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STABILIZATION OF RH IN EXHIBITION CASES: HYGROMETRIC HALF-TIME

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Abstract—A formula is derived with experimental support for predicting the RH changes inside an unsealed exhibition case containing a buffer such as silica gel. It is shown that a well-constructed case containing about 20 kg silica gel per cubic metre of case volume should constrain seasonal humidity variation within reasonable limits and in some climates make air conditioning unnecessary. However the formula proposed requires full-scale practical tests before adoption.

1. INTRODUCTION

It is very likely that the complete air conditioning of a museum to a high degree of RH (Relative Humidity) stability can do more for preservation than any other factor. Yet there is an uneasy feeling that a system developed in the energy-wasting days which are already behind us may not be the best for the future, and of course has never been even possible for the poorer museums.

But almost all museums use exhibition cases of some kind. Could we not banish the massive, noisy and costly machinery that is involved in air conditioning, and use instead a simple, cheap and maintenance-free control of the atmosphere within museum exhibition cases? The purpose of this article is to take a step in this direction by covering some necessary theoretical and experimental groundwork, making use of foundations already laid [1-4].

2. EXPONENTIAL DECAY AND HALF-TIME

2.1. *Exponential Decay*

The third part of this paper, from which a simple formula is derived, is necessarily mathematical. But the general tenor of the argument can be made clear without mathematics.

Many processes of change in nature work according to a simple rule, that of exponential decay, which can be understood as follows.

When we make a cup of coffee we start with water at 100°C, so the coffee starts out of equilibrium with its surroundings because its temperature is 100° and its equilibrium temperature (that of its surroundings) is, say, 20°C. Its rate of cooling, as Newton first recognized, will now be proportional to that difference in temperature. That is to say its rate of cooling will start by being proportional to (100 - 20), so that we could say the rate at time zero = $k(100 - 20)$ degrees per minute. We need not actually determine k unless we specifically want to. The point is that the coffee will continue to cool at a rate proportional to the difference between its temperature and the temperature of its surroundings. At 50°, for example, its rate of cooling will be $k(50 - 20)$ degrees per minute, a considerably slower rate. When its temperature has reached 21° its rate of cooling will be $k(21 - 20)$ degrees per minute, which is an 80th of its initial rate.

How long will it take to cool to equilibrium, which is at 20°? A mathematician would say 'never!', but this is, of course, never true in real life. The room temperature is itself fluctuating, and if it drops a little below 20° it gives the cup a chance to cool a little faster, and soon cup and room will be fluctuating within the same relatively narrow temperature range. The important fact to note is that the time taken to reach room temperature or equilibrium cannot be accurately determined, and if we do attempt to determine such a

figure by using a thermometer which only reads to $\frac{1}{4}$ degree so that $20\frac{1}{4}$ looks like 20 we will even then never get the same figure twice.

This is a situation typical of exponential decay. We might persist, however, intuitively realizing that some measure of the time involved in cooling would be useful. And indeed this is so. What we do is to measure the time taken to reach half way. The starting temperature is 100° , the equilibrium temperature is 20° , and the half-way temperature is the average of these two: 60° . We therefore measure the time taken to cool from 100° to 60° , and we call this the half-time.

A particularly useful property of the half-time is that we can start taking our measurement any time we like. Time zero need not be at 100° . Suppose we cool from 100° to 60° and find that this takes 5 minutes, making the half-time 5 minutes. We can immediately check this measurement by making our new time zero at 60° and timing the cooling to the new half way point, $\frac{1}{2}(60 + 20) = 40^{\circ}$. We will find that the cooling from 60° to 40° also takes 5 minutes although this is a fall of only 20° as opposed to the first reading over 40° . Similarly the time for cooling from 40° to $\frac{1}{2}(40 + 20) = 30^{\circ}$ is also 5 minutes, and so on. The half-time will always be 5 minutes for this particular cup of coffee.

The best-known example of half-time measurement is radioactive decay. A radioactive atom is matter in disequilibrium. It reaches equilibrium by disintegrating into stable atoms. Whether it does this within the next second or next year is a matter of chance. Because of these constantly occurring disintegrations a mass of radioactive material is never pure, so that we can never get an absolute time zero from which to start measuring its rate of decay. This is of no consequence, however, because the decay is exponential: its rate (number of disintegrations per second) is proportional to the number of radioactive atoms in the material, which is itself a direct measure of the amount of departure from equilibrium, just as much as the excess temperature of the coffee was. To measure the half-time, here usually called the half-life, of a radioactive element, we count the number of disintegrations per second at the start, at a time designated zero, and wait until the disintegration rate has dropped to half the rate at time zero. In practice there is a mathematical device for calculating half-time from any two count-rates and the time between them (see p. 96).

Our third example of exponential decay directly concerns the matter in hand: RH in an exhibition case.

If we could ensure by cheap and simple means, and without using machinery, that the RH in an exhibition case remained within a safe range right through a winter heating period or right through a tropical monsoon period, we could at a stroke make an important advance in conservation.

The purpose of this article is to show that an understanding of what might be called the hygrometric half-time of the exhibition case and its contents is a necessary step to the solution of this problem.

2.2. *The Hygrometric Half-time of an Exhibition Case*

An exhibition case holds water in the air within the case, in the contents of the case and in the materials used in making the case. To simplify our thinking let us consider a case, either made of metal or lined with a moisture-barrier. We then need only consider the water in the case air and in its contents.

The case is not sealed in any special way.

Now experience has shown us that if we place objects carefully seasoned to 55% RH in the case, close its lid and then proceed to subject it day after day to a much lower external RH, as during winter heating, the RH in the case will drift lower and lower, and the moisture-content of its carefully-seasoned contents will fall in consequence, though more slowly than if not protected by the case.

The reason for this is, of course, that the case does not constitute a complete barrier for air

and moisture. Air and water vapour can exchange in this way by three mechanisms: temperature change, pressure change and simple diffusion. Padfield, in an important article that covers a great deal of ground [2], has shown clearly that both temperature and pressure changes in museum conditions are relatively unimportant. The important cause of RH change within a case is diffusion of air, mainly through cracks in the unsealed case, but also through wood and even certain plastics used for glazing.

But, whatever the mechanism, the change in RH is one of exponential decay, and can therefore be characterized by a half-time. We measure the RH inside the case at time zero, and the room RH, which must be considered constant for simplicity (though a varying room RH can also be dealt with). Then the hygrometric half-time for the case with its contents is the time taken to reach the half-way RH state: $\frac{1}{2}(\text{case RH at time zero} + \text{room RH})$.

This hygrometric half-time will depend on two chief factors: (1) the air leakage rate of the case measured, say, as number of air changes per day, and (2) the buffering material in the case.

In this context a buffering material is any material which contains exchangeable water, that is to say any material which contains more water at high RH than at low. Wood, natural textiles, paper and silica gel are all buffering materials.

If there is absolutely no buffering material in the case—a rare situation—then its half-time will be precisely the time taken for half an air change, since a mixture of half outside and half inside air gives an RH halfway between the two. When we realize that even a well-fitting case might undergo one air change per day we see that this is a hopeless situation, and so buffering becomes very important.

Our primary objective might now be defined as follows: to make a case which does not require any elaborate sealing or unusual technology, and which contains enough buffering material to keep its contents safe through the dangerous part of the year.

We cannot hope for absolutely constant RH, since the buffering system cannot reverse a trend in RH, it can only slow it down. Taking 55% RH as the starting level, a winter heating RH of 30% and a monsoon RH of 80%, the half-way RHs would be 42.5% and 67.5% respectively. If we could accept these as the danger levels, then the half-time of case and contents is likely to be roughly the same as the danger period. Looking ahead (Figs. 2–4) it appears that a half-time of 150 days or about half a year would keep RH variation without about $\pm 8\%$ while buffering all sharp changes. This should cover many situations, and is enough to clarify our objective for the moment: *a half-time of about half a year*.

However it should be realized that, if our system is really going to work unattended year in and year out, smoothing out seasonal differences, it will find its own average RH, which may be different to the RH we chose at the beginning, and will in fact be the average indoor RH of the room in which the case stands. If this is too low, then some crude winter humidification of the room may become necessary, merely to bring up the annual average, and conversely for humid climates.

2.3. Extending the Half-time of a Case to 150 Days

There are two main things we can do to extend the half-time of a case: firstly we can reduce its leakage rate as far as possible, and secondly we can add buffer. (The use of stabilizing salts is a further possibility not discussed here since it poses certain maintenance problems.) To seal a case hermetically is more difficult than most people imagine, and makes it very difficult of access. But it is reasonable to expect a well-made case with snugly-fitting unwarped closure and a moisture-barrier to any wooden sides, to have a leakage rate of not more than one air change per day [2] (e.g. Case 2 of Fig. 6).

To estimate the amount of silica gel needed we must make use of the formula derived in Section 3:

$$N_{\frac{1}{2}} = 4 MB \text{ (approximately)}$$

$N_{\frac{1}{2}}$ is the number of air changes to the half-way stage. With one air change per day, $N_{\frac{1}{2}} =$ half-time in days. If we are aiming at half a year, $N_{\frac{1}{2}} = 150$.

B is the amount of buffer in the case, measured as the dry weight of buffer in kilograms per cubic metre of case volume.

M characterizes the moisture-holding properties of the buffer, and can be called its 'specific moisture reservoir'. If one kilogram of the buffer loses M grams of water when the RH falls by 1%, or vice versa, then its specific moisture reservoir is M.

Table 4 shows that M for silica gel is dependent on RH. In the middle of the range, $M = 2$. Therefore $150 = 4 \times 2 \times B$, and $B =$ about 20 kg silica gel per cubic metre.

We therefore need 20 kg of silica gel per cubic metre for a case which undergoes one air change per day, if it is to have a half-time of about 150 days. This is a not unreasonable amount, as Figure 6 shows. Of course any wood in the case, including the wood of the exhibits, will contribute to the buffering, but we can regard this as a bonus contribution to stability and retain our 20 kg/m³ of silica gel.

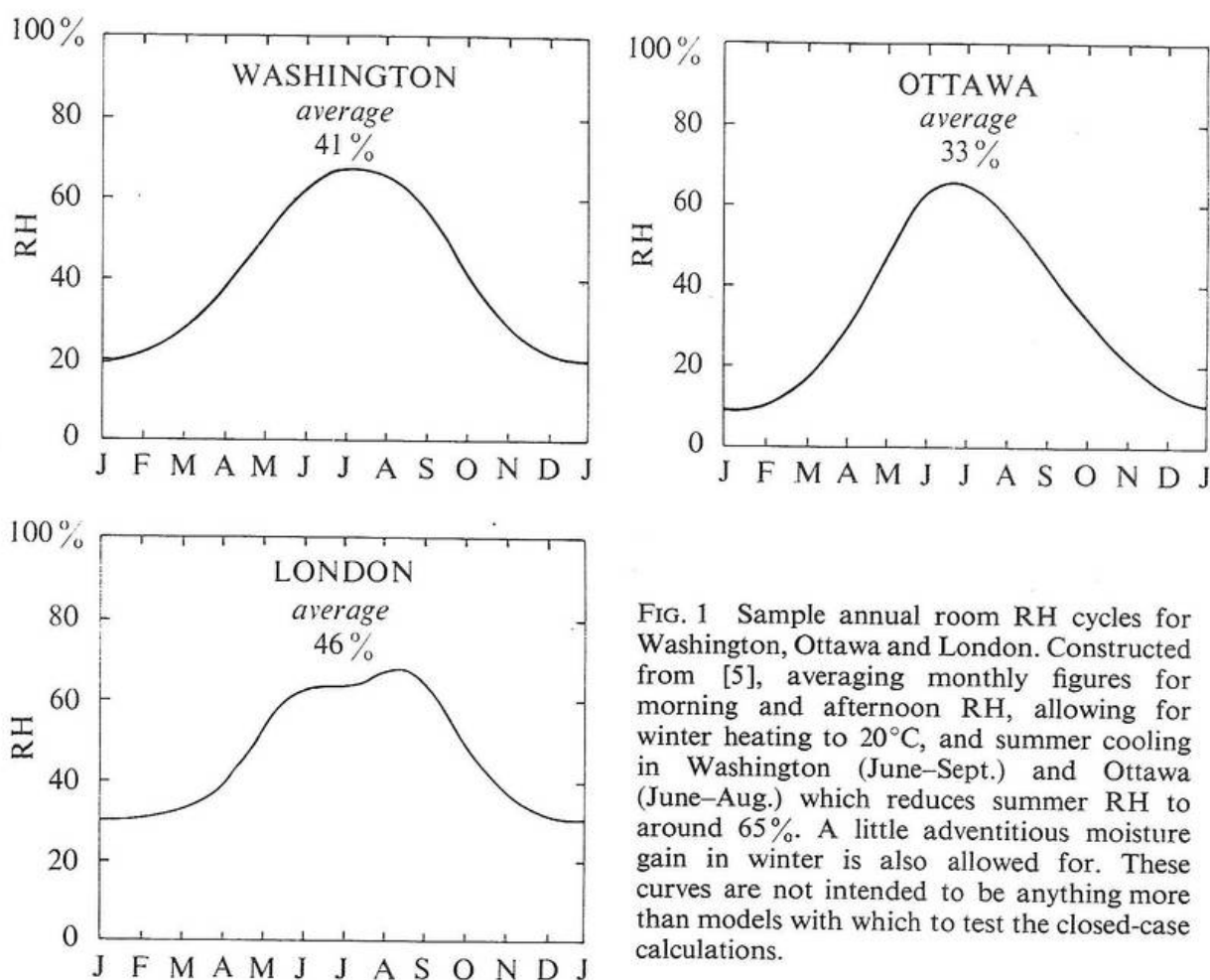


FIG. 1 Sample annual room RH cycles for Washington, Ottawa and London. Constructed from [5], averaging monthly figures for morning and afternoon RH, allowing for winter heating to 20°C, and summer cooling in Washington (June–Sept.) and Ottawa (June–Aug.) which reduces summer RH to around 65%. A little adventitious moisture gain in winter is also allowed for. These curves are not intended to be anything more than models with which to test the closed-case calculations.

| | J | F | M | A | M | J | J | A | S | O | N | D | Month |
|------------|----|----|----|----|----|----|----|----|----|----|----|----|-------|
| Washington | 19 | 21 | 27 | 38 | 52 | 61 | 67 | 65 | 56 | 41 | 28 | 20 | %RH |
| Ottawa | 10 | 10 | 16 | 27 | 46 | 62 | 66 | 59 | 45 | 32 | 20 | 13 | %RH |
| London | 31 | 30 | 31 | 37 | 53 | 62 | 63 | 67 | 62 | 48 | 37 | 32 | %RH |

2.4. Stabilized Annual RH Cycle in a Closed Case

It seems we now have the means of predicting the RH change in a case containing buffer when placed in a room of different but steady RH. Put another way, if a case has come to equilibrium with a steady room RH, and then this room RH changes suddenly to a new one, we can predict the lag in RH change within the case.

But in real life the RH in a non-air-conditioned room is not likely either to be steady or to change abruptly to a new steady value, but rather to be the result of all kinds of fluctuations in the weather and heating, both short-term (hourly and daily) and long-term (seasonal). For a reasonably well-fitting case we can ignore the short-term fluctuations, but the seasonal drift remains. That is to say a case with a half-time near one day will be affected by daily fluctuations, but if the case has a half-time of over one month but less than one year it is the seasonal fluctuations which will be our concern.

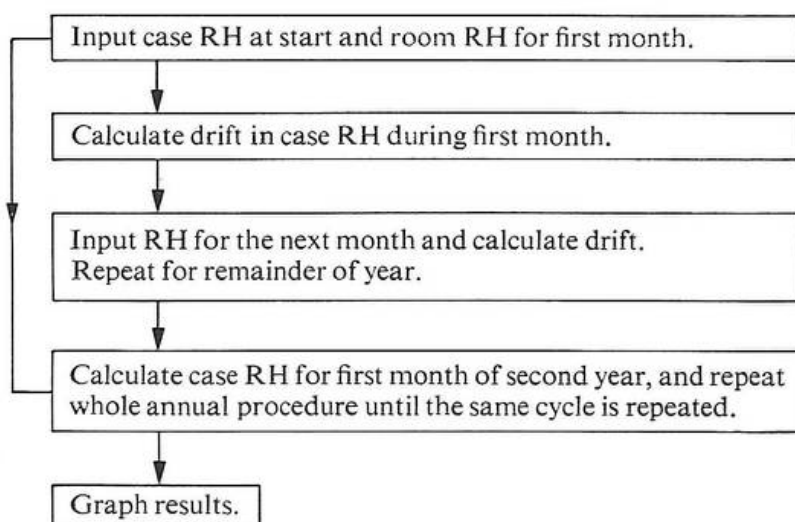
Let us take three cities as examples to work on: Washington as a city which requires both extensive winter heating and summer cooling, Ottawa to represent extremely low winter indoor RH, and London with a milder, semi-maritime temperate climate. The indoor RH curves representing these cities (Fig. 1) have allowed for winter heating to 20°C.

Concerning summer cooling, at the risk of over-simplification, one can assert from the standard hygrometric relations that the room RH resulting from use of a simple cooler will not be too far away from 65% except in dry climates, whatever the outdoor RH. Thus a city in the humid tropics such as Singapore, with outdoor RH in the 70s and 80s throughout the year might expect a cooled RH of 65% during exhibition opening hours, rising to 70 or 80% during the night, and yielding an average of over 70%.

The curves of Figure. 1 are not intended to be accurate predictors, but rather to be models with which to test the behaviour of our exhibition case.

The next step is to plot, with the help of the equations developed in the mathematical section (p. 93), the course of the RH within the case for various values of the half-time. If the annual fluctuations of case RH can be reduced to a safe value then we have solved the problem of RH stability.

TABLE 1
SIMPLIFIED OUTLINE OF ALGORITHM FOR FIGURES 2-4



Although computer simulation is no substitute for practical experiment it can be a most useful preliminary, giving us, if we work correctly, an impression in a few minutes of what takes years. The curves in Figures 2-4 are such simulations, using an algorithm for calculating the effect of room RH on case RH on a monthly basis, and graphing the results only after a sufficient number of annual cycles have been performed to reach a steady-state condition (Table 1).

From inspection of these sample annual cycles and others, it appears that, to keep fluctuations in RH within $\pm 10\%$, a reasonable aim for such a simple system in rather difficult conditions, we need a half-time of 150 days, or about half a year.

The effect of heating the case to a temperature different to that of the room, as by sunlight or strong spotlight, has not been taken into account. Good conservation should ensure that this does not happen to any marked extent.

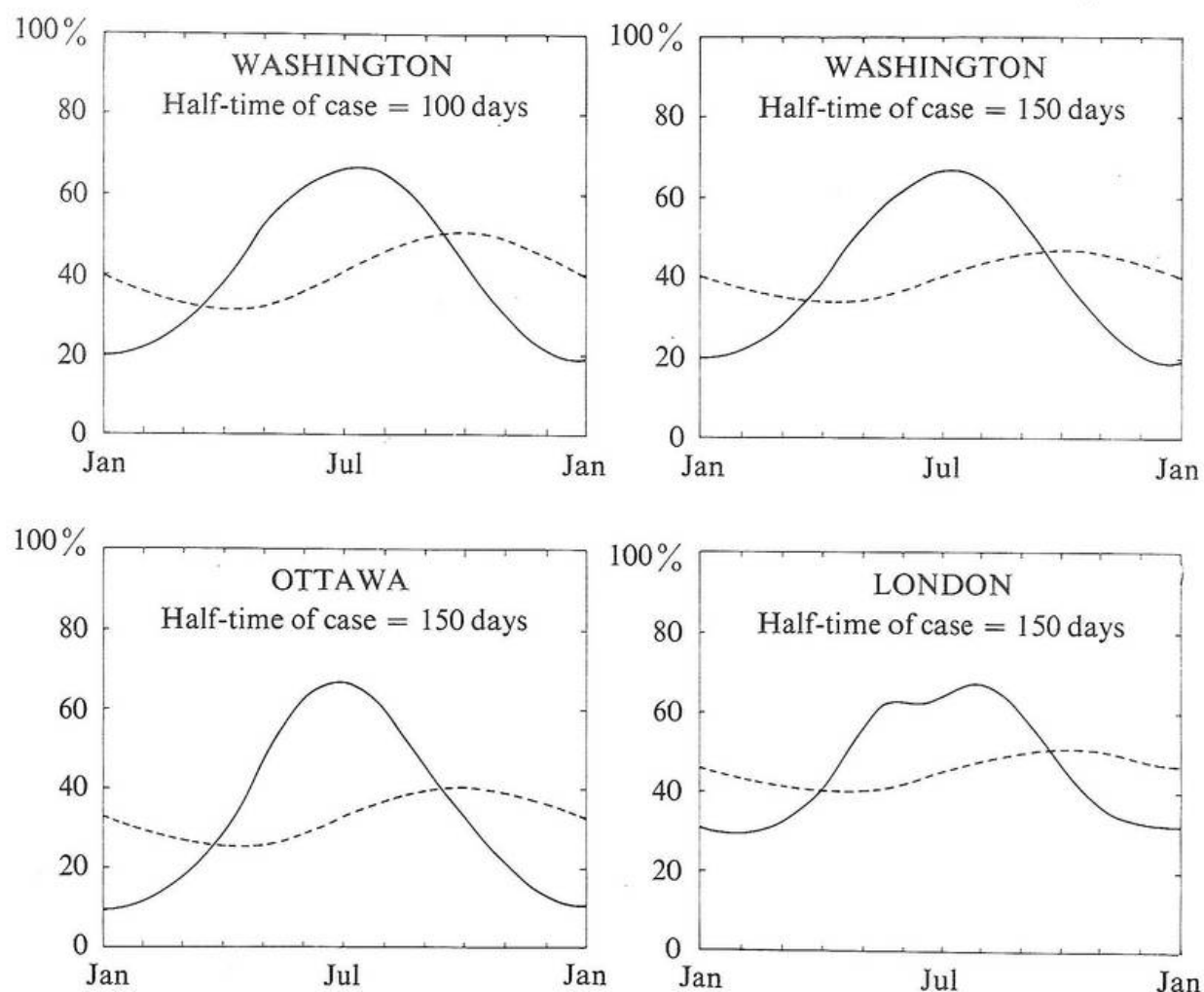


FIG. 2 Annual RH cycles in room and case. Room cycles are from Figure 1 (solid line). Case cycles are calculated (broken line).

| | Average | Max | Case Min (% RH) |
|---------------------------------|---------|-----|--------------------|
| Washington (half-time 100 days) | 41 | 50 | 32 |
| (half-time 150 days) | 41 | 47 | 34 |
| Ottawa (half-time 150 days) | 33 | 40 | 26 |
| London (half-time 150 days) | 46 | 51 | 40 |

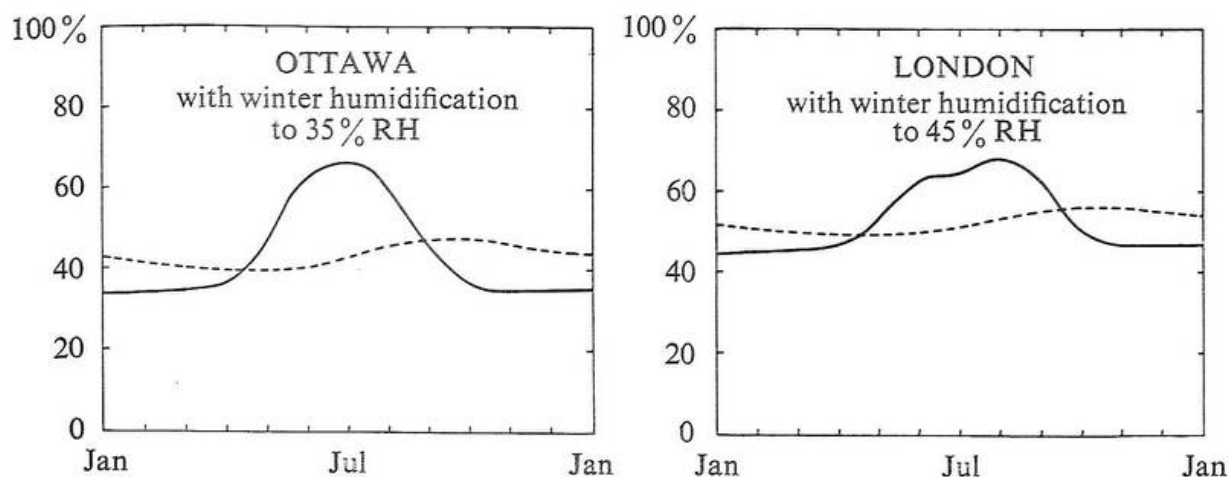


FIG. 3 The effect of some room humidification during winter. Ottawa humidification to 35%, giving case RH $43 \pm 4\%$. London humidification to 45%, giving case RH $52 \pm 3\%$. Half-times 150 days.

But there remains the problem that the average annual RH which the case settles down to—which is the average annual room RH—may be quite unsuitable (e.g. Washington about 40%, Ottawa about 33%, London about 46%, and probably over 70% in Singapore and the humid tropics). The closed but non-sealed case which we have been examining will cycle its RH gently through the seasons without further attention. However, although at the start of the operation the exhibits in the case were stabilized to 55% or some other chosen value, they will, as it were, lose all memory of this original value and settle down to a cycle the average RH of which will be that of the room, though with very much smaller fluctuations. The buffer literally only buffers against change, that is, slows it down and reduces it, but cannot positively force an RH higher or lower than the room average. This, of course, is rather disturbing news.

It is suggested that, to counteract the extreme dryness of winter heating, even from the human point of view, some humidification is desirable, but not necessarily to the high levels advocated in conservation (50–55%). For example, winter room humidification to 35% in Ottawa or 45% in London would raise the annual average case RH to 43% and 51% respectively (Fig. 3). These averages might well be acceptable, especially since the fluctuation

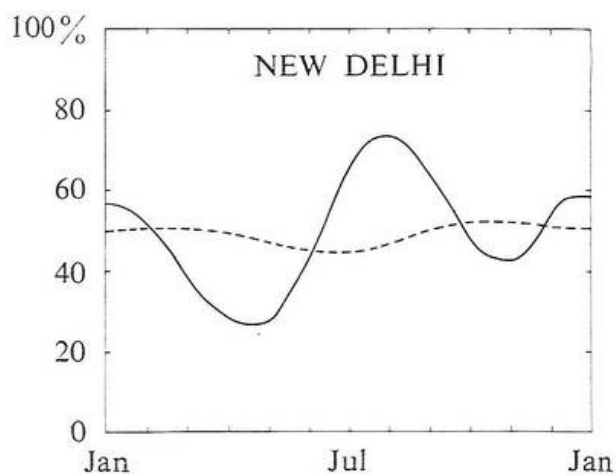


FIG. 4 The closed case with buffer in New Delhi (half-time 150 days). Room RH (solid) $47 \pm 22\%$. Case RH (broken) $47 \pm 4\%$. Half-time 150 days.

would be no more than $\pm 4\%$.

However, in the humid tropics, the problem is not easily solved. Here the characteristic is steady, not seasonal, dangerous RH, high in this case. Furthermore ventilation is a good prophylactic against mould-growth, and in a closed case the air is still.

On the other hand, in tropical inland areas with a wet season the closed case could prevent high monsoon RH from reaching the contents just as effectively as in cold climates it prevents excessive dryness (Fig. 4).

2.5. *Towards a Practical Solution*

This article only tackles half the problem. The rest lies in practical work and testing. The course that might be taken can be suggested.

1. *Case Construction.* There need be no onerous restrictions on design. The case itself should not be moisture-permeable. If of glass or metal this is no problem, but a wooden case should have, perhaps as an interlining, an effective moisture-barrier layer, such as metal foil, aluminized plastic foil, or polyvinylidene chloride film (Saran). This would be hidden from view by the case lining. Closures should fit very snugly. Fastenings should not distort, so opening up gaps elsewhere. Gaskets may be necessary in some cases.

2. *Buffering.* For RH conditions above 50% silica gel offers little advantage over wood, its M-value being about the same, but at lower RH values silica gel is the best buffer, and is in addition totally chemically inactive and fireproof. The silica gel should be used in paper or cloth bags, as regularly supplied for drying purposes. It should not, of course, be used in its dry form, but conditioned to the humidity required. This occurs without interference if the bags are kept in the right RH for some weeks. The buffer will need to be hidden from view, but at the same time free circulation of air between buffer and exhibits is essential. About 20 kg silica gel per cubic metre of case volume is suggested as a start.

3. In every exhibition case there should be an *RH meter* visible from outside the case. The simplest non-adjustable paper dial hygrometers cost very little. They should all be checked at yearly intervals against a wet-and-dry-bulb instrument, and if readings are more than about 3% out of true, they should be thrown away and replaced.

4. The next task is to find the *hygrometric half-time* of the case. This requires that it be placed, closed and complete with buffer and RH meter, in a fairly steady RH which is sufficiently different to that within the case to cause a change in a reasonable time. After a change of not less than 5%, and preferably 10%, has occurred in the case, the half-time can be calculated using the multiplying factors in Table 2. We are aiming at 150 days, and if the half-time is less than this improvements will have to be made in the case, or more silica gel will have to be added.

5. *Supervision and Record-keeping.* When a case is first fitted out for experiment, it should be checked at first daily, then weekly and ultimately monthly if all goes well. The first few days are particularly critical because there may be buffering material among the contents with an unexpected moisture-content which will throw the RH out as soon as the case is closed.

2.6. *A Summary of the Argument*

- The RH in a case containing buffer will decay exponentially towards the room RH.
- The rate of this process can be characterized by a 'hygrometric half-time', $t_{\frac{1}{2}}$, being the time taken to reach a point half-way between the case RH at start and the room RH.

- If the half-time is measured in number of air changes, $N_{\frac{1}{2}}$, rather than units of time, then it can be shown that

$$N_{\frac{1}{2}} = (\text{approximately}) 4 MB$$

where B = quantity of buffer in kg/m^3

and M = 'specific moisture reservoir', or the rise in moisture content of the buffer in g/kg for a 1% rise in RH.

- Due to the lag in RH change within the case, its RH fluctuations are smaller than those in the room, and can be reduced to less than $\pm 10\%$, even in the worst situations, if the half-time is at least 150 days.
- A carefully-made case might undergo about one air change per day. In such a case $t_{\frac{1}{2}} = N_{\frac{1}{2}}$, so that $t_{\frac{1}{2}} = \text{approx. } 4 MB$.
- Table 4 shows that M for silica gel is at least 2 in the middle of the range. Putting $M = 2$ and $t_{\frac{1}{2}} = 150$ days for a case with one air change or less a day, in the formula $t_{\frac{1}{2}} = 4 MB$:

$$150 = 4 \times 2 \times B$$
 so that B = about 20 kg silica gel per cubic metre of case volume for effective stabilization.
- Once things have settled down, the average annual case RH will be that of the room. Indoors in temperate zones this is usually too low for good conservation, and therefore a moderate amount of room humidification will still be required.
- Countries in the wet tropics, where the RH is constantly in the mould-growth range (over 65–70%) should not use buffered closed cases.
- On the other hand, tropical countries subject to seasonal monsoons (e.g. New Delhi) might find that the buffered closed case offered steady RH near to the required level.
- There should be a hygrometer in every closed case, visible from the outside.
- In favourable situations the closed case could give stable RH at a good conservation level without any maintenance and at low cost. But further experiment is necessary.

3. MATHEMATICAL AND EXPERIMENTAL SECTION

List of symbols used:

| | |
|-------------------|--|
| t | = time |
| R | = room RH at time t |
| C | = case RH at time t |
| C_0 | = original case RH ($t = 0$) |
| k | = rate constant of exponential decay |
| $t_{\frac{1}{2}}$ | = 'hygroscopic half-time' of case + contents |
| G | = moisture content of air (g/m^3) |
| E | = moisture content of buffer (g/kg) |
| B | = dry weight of buffer in case (kg) |
| M | = 'specific moisture reservoir' of buffer (moisture gain in g/kg for a 1% RH rise) |
| N | = number of air changes |
| $N_{\frac{1}{2}}$ | = half-time measured in air changes |
| N_D | = number of air changes per day |

3.1. The Exponential Decay of RH Difference Between Case and Room

At any time t the RH in the case will be approaching the room RH at a rate proportional to the difference in RH between room and case. Expressed mathematically,

$$-\frac{dC}{dt} = k(C - R) \quad \dots (i)$$

Note the negative sign for the rate, indicating that the gradient of the curve is negative when

$(C - R)$ is positive, or vice versa. Thus the formula reads correctly whether the room RH is high or low.

Rearranging for integration:

$$-\int \frac{dC}{C - R} = \int k \cdot dt.$$

The definite integral, where $C = C_0$ when $t = 0$, becomes:

$$\log_e \frac{C - R}{C_0 - R} = -kt \quad \dots (ii)$$

or

$$\frac{C - R}{C_0 - R} = e^{-kt} \quad \dots (iii)$$

At half-time, $t_{\frac{1}{2}}$, $\log_e \frac{C - R}{C_0 - R} = \log_e \frac{1}{2}$.

Therefore

$$t_{\frac{1}{2}} = -\frac{1}{k} \log_e \frac{1}{2} = 0.693/k \quad \dots (iv)$$

k is the general constant in equations of exponential decay, often called the rate constant of the process. In our exhibition case k will clearly be related to the leakage rate and to the amount and effectiveness of the buffer. We must now determine this relation.

3.2. Effect of Air Leakage and Buffer on the Half-time of the Case

We consider an exhibition case of one cubic metre volume with, for simplicity, a moisture barrier but no special sealing. In other words the case leaks, but the material of the case takes no part in the buffering. For buffering we add a known quantity, B kg, of silica gel or other buffering material. We are interested in following the amount of moisture in the air of the case, and this we will measure in g/m^3 , G , in preference to RH. But the two are linearly related because we shall hold the temperature constant. Because the process is slow, the moisture in the air will always be in equilibrium with the moisture in the buffer.

Our system works to reduce RH change in the case whether the room air is too damp or too dry.

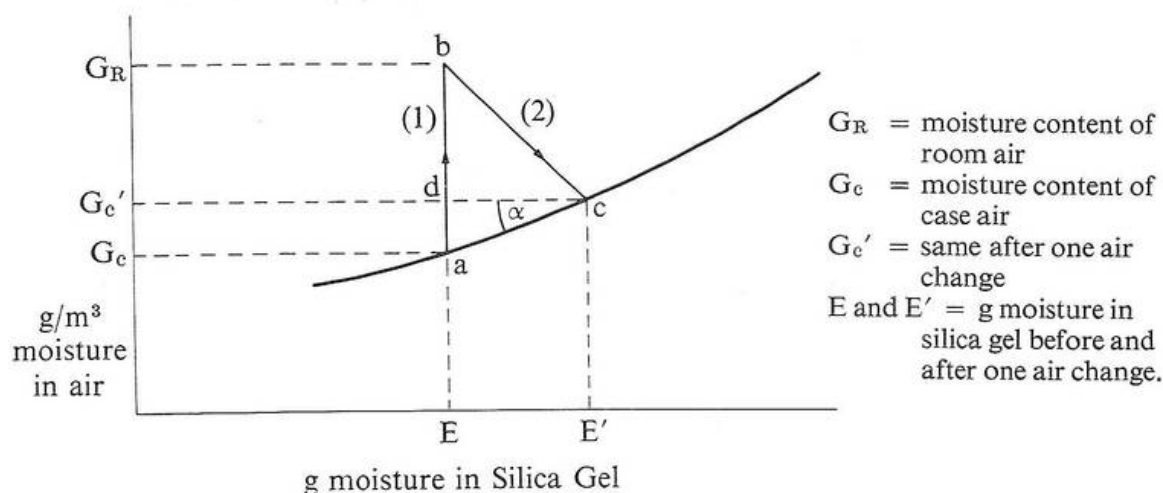


FIG. 5 Equilibrium curve for moisture in case air and silica gel (not drawn to equal axes).

We shall study a case which starts at around 55% RH standing in a room with a steady high RH, so that the case RH will creep upwards.

The first point to note is that, if we are to hope for any kind of stability, most of the moisture in the case must be in the silica gel and not in the air. For example a one cubic metre case with 20 kg of silica gel at 55% RH contains about 6 kg of water in the silica gel but only 8.65 g in the air of the case (0.14%). Then, since we want to follow the process by breaking it up into steps, a step which involves one complete air change will not amount to a very large change in the total moisture within the case.

Following Figure 5 we break the consequence of one air change into two steps:

Step (1): A complete air change takes place, so that, in the first place, case air changes from G_c to G_R , while E remains constant.

Step (2): In response to the dampness of the room air which has entered the case, the silica gel takes in some of this moisture until equilibrium is restored.

As a result of these two steps, which in reality would be blended together, there is a slight increase of moisture both in the air of the case and in the silica gel. This is shown by the movement from a to c on the equilibrium curve, Figure 5.

The important point is that the final moisture loss (gain) by the gel is equal to the final moisture gain (loss) by the case air. That is to say, provided we have drawn x - and y -axes to the same scale, $bd = cd$, and the triangle bcd is a 45° , 45° , 90° triangle.

From this we can deduce trigonometrically that

$$ad = ab \frac{\tan \alpha}{1 + \tan \alpha}.$$

Or, referring to the axes on Figure 5,

$$(G_{c'} - G_c) = \frac{\tan \alpha}{1 + \tan \alpha} (G_R - G_c).$$

Now $(G_{c'} - G_c)$ is the small change in the moisture content of the case air following one air change. In other words it is the air moisture content change per air change, or the rate of moisture content change measured in time units each of one air change. If we call the number of air changes N ,

then our rate of moisture change = $\frac{dG}{dN}$, and

$$\frac{dG}{dN} = \frac{\tan \alpha}{1 + \tan \alpha} (G_R - G_c).$$

Dividing throughout by the moisture content of saturated air at the temperature of the case converts moisture content to RH. Using the symbols of equation (i) the above equation then becomes

$$-\frac{dC}{dN} = \frac{\tan \alpha}{1 + \tan \alpha} (C - R).$$

Finally,

$$\tan \alpha = \frac{\text{moisture gain of air}}{\text{moisture gain of buffer}}$$

for a small RH rise, say of 1%.

Saturated air at 20°C contains 17.30 g/m^3 moisture, therefore the moisture gain of air for a 1% change in RH = 0.173.

The moisture gain of the buffer = MB

where

B = wt of buffer in kg

M = moisture gain in g per kg for a 1% RH rise.

Therefore

$$\tan \alpha = \frac{0.173}{MB}$$

and

$$\frac{\tan \alpha}{1 + \tan \alpha} = \frac{0.173}{MB + 0.173}$$

$$-\frac{dC}{dN} = \frac{0.173}{MB + 0.173} (C - R) \quad \dots (v)$$

It is evident by comparing (i) and (v) that, provided time is measured by number of air changes, N ,

$$\text{the rate constant } k_N = \frac{0.173}{MB + 0.173} \quad \dots (vi)$$

This value of the rate constant can now be used in all forms of the exponential equation. But many people will find it easier to avoid exponential expressions, and to use instead the half-time, found by equation (iii) to be equal to $0.693/k$. Since our half-time is measured in number of air changes, we can use the symbol $N_{\frac{1}{2}}$:

$$N_{\frac{1}{2}} = 0.693/k_N = \frac{0.693(MB + 0.173)}{0.173} = 4.006 MB + 0.693.$$

In any workable situation there are several air changes to the half-time, so that we can ignore 0.693, making

$$N_{\frac{1}{2}} = \text{approx. } 4 MB \quad \dots (vii)$$

or $t_{\frac{1}{2}} = 4 MB/N_D$ where N_D = number of air changes per day.

As it stands this formula is dimensionally incorrect. This is because we have taken B to equal the mass of buffer per unit volume of air. Strictly B should be entered as the mass of buffer per unit mass of air. But this is a clumsy form, and in any case is unnecessary under approximately constant temperature conditions, i.e. constant density of air.

The formula in dimensionally correct SI units becomes:

$$t_{\frac{1}{2}} = 4760 MB/N_D$$

where the units must be altered as follows:

- M = specific moisture reservoir in kg/kg
- B = kg buffer per kg air in case
- N_D = number of air changes per day (no change)
(density of air at 20°C, 50% RH = 1.19 kg/m³)

However, this SI form of the formula will not be used.

3.3. Measuring the Half-time of an Exhibition Case

Equation (vii) shows that the half-time of a case, so long as it is measured in air-changes rather than in the more usual units of time, is determined solely by the product of B , the amount of buffer per cubic metre, and M , which might be termed the specific moisture reservoir of the buffer.

Although this formula has a pleasing generality and simplicity, there remains the difficulty of using air changes as units of time, because the rate of air change of a case is usually not known. This difficulty can be side-stepped as follows.

It will take an inconveniently long time to measure the half-time directly of a well-made case. Instead, we measure, not the time taken to reach half way, but the time taken to reach a less complete state.

It will be recalled that at half-time $(C - R)/(C_0 - R) = \frac{1}{2}$. Table 2 shows the factor by which our time must be multiplied to obtain $t_{\frac{1}{2}}$ for various other values of $(C - R)/(C_0 - R)$.

TABLE 2

| $\frac{C - R}{C_0 - R}$ | Multiplying factor | (The multiplying factors have been calculated by assuming simple exponential decay) |
|-------------------------|--------------------|---|
| 0.9 | 6.6 | |
| 0.8 | 3.1 | |
| 0.75 | 2.4 | |
| 0.7 | 1.9 | |
| 0.6 | 1.4 | |
| 0.5 | 1.0 | |

Example: RH of case at start of timing 50%
 RH of room 26%
 Time taken to reach 44% 50 days
 $\frac{C - R}{C_0 - R} = \frac{44 - 26}{50 - 26} = 0.75$
 Multiplying factor from table = 2.4
 Therefore half-time $t_{\frac{1}{2}} = 2.4 \times 50 = 120$ days

3.4. Experimental

To test the formula for decay of RH difference in a case containing buffer, two small exhibition cases were prepared by lining them inside with aluminized plastic foil (Fig. 6). The dual purpose of this moisture barrier was, first, to ensure that the moisture reservoir within the case was negligible compared to that in the silica gel which would be added, and second to be able to experiment at high and low RH without prior conditioning.

Leakage rates were determined by filling a graduated cylinder with distilled water, allowing the water to soak up to a circle of filter paper, and placing the whole in the closed case. Once the closed case had settled down to 100% internal RH, as checked by hygrometer, a plot of water loss against time allowed calculation of the leakage rate of water-saturated air at room temperature. Though

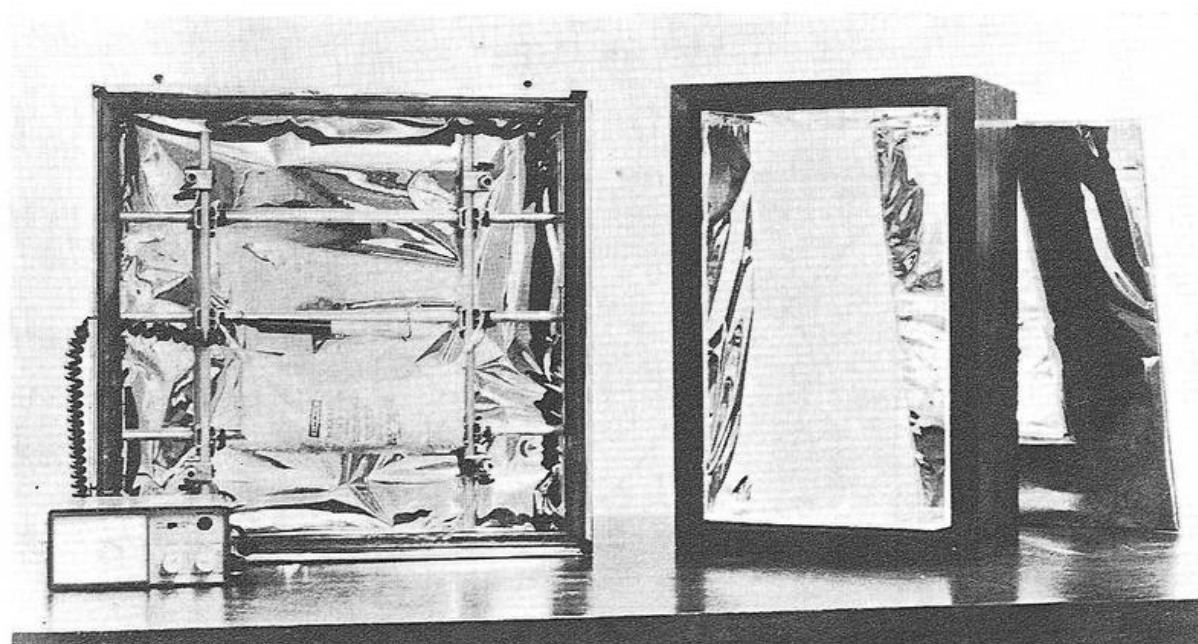


FIG. 6 The two cases used in the experiment, lined with aluminized plastic foil. The framework for the attachment of the hygrometer and bag of silica gel is shown in the smaller case.

the cases were of comparable size they had very different leakage rates. Case no. 1, the smaller of the two, was opened by removing its glass front, which was quite loose-fitting. Its leakage rate was about one air change every two hours (0.53 air changes/hr or 12.7 per day). In case no. 2 the back was screwed in to a snug fit, so that it took almost a day for an air change (0.0525 air changes/hr or 1.26 per day). It is worth repeating here that the temperature changes experienced during the experiment (around $\pm 3^\circ\text{C}$) would have had only a small effect on the leakage, which is predominantly by diffusion through cracks.

Since the laboratory is air-conditioned, supposedly to $55 \pm 4\%$ RH, it was planned to place in the cases 1 lb dry weight (0.454 kg) bags of silica gel conditioned to an RH either considerably higher or considerably lower than room RH and follow the drift back to room RH. Though this is the reverse of the real-life situation, where it is the room which has the abnormal RH, it is equally good for test purposes. In the event the air-conditioning was far from stable, so that only the first part of each run was usable, when the difference between case and room RH was large enough to dwarf room RH variation.

It will be recalled from equation (ii) (p. 94) that

$$\log_e \frac{C - R}{C_0 - R} = -kt.$$

This equation can equally well be expressed by measuring time in number of air changes:

$$\log_e \frac{C - R}{C_0 - R} = -k_N N.$$

To find k_N by plotting, we put this in the form:

$$k_N = \frac{\log_e(C_0 - R) - \log_e(C - R)}{N}.$$

Then a plot of log (difference between case and room RH) against time will give a gradient equal to the rate constant, k_N .

Our theory, however, predicts the value of k_N from (vi):

$$k_N = \frac{0.173}{MB + 0.173}.$$

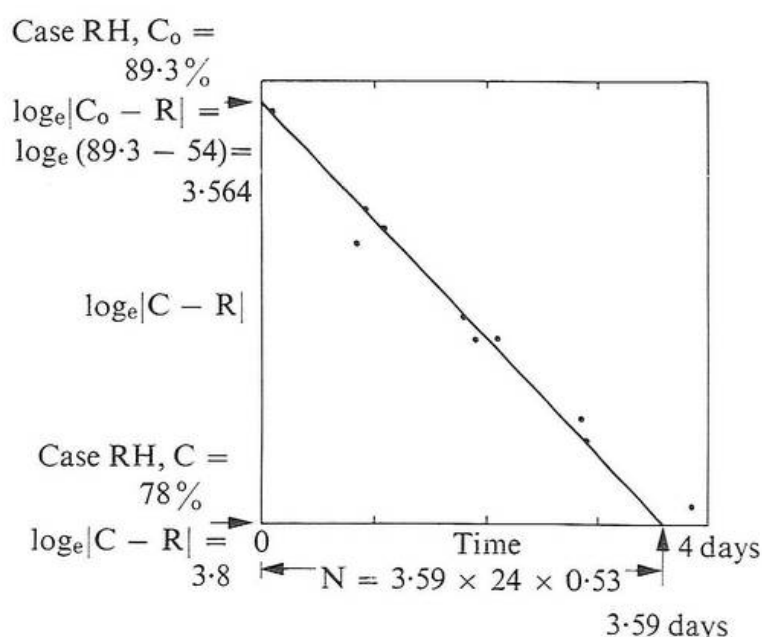


FIG. 7 The experimental results plotted.

Case 1, run 1. 0.53 air changes/hr. Room RH = 54%
 Case RH extrapolated back to time zero, $C_0 = 89.3\%$
 Case RH at 3.59 days, $C = 78\%$
 From graph,

$$k_N = \frac{3.564 - 3.178}{3.59 \times 24 \times 0.53} = 8.45 \times 10^{-3}$$

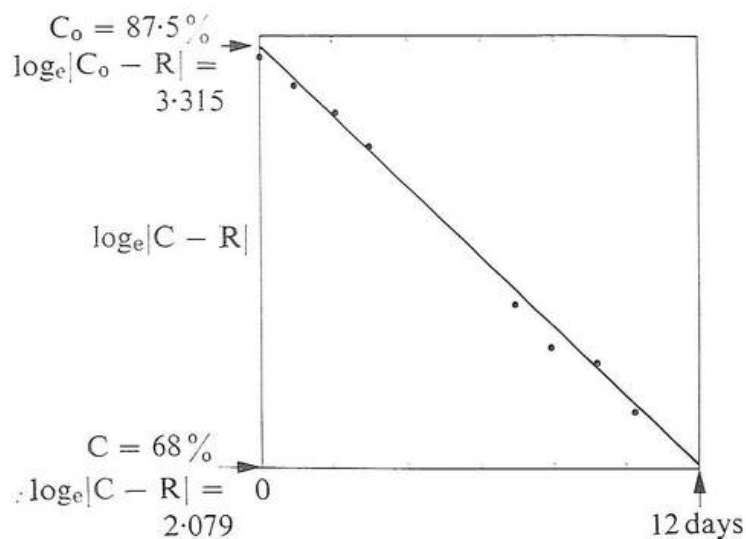
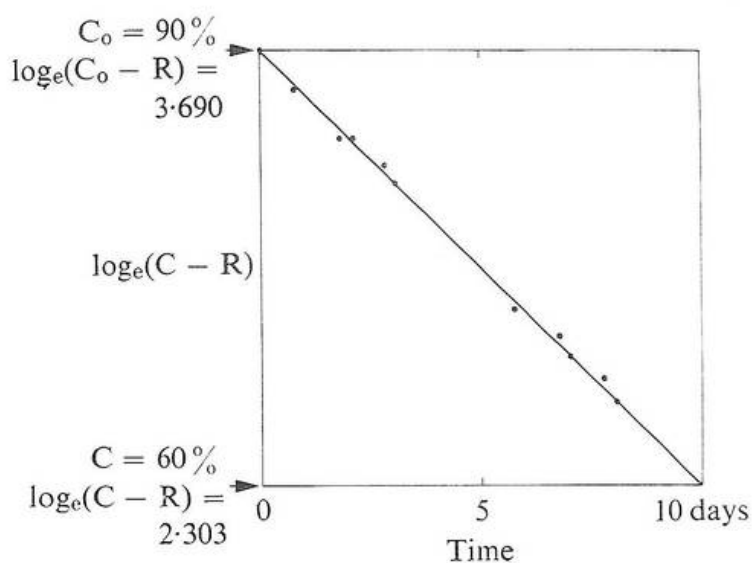


Fig. 7 continued

Case 1, run 2. 0.53 air changes/
hr. Room RH = 60%

$$k_N = \frac{3.315 - 2.079}{12 \times 24 \times 0.53}$$

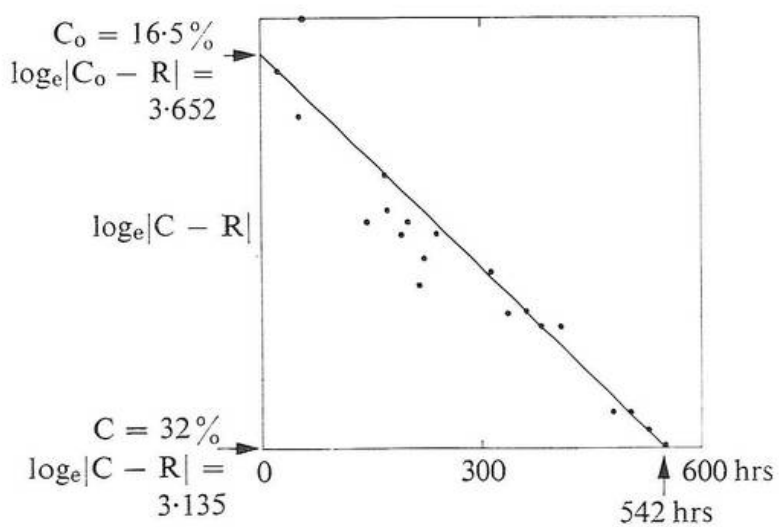
$$= 8.10 \times 10^{-3}$$



Case 1, run 3. 0.53 air changes/
hr. Room RH = 50%

$$k_N = \frac{3.690 - 2.303}{10 \times 24 \times 0.53}$$

$$= 0.0109$$

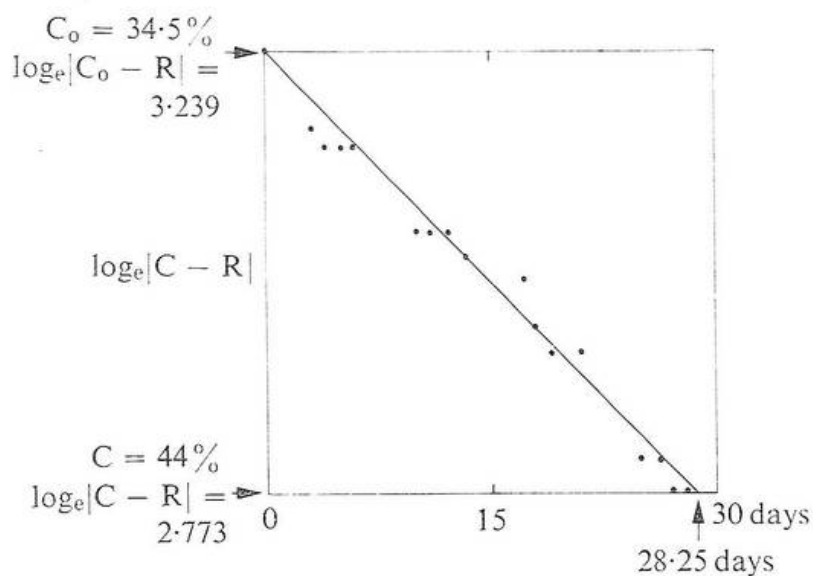


Case 1, run 4. 0.53 air changes/
hr. Room RH = 55%

$$k_N = \frac{3.652 - 3.135}{542 \times 0.53}$$

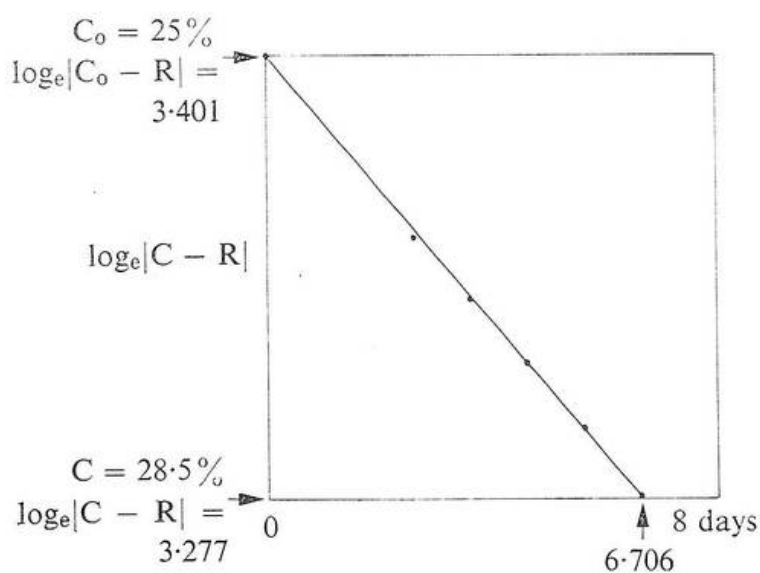
$$= 1.80 \times 10^{-3}$$

Fig. 7 continued



Case 2, run 1. 0.0525 air changes/hr. Room RH = 60%

$$k_N = \frac{3.239 - 2.773}{28.25 \times 24 \times 0.0525} = 0.0131$$



Case 2, run 2. 0.0525 air changes/hr. Room RH = 55%

$$k_N = \frac{3.401 - 3.277}{6.706 \times 24 \times 0.0525} = 0.0147$$

TABLE 3
VERIFICATION OF THE FORMULA $k_N = 0.173/(MB + 0.173)$ BY FINDING k_N EXPERIMENTALLY FOR KNOWN B AND HENCE DEDUCING M

| Case | B | Run | RH range | k_N | M |
|------|------|-----|----------|-----------------------|-----|
| 1 | 20.6 | 1 | 90-78% | 8.45×10^{-3} | 1.0 |
| | | 2 | 87-70% | 8.10×10^{-3} | 1.0 |
| | | 3 | 90-63% | 0.0109 | 0.8 |
| | | 4 | 16-32% | 1.80×10^{-3} | 4.7 |
| 2 | 13.2 | 1 | 34-44% | 0.0131 | 1.0 |
| | | 2 | 25-29% | 0.0147 | 0.9 |

We know the leakage rate, and therefore can express time in air changes, so obtaining values of k_N by plotting. We also know the amount of buffer, B, in the case, and so can find values of M from k_N and B. These experimentally determined values of M can then be compared with the expected values.

This has been done in Figure 7. Concerning positive and negative signs the treatment may look a little cavalier but is not. Whether the RH is rising or falling logs are made positive. The number of air changes, N, and the rate constant, k_N , are both positive. The gradients have all been plotted to the same format (negative) for consistency.

Each case contained 0.454 kg silica gel, and the volumes of the cases were 0.022 and 0.0345 m³, so that B for the cases was 20.6 and 13.2 kg silica gel per cubic metre respectively.

Table 3 gives a summary of the experimental results.

TABLE 4

M (g MOISTURE GAINED (LOST) PER KG SILICA GEL PER 1 % RISE (FALL) IN RH) FOR FRESH SILICA GEL [6]

| RH % | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
|------|----|----|----|----|----|----|----|----|----|
| M | 8 | 8 | 6 | 3 | 2 | 2 | 1 | 1 | 1 |

Comparison of Tables 3 and 4 shows that at high RH the values of M determined through applying the formula developed to a practical situation agree well with published figures. At low RH the M value for the silica gel in case 1 is too small (4.7 against an expected 7 or 8). The silica gel in case 2, however, appears to have behaved very poorly indeed. Both bags had, in the course of their experimental lives, been conditioned more than once to very high RH by standing over water in closed containers for a week or two, and it was suspected that this treatment might have caused deterioration. The bag for case 1 could not be tested since it fell to pieces during a further conditioning process! Bag 2, however, was dried to 25% RH, placed in a polythene bag with a hygrometer, and weighed at intervals. The polythene slowed down moisture gain to about 3% RH per week. These measurements showed that the silica gel had indeed deteriorated to an M at 25% of no better than 1.6. In effect this unexpected result added a little confidence to the theory, though further testing is obviously required, using different types of container. It should also be borne in mind that a quick run of a week or so does not allow the silica gel time for equilibrium and would lead to too low a value of M.

3.5. Summary of Formulae Used (for symbols see p. 93)

The basic formula is

$$N_{\frac{1}{2}} = 4 MB \text{ air changes (approximately)}$$

or

$$t_{\frac{1}{2}} = 4 MB/N_D \text{ days}$$

since

$$N = N_D \cdot t$$

The rate constant for the exponential process, following a standard form, is

$$k_N = -\frac{1}{N} \log_e \frac{C - R}{C_0 - R} \text{ air changes}^{-1}$$

or

$$k = -\frac{1}{t} \log_e \frac{C - R}{C_0 - R} \text{ days}^{-1}$$

where t is in days

and

$$k = N_D \cdot k_N$$

By using Figure 5 from which the basic formula was derived, the rate constant can also be expressed as

$$k_N = \frac{0.173}{MB + 0.173}$$

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REFERENCES

- 1 TOISHI, K., 'Humidity Control in a Closed Package', *Studies in Conservation*, 4 (1959), 81-87.
- 2 PADFIELD, T., 'The Control of Relative Humidity and Air Pollution in Show-cases and Picture Frames', *Studies in Conservation*, 11 (1966), 8-30.
- 3 STOLOW, N., *Controlled Environment for Works of Art in Transit*, Butterworths, London, 1966.
- 4 THOMSON, G., 'Relative Humidity—Variation with Temperature in a Case Containing Wood', *Studies in Conservation*, 9 (1964), 153-169.
- 5 Meteorological Office, London. *Tables of Temperature, Relative Humidity and Precipitation for the World*. Met. 0.617e. Her Majesty's Stationery Office, London, 1966.
- 6 STOLOW, N., 'Fundamental Case Design for Humidity Sensitive Museum Collections', *Museum News* (Technical Supplement), (Feb. 1966), 45-52.

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Abstrait—Une formule est établie avec appui expérimental pour prévoir les changements RH dans une vitrine d'exposition non étanche contenant un tampon tel que de la gelée de silice. Elle a révélé qu'une vitrine bien construite contenant environ 20 kg. de gelée de silice par mètre cube de volume de vitrine devrait contenir les variations d'humidité avec les saisons dans des limites raisonnables. Sous certains climats une climatisation n'est pas nécessaire, mais la formule proposée nécessite cependant des essais pratiques et à grande échelle avant d'être adoptée.

Kurzfassung—Eine Formel wurde an Hand von Versuchen aufgestellt, die Vorhersage der Veränderungen in der relativen Feuchtigkeit in einem undichten Schaukasten ermöglicht, der Puffermaterial wie z.B. Kieselgel anthält. Es wird beschrieben wie ein gut gebauter Schaukasten mit zirka 20 kg Kieselgel pro Kubikmeter Kastenvolumen die saisonbedingten Feuchtigkeitsschwankungen innerhalb angemessener Grenzen hält und unter manchen klimatischen Bedingungen Klimatisierung erübrigt. Die vorgeschlagene Formel erfordert jedoch praktische Grossversuche bevor sie angenommen werden kann.