THE MEASUREMENT OF EQUILIBRIUM RELATIVE HUMIDITY

PART I

By

L. IMRE

Department of General Mechanics, Polytechnical University, Budapest

(Received December 16, 1963)

Presented by Prof. J. Sváb

The interpretation of moisture equilibrium and its characteristics

The characteristics defining the moisture equilibrium condition of wet materials are of great importance from the point of view of technological processes such as dehydration, storage, packaging [1, 2] etc.

A wet material is considered to be in the state of moisture equilibrium if it neither gains nor loses moisture. Since moisture transfer is a function of the mutual correlation of the sample and its environment, when considering the problem of moisture equilibrium the environment has also to be taken into consideration. This mutual correlation manifests itself in the alteration of the vapour tension, in the following way: when on the surface of the material the relative vapour pressure is higher than that of the atmosphere, dehydration (desorption) occurs. On the other hand if it is lower, the process is reversed and adsorption occurs. Thus the state of equilibrium, at a given temperature and moisture contents, exists only at a given relative vapour tension. If the hygroscopic material is surrounded by air the equilibrium relative vapour pressure may be characterized by the relative humidity of the air (ERH — equilibrium relative humidity). Thus ERH is a function of both the moisture content of the sample in question and the temperature.

At a given temperature (T), ERH values (Φ_e) vary considerably with the various moisture levels of the material (W). This correlation may thus be expressed

$$\Phi_e = \Phi_e(W)_T. \tag{1}$$

This equation and its graphical presentation are termed the sorption isotherm of the material (SI). It is known that in most materials the ERH values as approximated by desorption and adsorption, respectively, do not agree over the total range of moisture-contents (sorption hysteresis). Therefore, it is desirable to distinguish the adsorption isotherm (ASI) and the desorption isotherm (DSI).

The SI may be established by the determination of pairs of values $(\varPhi_e, W)_T$. Dependent on the method of derivation and measurement of the pairs of values various procedures were developed.

If ERH values of a certain material, obtained by various methods, are compared often essential discrepancies may be observed. The differences are due mainly to varying conditions of measurement and the errors inherent in the various determination methods.

It is, therefore, advisable to choose, after the critical evaluation of the available methods, the one which is the most suitable to the given task. In this paper an assay was made to evaluate the various methods available.

Theoretical principles underlying the measurement of ERH

The determination of $(\varPhi_e, W)$ pairs of values falls into three distinct steps:

a) The development of the pair of values to be measured, confirming to $T = $ constant conditions.

b) The determination of $\varPhi_e$.

c) The determination of W.

The determination is usually carried out with a test sample, in a thermostatically controlled chamber which is generally closed, in accordance with the procedures as given under paragraphs *a)* and *b)*. The various ways in which the pairs of values may be developed are as follows:

I. The vapour pressure in the measuring chamber is a given constant value, the determination is continued by way of changing moisture content till $W = W_e$ will developed with satisfactory accuracy. Thus, the $\varPhi_e$ value is determined by the vapour pressure of the atmosphere (tensimetric procedure), and step *b)* therefore means the determination of the tension in the closed chamber.

II. The equilibrium vapour tension of the measuring chamber ($\varPhi_e$ value) is developed by the adsorption or desorption of the sample. However, in the case of measurement of desorption the initial tension of the chamber should be lower, whereas in the case of measurement of adsorption it should be higher than that of the sample. The determination is continued till the measuring chamber or the sample reach saturation limit.

Measuring-technical and evaluation aspects of ERH determination

Results of acceptable accuracy in ERH measurement may be obtained only when several requirements are at the same time satisfied. These requirements may serve as criteria on which evaluation may be based in accordance with the degree of satisfaction. These criteria are as follows:

1. Is the test sample an unambigious represantative of the material to be tested?

2. Will the moisture distribution of the sample change during measurement and to what extent this change may be followed?

3. Will a substantial change occur in the moisture content of the sample during measurement?

4. In what way will the thermodynamic equilibrium develop during measurement; is it possible to assure isothermic development?

5. At what pressure is the determination carried out and is the result valid at a different pressure?

6. In what kind of environment is equilibrium attained?

7. Do the premeditated conditions of determination come into existence and to what measure can this be verified?

8. Is it to be expected for the test material to suffer substantial change during determination, such as spoilage?

9. Is the method equally suitable for the determination of both desorption and adsorption isotherms?

10. How long should the period of measurement last and how can the development of the pair of values to be measured, be observed?

11. What kind of equipment and technical training is necessary to apply the procedure correctly?

12. To what extent is the procedure and the necessary equipment controllable and well arranged.

The following chapter deals with the measuring-technical aspects of ERH determination methods.

Procedures carried out in a chamber having constant tension

Tensimetric procedure

Using the tensimetric method — generally applied for the determination of desorption ERH values — the test sample has to be placed into a closed chamber having a constant temperature. The desired tension may be achieved with a sulfuric acid solution of given concentration [3] or a salt solution [4, 5, 6] or with conditioned air [7] respectively. The test sample placed into the chamber aspires to attain the equilibrium moisture content as determined by the tension of the atmosphere. The state of equilibrium is reached when at several consecutive measurements the weight of the sample is constant (Fig. 1. t_m). When equilibrium is reached the tension Φ_e of the chamber has to be determined. Finally W_e is obtained by determining the moisture content of the sample, eg. in a drying cabinet at 104° C.

The measurement is usually carried out in air. With the pair of values thus obtained a sorption isotherm may be plotted. Using a sample of given dimensions, the time (t_w) needed to reach practically constant weight in the measuring chamber, generally increases with increasing vapour tension of atmosphere. (In Fig. 2 the $W(t)$ curves at different Φ_e tensions of the chamber for natural salami casings as determined by the author with the tensimetric method may be seen.)
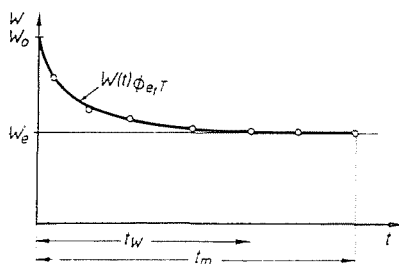

Fig. 1. Change of the moisture content of the sample plotted against time (Drying curve) W_0 = the initial moisture content of the sample. W_e = equilibrium moisture content t_m = the determination period. t_w the actual time of equilibration

Thus, the final value established in tensimetric measurements is achieved when the sample — air — absorbent multicomponent system reaches equilibrium. During desorption measurements, in the phase of equilibration the superfluous moisture content of the test sample is transferred in the absorbent by the ambient air as an intermediate medium. Thus it is evident, that during the determination the initial concentration of the absorbent will change in proportion to the water absorbed. The smaller the change of weight suffered by the test sample, in proportion to the amount of water (x_0) in the absorbent solution, in other words the smaller the $\pi = \dfrac{\varDelta x}{x_0}$ relative solvent increase, the more negligable is the disturbing effect of the change of concentration. (Here $\varDelta x = (W_0 - W_e) \cdot G_d$ and G_d is the dry weight of the sample.) It is deemed advisable to keep π low because in this case it becomes possible to carry out the determination at the desired Φ_e values by setting the initial concentration by exact weighing. By decreasing the weight of the test sample, while the weight of the absorbent is increased, the value of π may be kept low.

Though at $\pi < 5 \cdot 10^{-3}$ values the change of the tension of the chamber is negligable, and the change of concentration as concluded from the change of weight should be taken into consideration, in order to avoid errors caused

by faulty weighing, or by insufficient purity of components, or by change of sample weight for some other reason, it is advisable to control the composition of the absorbent, e.g. by titrimetry.

Data on the tension belonging to absorbents of varied concentration are available in the literature. Several series of data on sulphuric acid and salt solutions have been determined, although these show some discrepancy [3, 8, 9, 10, 11, 12, 13].
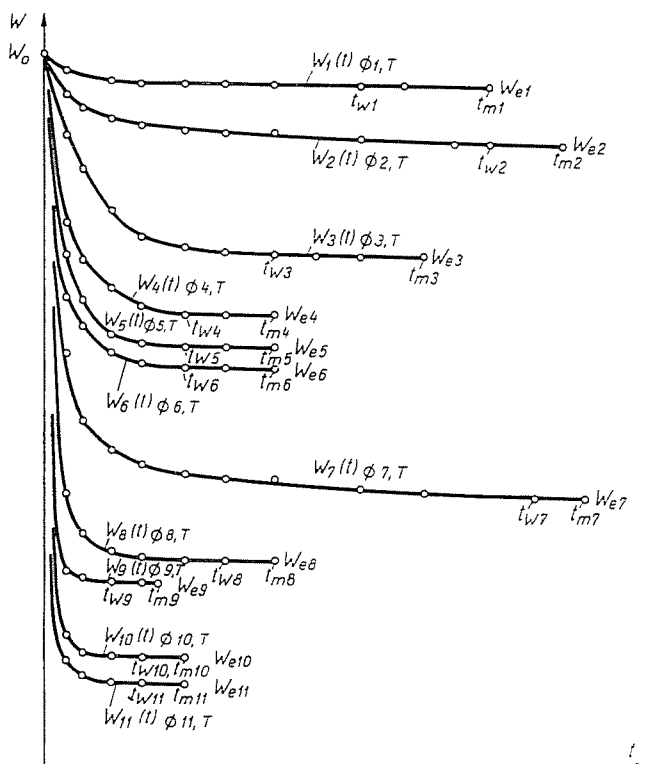

Fig. 2. Tensimetrically determined drying curves in chambers of various humidity

In consequence of the moisture exchange occurring in the measuring chamber the vapour tension of the absorbent asserts itself on the surface of the test sample only after an infinitely long time, theoretically. It is for this reason and because of the error caused by the inevitable temperature fluctuation, that only a quasi-stationary state sets in. The longer the time needed for the determination (t_w, Fig. 3.) the more is the surface tension of the absorbent (Φ_a) approximated by the tension of the chamber (Φ_m). The time needed to accomplish determination may be decreased by keeping the

factors affecting the moisture transfer at an advantageous level. It is of advantage, for instance, to increase the surface area of the sample and that of the absorbent, to decrease the thickness of the sample, — causing the moisture gradient to be of little significance. The determination period may be decreased by the agitation of the ambient air, or, if the absolute moisture content (x_1) of the air in the chamber, at tension belonging to the concentration of the absorbent, is small as compared to the moisture content of the sample (x_a), — in other words $\sigma = \dfrac{x_a}{x_1}$ ratio is large.
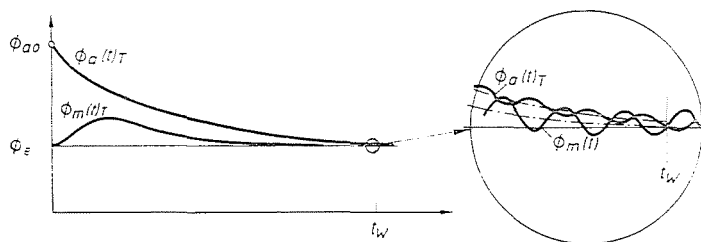

Fig. 3. The change of the relative vapour tensions belonging to the sample and the measuring chamber, respectively, during tensimetric determination

Because of the irevitable, though small, fluctuation of the temperature in the chamber it is possible to observe the constant weight within a practically finite period. During the progress of drying the sample the fluctuation of the temperature causes the tension in the chamber to fluctuate around the nominal value, and thus, the sample may come in the range of hysteresis. In this case, provided the customary analytical balance of 0.1 mg accuracy is used, small positive and negativ changes of the weight are to be observed. The fluctuation of the amplitude and frequency depending on the temperature control is superimposed on the curve $\Phi_m(t)_T$ (see in Fig. 3.) which is followed by a certain lag and decreased amplitude by the $\Phi_a(t)$ curve (see Fig. 3., part a.).

The temperature of the test sample during drying remains below the dry bulb temperature of the chamber, till equilibrium is attained. To ascertain whether the state of equilibrium is reached, it is advisable to check the weight without opening the measuring chamber [4,7], otherwise it would be inevitable to await the development of the equilibrium relative vapour pressure each time. The opening of the measuring chamber would increase the determination period, with the simultaneous change of the moisture content of the sample as well as that of the absorbent solution, dependent on the atmospheric and weighing conditions.

The advantage of the tensiometric method lies in its simplicity and controllability. However, the comparatively long determination period, even with samples of minute quantity is disadvantageous, and therefore, its applicability is restricted.

The weight and dimensions of the sample cannot be decreased beyond a certain limit, even in homogeneous materials, because of the increase of the relative error caused by the inaccuracy of weighing. In the case of composite materials the decrease of the sample weight may involve difficulties in sampling and may result in samples not representing the true composition of the material to be tested. According to the experiences of the author the long determination periods, which may account for the order of magnitude of 200 to 500 hours with samples of 2 to 3 g and at $\Phi_e > 70\%$ relative humidity, and besides the varied composition of the samples, are due to the thickness of the sample. The thickness of the sample determines the development of the moisture gradient. Figure 2. shows how the thickness of samples 2 and 7, particularly that of the latter, influenced the length of the determination period. The ERH determination in larger samples is impracticable, because at generally needed temperatures and above $\Phi_e > 70\%$ values on certain samples, particularly on food, mould or bacterial cultures develop and, frequently, microbial spoilage may not be inhibited.

By causing the air to flow through the measuring chamber the period of determination may be somewhat shortened [3, 7, 16]. However, this may involve mechanical and other difficulties, such as the continuous deflection of the heat equivalent of the ventilator work, the strict control of the temperature. These difficulties may decrease the accuracy of the determinations.

A disadvantage of the tensimetric method lies in the fact that the determination of the ERH value belonging to a given moisture content of a material is not possible by a single measurement. This only becomes possible after the isotherm had been plotted. However, when the method is carried out with laboratory accuracy, care and efficiency, and the analyses and weighing are exact, it will give reliable results.

The bi-thermal method

The bi-thermal method, suggested by A. R. WEIR [17] and further developed by R. H. STOKES [18] is also based on the production of a given vapour tension. This method differs from the tensimetric method in the way in which the desired tension is achieved. However, the pair of values to be determined, in other words the state of equilibrium, is developed by way of changing the moisture content of the test sample.

The measuring chamber wanted for this method consists of two containers having different temperatures, connected by a tube (Fig. 4). The sample is

placed in the first container, thermostatically controlled at T_1 temperature. The second container, thermostatically controlled at T_2 temperature, contains distilled water having a free surface.

After evacuation and the consolidation of the temperatures the whole system aspires to attain a state of sorption equilibrium at a pressure corresponding to $T_2 < T_1$ temperature. During equilibration the water in container 2 becomes an absorbent of dewpoint temperature and equilibration lasts till the vapor pressure reaches the level corresponding to the saturated vapor pressure at T_2 temperature.
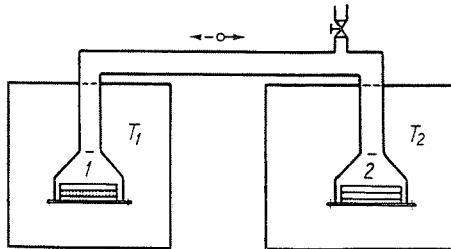

Fig. 4. Schematic arrangement of the measuring chamber in the bi-thermal method

The method has an inherent sensitivity to temperature. It is particularly important to set the temperature-difference between the two containers to be more exact by at least with one order of magnitude than the temperature of the two containers. The accuracy of results mostly depends on the control of the temperature and exact knowledge of the actual temperatures.

In the course of determination, the condensation of water vapor on the tube surface may cause difficulties. To avoid this, care must to taken in the choice of temperature of the colder container as compared to the initial temperature of the air enclosed in the containers.

The thermal conductivity of the tube section connecting the two containers may also cause some trouble. It is for this reason that the thermal equilibrium does not set in and the containers (sample and water) do not attain the exact temperature of their respective thermostats. This effect may be reduced by adjusting the equipment, for instance, by enlarging the immersed parts.

There are problems involved in the establishment of the state of equilibrium. The time needed for equilibration is influenced by the amount cf gase enclosed. These gases retard equilibration. It is therefore advisable to control the equilibration period by several determinations before serial tests are started and sufficient time must be allowed for the determinations. In the case of testing liquid samples (eg. solutions) the test period may be shortened by periodical agitation of the system.

During determination the thermodiffusion effect of the enclosed gases, generally a negligable value, is dependent on the degree of evacuation.

This method requires a sensitive apparatus, great care in manipulation and then accuracy of measurements is quite satisfactory. The results compare well with other results, described in the literature and deemed to be sufficiently exact [19, 20].

The applications are restricted. It may be used advantageously for the determination of equilibrium vapour-pressure of liquids (solutions), since in this case the moisture gradient in the sample is negligable and no difficulty is involved in obtaining a large evaporating surface.

The method was adapted by K. MAHLER [21] for the automatically obtaining sorption isotherms. By the gradual changing of T_2 temperature the vapour tension of the chamber is varied and the change of weight of the sample is registered by an analytical balance. All other parameters of importance are registered at the same time.

The automated procedure is extremely convenient but at the same time requires an expensive and precise apparatus.

The change of temperature ratio $\dfrac{dT_2}{dt}$ and thus the determination period is assumed to be predetermined in a preliminary test.

An interpolation method based on the determination of change of weight

In this method, as suggested by LANDROCK and PROCTOR [22], little samples are placed simultaneously in several chambers of different relative humidity. After the elapse of a certain period the change in the sample weight, as caused by desorption or adsorption, respectively, is determined. Results are plotted and the relative humidity value, at which no change could have occurred may be interpolated. This value is taken for the ERH value belonging to the sample of given moisture content (Fig. 5.). The desired humidity in the chambers is achieved by the application of predetermined salt or acid solutions. The temperature of the chambers is thermostatically controlled.

In the interpolation method based on the change of weight, the desired value is never actually produced. It is also difficult to obtain the conditions theoretically presumed. During the determination the relative humidity values belonging to the given salt and acid concentrations would have to be present. However, this could be achieved only if the amount of the solution would be infinitely large in comparison to that of the sample and the enclosed air (and π would be very small). The sample in a desorption chamber serves as a source of moisture and a constant stream of humidity will migrate therefrom in the direction of the solution as an absorbent. The momentary equi-

librium will set in at the relative humidity value of the atmosphere where the amount of moisture evaporating from the sample equals that transferred by the air to the absorbent. Thus the vapour tension in the chambers depends on a series of factors. (In an experiment carried out by the author a sample was placed in a chamber with a sulphuric acid solution of 70% ERH. The weight of the sample amounted to 6.7% of that of the acid solution and it was initially of 95% ERH. The RH value as measured in the chamber amounted to 89%, in spite of the fact that the free absorbent surface of the sample was one fifth of that of the solution.)

The samples placed in the different chambers show various drying rates and these transient processes increase the instability of the method in proportion to the determination period.
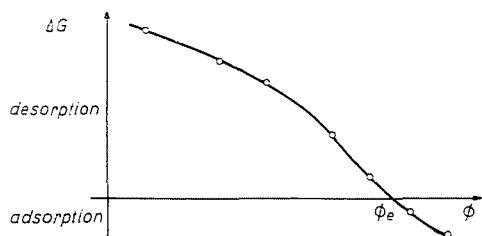

Fig. 5. The diagram of change of weights, as measured in various measuring chambers in identical determination periods with the interpolation method

It is disadvantageous to leave the sorption hysteresis out of consideration and plot a single curve from the results obtained in desorption and adsorption measurements. For the determination of a single ERH value several determinations have to be carried out with samples of identical moisture content, at identical temperatures and at an identical test period.

Difficulties may arise owing to sampling problems. Since it is essential to have a sample of minute quantity in comparison to that of the solution, the testing of composite materials or individual samples is impracticable, for it is theoretically not possible to draw several individual samples of equal composition, equal moisture content and equal moisture distribution.

The method is very sensitive to changing temperature levels, and small fluctuations affect the determination and in chambers near to the ERH value an atmosphere of desorption character may change to one with adsorptive character or vice versa.

Though simple and ingenuous, this method is in many cases of limited accuracy and thus it may be used mainly for approximation. Its accuracy would suffice only in cases where sorption hysteresis does not occur, or is of negligable extent, when the taking of small samples does not encounter

difficulties, the material to be tested is homogeneous and all the samples may be placed in a single thermostatically controlled chamber. In the interest of measurements of adequate accuracy it would be desirable to increase the determination period, however this period must not be too long, since the moisture content of the various samples in the different chambers may alter and the changes of weight do not belong to identical moisture contents.

Literature

1. IMRE, L.: Monográfia. Bp. Müsz. Egyetem, (1961).
2. IMRE, L.: Húsipar, **6** (1962).
3. LIKOV, A. V.: A szárítás elmélete. Nehézipari Könyvkiadó. Bp. (1952).
4. GÖRLING, P.: Diss. Darmstadt. (1954).
5. SOMADE, J.: Sci. Food Agric. **6**, 426 (1955).
6. JOHANSSON, C. H. & PERSSON, G.: Byggmästaren. **17**. 311 (1946).
7. KAMEI, S.: Dechema-Monogr. **32**. 305—337 (1959).
8. HODGMAN. C. D.: Handbook of Ch. & Ph. Chem. Rubber Publ. Co. Cleveland, (1961).
9. JONES. R. R.: J. Appl. Chem. **1**. 144 (1951).
10. STOKES, R. H. & ROBINSON, R. A.: Ind. Eng. Chem. **41**. 2013 (1949).
11. HEPBURN, J. R.: Proc. Phys. Soc. **40**. 249 (1928).
12. OBERMÜLLER. J.: Z. Phys. Chem. **145** (1924).
13. O'BRIEN. F. E. M.: J. Sci. Instr. **25**. 73—76 (1948).
14. D'ANS. J. & LAX, E.: Taschenbuch für Chemiker und Physiker. 2. Aufl. 888. Berlin. (1949).
15. VAS, K. & PROSZT. G.: Élelm. Ipar. **9**. 6 (1955).
16. KNEULE. F.: Das Trocknen, Verl. H. R. Sauerländer & Co. Aarau und Frankfurt am Main, (1959).
17. WEIR. A. R.: Coll. Czech. Chem. Comm. **8**. 149 (1936).
18. STOKES, R. H.: J. Am. Chem. Soc. **69**, 1291 (1947).
19. BOUSFIELD, W. R.: Trans. Farad. Soc. **13**, 401 (1918).
20. SCHANKMAN, S. & GORDON, A. E.: J. Am. Chem. Soc. **61**. 237 (1939).
21. MAHLER, K.: Chemie Ing. Techn. **33**. 9. (1961).
22. LANDROCK, A. H. & PROCTOR, B. E.: Food. Techn. S. 332 (1961).

László IMRE. Budapest, V., Szerb u. 23. Hungary