptable for illumination of the Ravenscroft glass in its unstable condition. When a plate of heat-absorbing glass and a piece of diffusing material were placed between the lamp and the exhibition chamber proper, the surface temperature of the glass dropped to 32.5°C, which was still

12. There are numerous accounts of Ravenscroft's early experimentation. One is: A. Hartshorne, *Antique Drinking Vessels*, New York: Brussel and Brussel, 1968, pp. 240-241.

regarded as a bit high, and which was still warmer than the air in the chamber. The spotlight was replaced with a fluorescent lamp having external circuitry and the temperature then held at about 25°C, and did not differ measurably from the temperature of the surrounding air. Therefore, the modified lighting was deemed safe for the Ravenscroft object.

In an effort to make the exhibit more instructive, a volume from the rare book collection of the Museum Library was placed in the case with the goblet. This is a 1662 edition of Neri's *The Art of Glass* (Special Collection no. 327). The volume was opened to a page relevant to the chemistry of the Ravenscroft goblet. When placed in the case, the book produced a startling drop in RH. It absorbed water vapor rapidly, because it had been shelved under low-humidity conditions for several months prior to being incorporated in the exhibition. This is dramatic evidence that the presence of additional absorbent materials—in this case the felt and the book—has an important effect on the RH finally attained. Even as effective a controlling agent as the silica gel had a hard time coping with these complications. If one is attempting to control a case with a material like silica gel, we believe it is inadvisable to introduce any strongly absorbent materials unnecessarily. For our installation of the Ravenscroft object, water was added to the system in order to elevate the RH somewhat. After the addition of 65 g of water to the 1,500 g of gel, a safe and stable RH of 42–45% was established and maintained for twenty-four weeks, after which the exhibition was dismantled. The Ravenscroft object appears to have been completely unaffected by its exhibition experience.

THE HYGROMETRIC HALF-TIME

Garry Thomson's treatment of the stabilization of relative humidity in exhibition cases¹³ makes use of the concept of a hygrometric half-time,

that is, the time required for the RH of a case to drop halfway to the RH level of drier ambient air. His mathematical treatment assumes an exponential decay of the RH in the case and takes into account the rate of air leakage and characteristics of buffering materials within the case. We have tested Thomson's model by comparing it to the empirical data collected during the monitoring of our own Crizzling Case. Thomson's model predicts that a plot of $\ln(C-R)$ vs. t should yield a straight line. (C is the RH within the case at time t and R is the RH of the surrounding air.)

A plot of our data for the interval between December 12, 1977 until January 23, 1978 (Fig. 5) does indeed yield a straight line verifying that the decay is exponential. (R is known to have averaged about 22% during this period.) From the slope of this plot the decay constant, k , was found to be 0.0192 per day, and the calculated half-time is 36.1 days. From our EMC vs. RH curve an average value of M -5.9 was assumed, and in our experiment, B is known to have been -3.5 kg/m³. Therefore, by using Thomson's equation *vi*¹⁴ and our own experimentally determined rate constant (k), it was possible to calculate that during that interval our case was undergoing about 2.3 air exchanges per day with the ambient air. This figure seems somewhat high and may not be real, because there could have been another factor contributing to the downward drift. Water had recently been added to the system and the silica gel might still have been in the process of reequilibrating. This would cause a downward drift if the rate of diffusion of water into the interior of the gel grains was relatively slow.

In our designs for cases for the new museum building, we will make use of Thomson's model

13. Thomson, *op. cit.*

14. Thomson, *ibid.*, p. 96.

$k_N = \frac{0.173}{MB + 0.173}$ where M = moisture gain in g per kg for 1% RH rise and B = dry weight of buffer in kg/m³.

and equation by increasing B, the quantity of buffering gel used, and attempt to reduce k by improving sealing so as to reduce leakage. In addition we shall explore still another approach.

Thomson's explanations make clear the fact that the leakage rate of the case is dependent upon the RH gradient between the case and its surroundings. His treatment quantifies the intuitive notion that the driving force behind leakage is the difference in RH and suggests that one way of extending the half-time of the drying process is to find some means to reduce the term (C-R). This, in turn, suggests that the presence of an air envelope of RH close to C surrounding the case would inhibit loss of moisture from the case and brings to mind the possibility of using a double barrier to further stabilize the case. This is just another way of looking at the rather obvious fact that a double-walled container would be slower to dry out but emphasizes that this would be especially true if the space in between also contained buffering material.

We have explored this possibility from a mathematical viewpoint and believe that a considerable extension of hygrometric half-time could be realized. The ultimate value of such a system would be determined by balancing the advantage of increasing the half-time against the inconvenience and expense of constructing a more elaborate case. Such a balance can be made favorable only by the ingenuity of the case designer.

SOME MISCELLANEOUS NOTES

"The Vapor Pressure" of a Crizzled Glass

A group of five badly-crizzled eighteenth-century French goblets was placed in a chamber with one of the same sensor probes used for monitoring the crizzling case. The chamber

used was a 9.7-liter laboratory desiccator, although only the crizzled glass was placed in the chamber and no desiccant or other materials. When the experiment was started the relative humidity was 46%. The RH slowly drifted downward and after eight weeks, leveled off at 41%. If one disregards the effect of absorption and desorption of water vapor on the walls of the chamber itself, it might be inferred that the "vapor pressure" of the adsorbed water and water of hydration of this particular crizzled object is -7.2 mm Hg, or an RH of 41% at 20°C. This corresponds, within experimental error, to the value of 42% given as the equilibrium RH for the monohydrate of potassium carbonate cited by Robert Organ.¹⁵ It also makes sense that the vapor pressure of water on—and/or in—a crizzled glass should be of the order of 40% or greater. Historically, the glass would have become hydrated to the extent that its equilibrium vapor pressure, expressed as an equilibrium RH, would be close to that of the average ambient RH it experienced over the past three centuries, and that value probably would have been of the order of 45%.

In a separate experiment, one of these goblets was heated at 110°C for one hour and its loss in weight, presumably consisting of evolved adsorbed water and water of hydration, amounted to 0.13 g or 0.12% of its weight.¹⁶ The surface area of the goblet is about 278 cm², so its water content had been about 0.00047 g/cm². The same object was then saturated with water by letting it stand in a chamber at 100% RH for several days, and the heating repeated. This time the loss in weight amounted to 0.17 g or 0.16% of its weight, and a water content of about 0.00061 g/cm².

15. R. M. Organ, "The Safe Storage of Unstable Glass," *Museums Journal*, 56, February, 1957, pp. 265-272.

16. We thank Dr. Yao Su and Theresa Magliocca of Corning Glass Works for carrying out this determination.

Reequilibration Times

For the system being tested to be used successfully, it is necessary not only that the silica gel release or absorb water as required, but also that it do so quickly enough so as to prevent the RH from wandering outside the safe levels specified. In order to evaluate the gel in this respect, a few simple experiments were conducted in laboratory desiccator chambers.

The capacity of the chambers used was 9.7 l. Approximately 90 g of silica gel removed from the enamel trays of the experimental case was placed in a covered glass dish inside the chamber. Then either a small quantity of freshly dried silica gel desiccant or a small quantity of liquid water was placed alongside the dish. The chamber was closed and allowed to dry out or build up a high RH. The chamber was then opened slightly and the dish of equilibrated silica gel was uncovered and the desiccant or any remaining water removed. Thus, the uncovered dish of gel was exposed suddenly to rather high or low RH conditions, and the time it required to restore the RH to its own equilibrium RH was recorded by a sensor probe enclosed in the chamber. In both cases the gel responded quickly.

In one experiment, the gel adjusted a starting RH of 69% to 41% in about two hours. In another experiment, it adjusted a starting RH of 13% to 40% in about four hours. It is probably true that a small-volume system reequilibrates more efficiently than a large system, but since the ratio of the chamber volume to exposed gel area was about the same in these experiments as it was in the large experimental case, it was surmised that the recovery time of the large case must be well within acceptable limits.

An experiment on the Crizzling Case itself showed that when the case was flushed out with ambient air at 17% RH, the silica gel reestablished its equilibrium RH of 40% within about

eight hours. (The increase to 35% RH, 75 per cent of the way, required only two hours.)

A Special Precaution

Usually, when water had to be added to the system, this was done by removing the trays of silica gel and spraying or squirting a measured volume of distilled and deionized water onto them. On a few occasions, however, liquid water was added by placing it in twelve small beakers distributed throughout the case. In these instances, the RH rose temporarily, but not excessively, because the water evaporated more quickly than the gel could take it up. No harmful effects were noticed until the third time this was done. On that occasion, some water was sprayed onto the gel and some placed in the beakers. The moistened gel was evidently even slower in taking up water vapor from the air. The RH rose to a level of 70–80% and stayed in that range for about fifteen hours. At that time, it was noticed that one of the objects, a Venetian goblet (CMG no. 59.3.20), had become separated at an old repair and collapsed sideways. Fortunately, it did not fall, for if it had, it certainly would have broken badly, and could have taken other objects with it. Upon examining the rest of the objects in the case, it was found that two others had similarly become unglued. No real harm was done, because all of the separations were at old breaks. We mention this not only as a precaution against adding water to a system in this way, but even more importantly, as a warning that edge-to-edge joins made with epoxy resins, as these had been, can apparently be loosened by rather short-term exposures to an RH of the order of 70–80%. This was totally unexpected by us and should be noted very carefully by all those who handle repaired glasses.

Short-term Variations in Relative Humidity

Careful observations were made of small variations in RH which occurred over a matter of a few hours or a day. Normally, these variations

were no greater than one or two percentage units of RH, but a few changes as great as three or four percentage units were observed. Generally these larger changes were accompanied by changes in temperature. When a temperature change of five or six degrees occurred, which occasionally happened, the RH would usually change correspondingly; that is, a rise in temperature would cause a decrease in RH until the silica gel could reequilibrate the system. But sometimes a rise in temperature was associated with a rise in RH, as if one were watching a classical adsorption experiment, in which the substrate releases the adsorbate as the temperature rises. These are small but interesting effects, and the processes should be studied further. In this connection, the fact that the RH of a given silica gel is thought to be relatively insensitive to temperature changes implies that the equilibrium partial pressure of water vapor over the gel must rise with temperature at about the same rate as the vapor pressure of water does.

Storage at Low Relative Humidity

In our earlier research several experiments were carried out on a Silesian goblet dated to 1820 which was donated for experimental purposes by Mr. Jerome Strauss.¹⁷ The object, sample no. 4011, showed typical incipient crizzling. Chemical analyses were made of the glass, an electron microbeam probe profile analysis was made of the surface, and several experimental pieces were sawed from the rim and foot.

After the experiments were completed, a few of the sawed pieces were placed in chambers with controlled relative humidities. As reported earlier, when stored overnight at near-zero RH, the glass degenerated dramatically to a severely crizzled state. But it was not then known how low the RH could go without causing degeneration. We now have some further information on that subject. The chamber with the next lowest RH had a level of 12–14%, which was established over a saturated solution

of lithium chloride. Before the fragment of glass was placed in this chamber, a series of photomicrographs was taken of its surface. The glass was placed in the chamber on January 31, 1975, and removed on October 25, 1977. (A few casual examinations had been made in the interim.)

It appeared to the author that this glass sample showed somewhat more prominent crizzling after the two years and nine months storage at the low RH than it did at the beginning of the experiment. A microscopic examination was made, and the results were compared to the photomicrographs taken at the beginning. Most of the fissures which could be seen after the storage at low RH were also visible in the original photomicrographs, there being only about a 2–3% increase in the number of fissures. This relatively small increase in the number of fissures would not account for the apparent degeneration toward severe crizzling, but a microscopic comparison between this sample and another sample stored at 70% RH did provide evidence which could explain it. The fissures in the glass stored at the lower RH were noticeably more prominent. They had the appearance of being wider and "more open" than those on the glass which had been stored at the higher RH. Therefore, although storage at the low RH had not appreciably increased the number of fissures in the surface, it had opened them up. Consequently, one must conclude that storage at an RH in the range of 12–14% for two to three years promotes a degree of dehydration, which is dangerous for glass with incipient crizzling.

A Comment on Treatment

Although the corrosion of glasses has been extensively studied, there is not complete agreement upon the details of the chemical mechanism by which the attack of water proceeds.

¹⁷ Sample no. 4011, Figure 3, in reference cited in footnote one.

The mechanism may be complicated and indeed may vary from situation to situation and from one glass system to another. Some knowledge of the details of the mechanisms (or, at least, a working hypothesis about them) is always necessary when attempting to devise treatments for various types of early glasses. This is true for stained glasses and ancient glasses as well as for crizzled glass objects. We have some thoughts on the matter and some experiments to suggest, but, by and large, details of the mechanism can be established and accepted by the community of glass scientists only after a great many experiments on many different glasses under varying and carefully-controlled conditions have been carried out. Such an undertaking is well beyond the scope of our Museum's scientific program, but we wholeheartedly encourage others to pursue such studies.

One point upon which there is general agreement is that the hydrolysis of glasses, their chemical attack by water, results in a depletion of alkali at the affected surface of the glass, and the conversion of the glass into a hydrated state. Numerous experiments, including several done on crizzled objects at our Museum, have confirmed this depletion of alkali.

An important point we wish to make here is in response to a suggestion which has frequently been raised, to the effect that if crizzling is caused by the removal of alkali, why not simply replace the alkali to reverse the process and restore the glass? The problem is that when the alkali is removed and the glass becomes hydrated, the molecular structure of the glass is altered. That is to say, its silicate network, or the "skeleton" of the glass, is also almost certainly disintegrated by the same process that causes the leaching of the alkali. The resulting structure is probably more like that of a hydrated silica gel than that of the original glass. Therefore, simple replacement of the alkali to its original concentration level should not be expected to transform the hy-

drated material back into a glass any more than the addition of carbon dioxide and water to a piece of charcoal should be expected to transform it back into an oak log. It is the way atoms are bound together—as much as what atoms are present—which determines the physical nature of matter, in this case the glassy character. Therefore, there is little hope, in the author's opinion, that the process of crizzling can be reversed chemically without some high-temperature process which would fuse the surface of the material and reconstitute it into a glass. Because high-temperature treatments are not likely to prove both feasible and effective, we are left only with applications of coatings or impregnations to consolidate a crizzled surface into something resembling its original glassy state.

Until now, most efforts at consolidation have proven unsuccessful in that the resulting appearances of the treated objects have been, if not displeasing, at least not glasslike. It may be that recent research at The Corning Museum of Glass¹⁸ will offer some hope in this regard. Pretreatment of other types of deteriorated glasses with silanes has improved adhesion and penetration of consolidants. Such treatments may allow greater latitude in the selection of consolidants and their means of application to crizzled glasses, so that appearances can be achieved which more closely resemble the original glass surfaces.

A Final Note

As this article was going to press, we had a most informative discussion with Dr. Stolow regarding the construction of a new case to be installed in our existing gallery. This case, which will contain ancient glass, will be controlled with silica gel and will be used as an

18. Unpublished work by Raymond Errett of the Museum staff and Shelley Reisman, then an intern at the Museum, in consultation with Dr. Merrill Lynn of Corning Glass Works.

experimental installation for the new building. Dr. Stolow made many very helpful suggestions and comments, some of which have a direct bearing on the contents of this article. Readers interested in this subject should watch for his forthcoming publications in the conservation literature.

It will be recalled that in several instances we added water to silica gel by spraying or misting it directly onto the surface with raking. Dr. Stolow does not recommend this procedure for several reasons. First, it can lead to decrepitation of the gel, that is, the gel may break up into smaller particles. This can be a disadvantage in systems where the gel is supported in fabric-covered panels, as the smaller particles fall out more easily; and also, small particles produced by decrepitation may cause dusting. Perhaps the most serious objection to adding liquid water directly to the gel is that it is difficult to add the water uniformly—and this difficulty becomes accentuated when one has to deal with large quantities of gel. In a paper presented at the meeting of the American Institute for Conservation in Fort Worth during June, 1978, Dr. Stolow discussed systems for conditioning silica gel in controlled-humidity chambers.

Dr. Stolow feels that the presence of other water-abundant phases in a system controlled by silica gel can have a beneficial effect by helping the gel to buffer the system, even

though it does introduce another variable. He also prefers the use of larger-sized particles in order to prevent their escaping through the fabric covers of panels supporting the gel. Because our trial installation will involve the use of such panels, a mesh size of 3–8 will be used in accordance with Dr. Stolow's recommendation.

Acknowledgements

It would be difficult to list here the names of all those who contributed to this complicated project. The author hopes that those whose names are not mentioned below will accept his thanks anonymously and take satisfaction in knowing their efforts were directed toward a worthwhile cause. Special thanks are due Judy Snyder, who for three years recorded the data and looked after the experimental cases. She also assisted in the preparation of the manuscript. In the later stages of this work, Susan Johnson ably carried out these same responsibilities. Dr. David J. Fischer conducted several preliminary studies which, although they are not discussed in the text, were essential to the project. He was assisted by Joseph Maio, who also helped in maintaining the experimental cases. All too often the efforts of members of museum security staffs go unnoticed, so it is a special pleasure to acknowledge here the willing cooperation of the guards who took data during those times the Museum was closed. They are: William Buchko, Patrick Eldred, Charles Gardner, Harold Gray, Ronald Ogden, Kerry O'Shanick, Walter Schroeder, Deborah Tally, Joseph Turchick, Roswald Viele, and Paul Yorio.

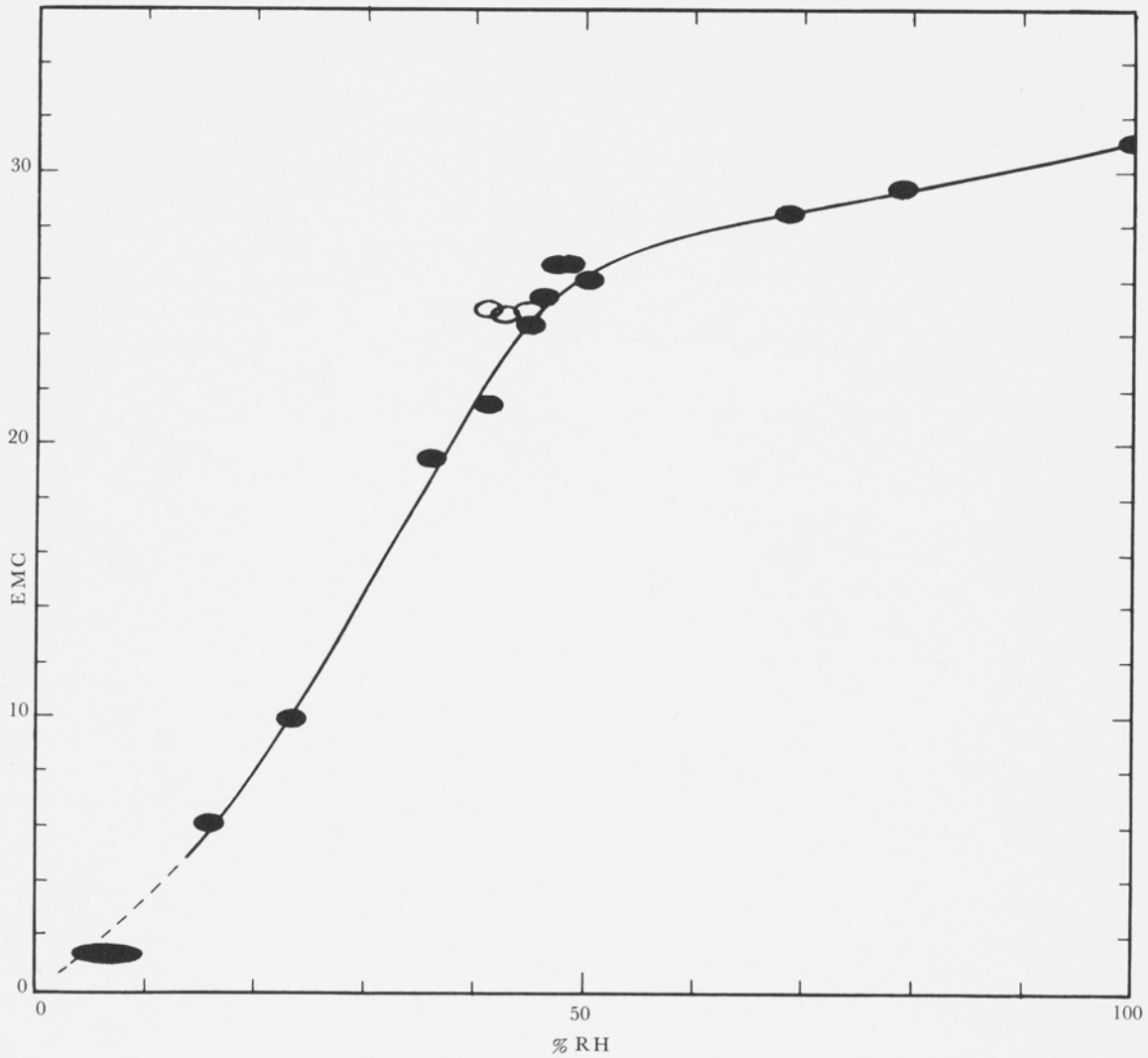


FIG. 1. Equilibration curve for silica gel used in the Crizzling Case experiment. The curve shows the equilibrium RH of air in contact with prepared samples of silica-gel having various moisture contents. (EMC is expressed as percentage of water relative to dry weight of gel.) Hysteresis is not indicated because of the small number of points determined. Open ellipses are data for samples of gel removed from the case at three stages of the experiment.

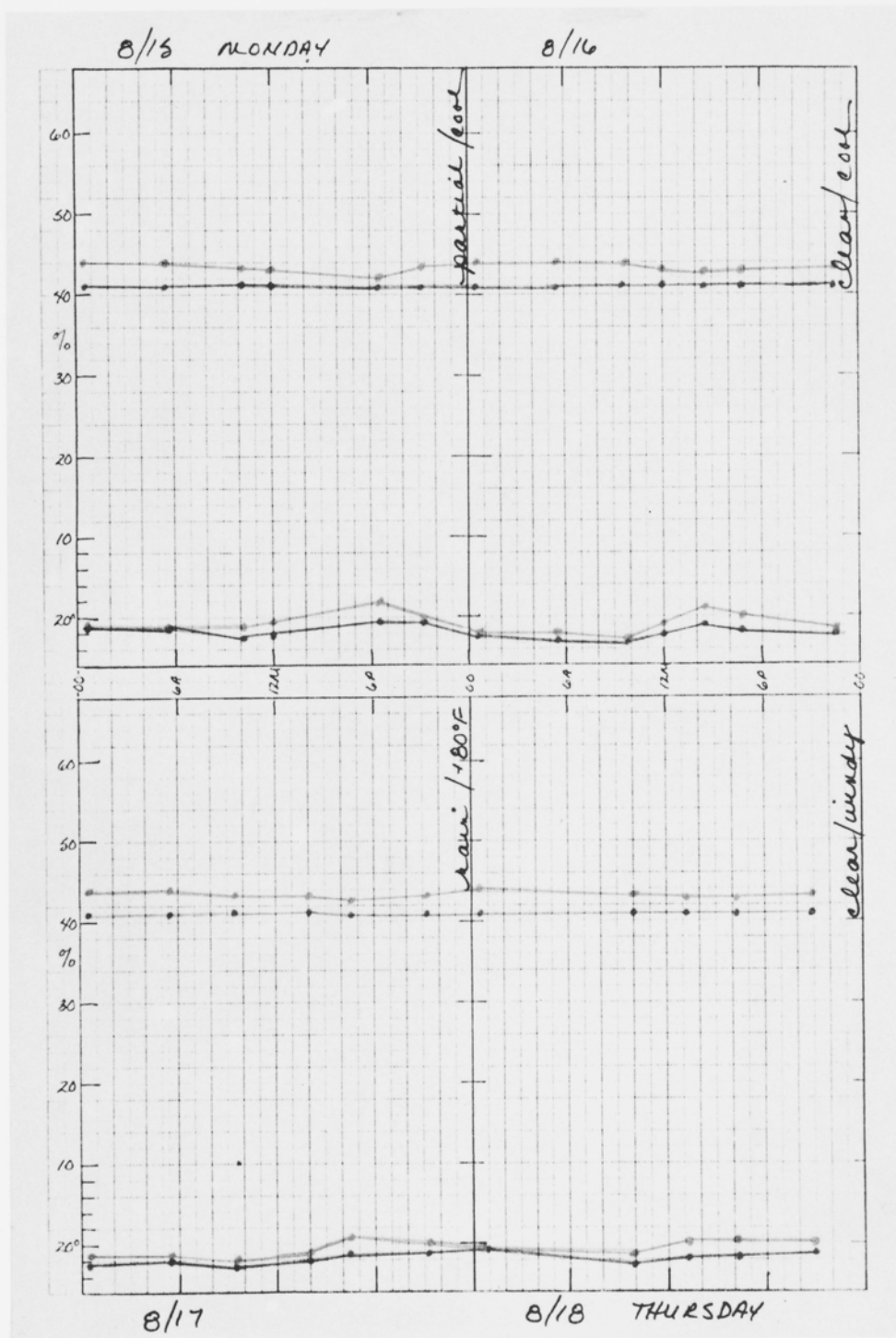


FIG. 2 . Page from Mrs. Snyder's and Mrs. Johnson's daily log book. Data are for four mid-summer days in 1977 and are typical of periods when the Crizzling Case was well stabilized. The plot shows raw data, not yet corrected for a slight calibration difference between the two probes.

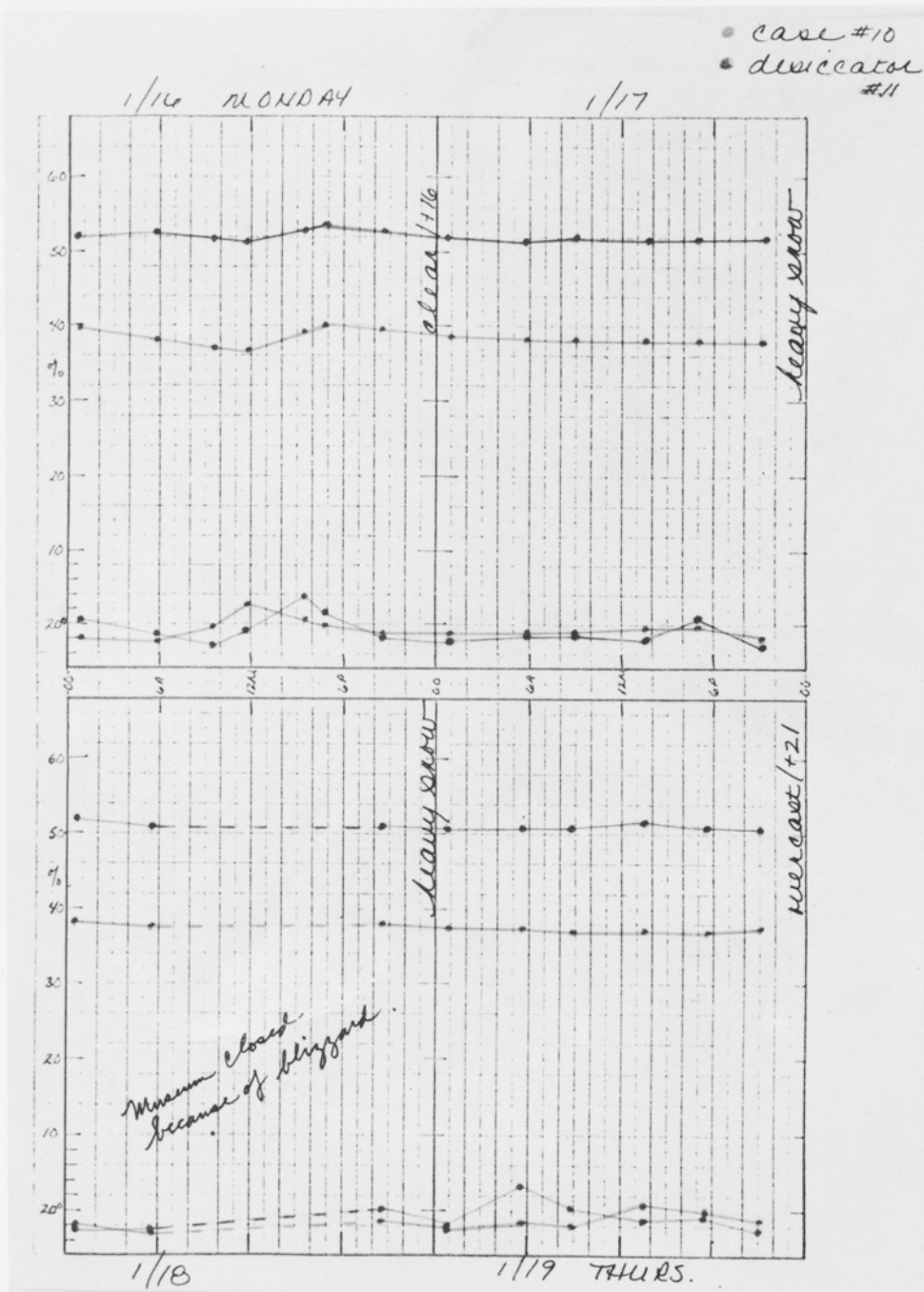


FIG. 3. Page from Mrs. Snyder's and Mrs. Johnson's log book. Data are for four mid-winter days early in 1978 when there was a heavy snowfall. The lower of each pair of RH curves is for the Crizzling Case while it was drying out exponentially. The upper RH curve is for one of the chambers of silica gel used in establishing the RH versus EMC curve ($EMC = 26.1\%$), which was just approaching its equilibrium state. The peaks in the temperature curves at the bottoms of the graphs result from occasional increases in the ambient temperature owing to some peculiarity of the building's heating system.

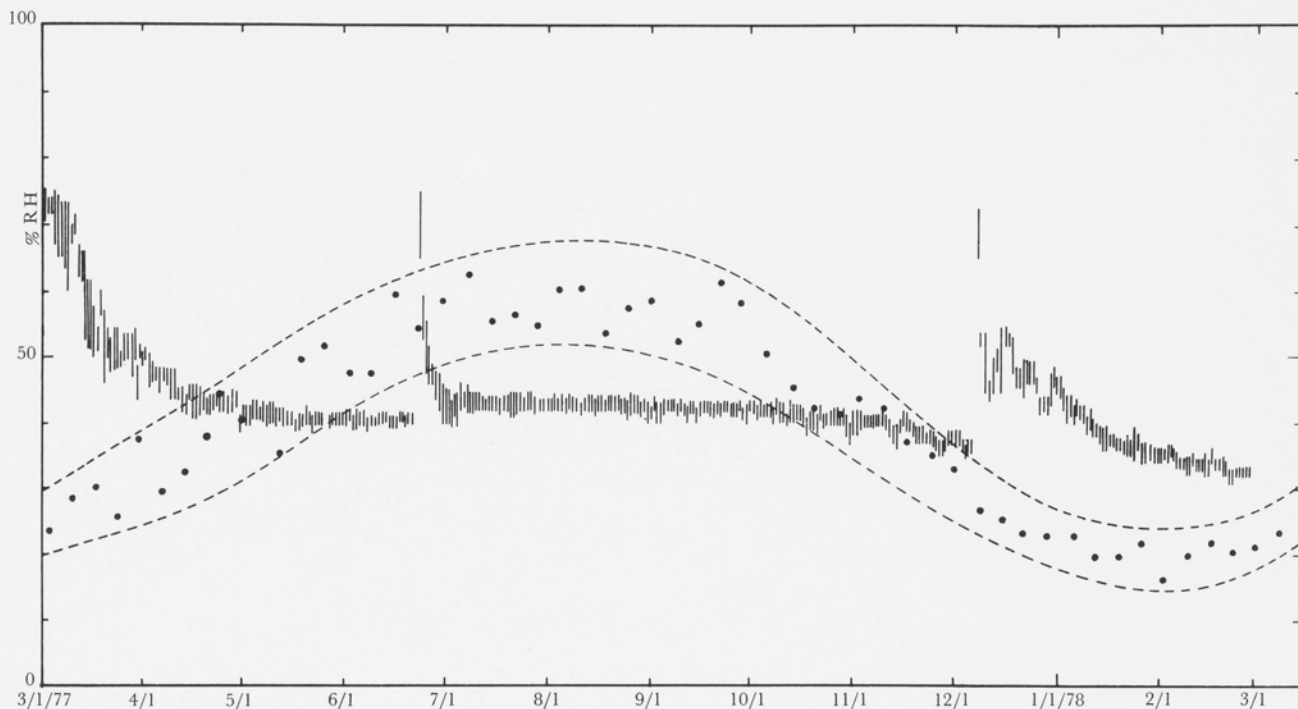


FIG. 4. One-year RH history of the experimental Crizzling Case plotted as a daily record. RH values measured at two locations within the case are plotted as vertical lines. The length of each line represents the daily range. Additions of water to the system are evident in early March 1977, late June 1977, and early December 1978. In all, some 5000 measurements were used to construct this curve. Solid dots indicate weekly mean

ambient RH values immediately outside the case. The broken curves are RH limits which include approximately 95% of the recorded data. The central tendency of RH values measured in a different part of the Museum, the Ancient Gallery, generally falls within the same limits, but the RH tends to wander outside the limits more frequently to temporary extremes of higher or lower RH.

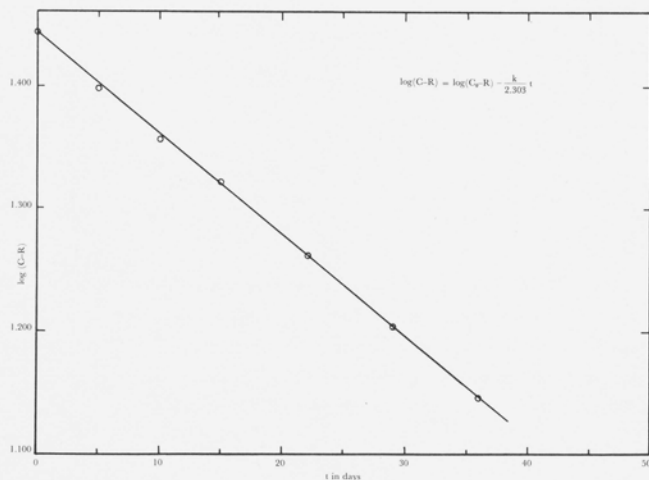


FIG. 5. Plot of $\log (C-R)$ versus time for RH data recorded in the Crizzling Case experiment during the interval December 17, 1977 till January 23, 1978. C is the RH measured within the case at time t , R is the average ambient RH, which is known to have been about 22%, and C_0 is the RH within the case at $t = 0$. The resulting straight line indicates that the drying out of the case is exponential with time, in accordance with the model proposed by Thomson. From the slope of the line, a rate constant of $k = 0.0192$ per day was calculated, which yields a hygrometric half-time of 36.1 days.