THE MEASUREMENT OF EQUILIBRIUM RELATIVE HUMIDITY

PART II

By

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Methods based on the development of equilibrium vapour tension

In the generally applied sequence of steps, as described in the first publication of this paper [23] the development of the pair of values (step a.) is usually determined by the moisture content or the moisture absorption of the sample. In desorption tests equilibration, i.e. the period of measurement lasts till the tension increased by the water evaporating from the sample practically reaches the ERH value (Fig. 6a). In adsorption tests determination is finished when the tension of the chamber is decreased by the water adsorption of the sample to the ERH level (Fig. 6b). This is followed of necessity by the change of moisture content in the sample. However, there are ways of keeping this at a negligable extent by the adjustment of the values ($W_0 \cong W_e$, Fig. 6), and so this method may be considered suitable for the determination of the ERH values by a single measurement, in samples of given moisture content. It has to be pointed out, however, that the establishment of W_e being the last step of the test, the results of the determination may be presumed to be correct even if $W_0 \neq W_e$, provided the gradient as developed in the sample is negligible. In order to extend the applicability of the method, it is, nevertheless, desirable to aim at keeping $W \cong W_e$.

The second step of the test is the establishment of the Φ_e as formed and stabilized in the measuring chamber. This step may be carried out in various ways, and a number of methods and arrangements were formed for this purpose.

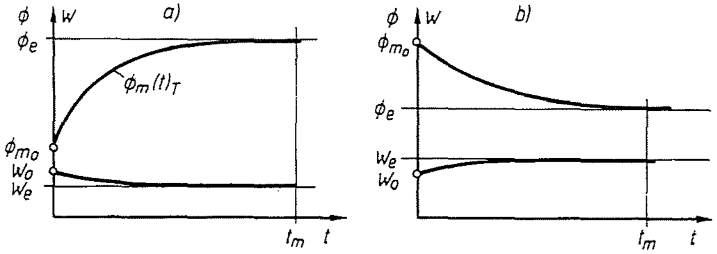

Fig. 6

The method based on the measurement of vapour tension (static method)

The theoretical principles underlying the method are simple and lucid [20, 24, 25]. According to the principle, after placing the sample in the measuring chamber this has to be evacuated to the order of 10^{-2} Torr. In this chamber, provided the temperature is kept constant, the sample will lose moisture, until the tension of the chamber equals that of the sample. The growing pressure in the chamber may be observed with a liquid micro-manometer of great sensitivity. When the manometer comes to a standstill, the equilibrium is practically attained and the reading may be noted. To establish the pressure of the sample the chamber has to be removed from the thermostat and chilled to —20°C, for instance, in a mixture of solid CO_2 and alcohol, and the manometer reading noted. By freezing all the condensable vapour, the vapour pressure value of the sample is given by the difference between the two manometer readings. The saturation water vapour pressure can be established when the measurement is carried out with distilled water under identical conditions. The ERH value belonging to W_e moisture content of the sample is determined by the quotient of the two values.

In this method, particularly in the case of high moisture contents (Φ_e values) equilibrium may be attained in 10—20 hours this being a great advantage.

The most important part of the equipment is the manometer, for which several suggestions have been made [4, 15, 26, 27].

Though this method is based on a simple principle, several difficulties may arise in its application. This fact emerged when the results obtained were not always reproducible.

The cause of some of the disturbing effects is known, therefore they may be corrected, at least in principle. However other reasons are not elucidated yet, and though their underlying causes are known, later they cannot be taken into consideration.

For instance, in principle the respective effects of the change of tension of ice or the change of environmental air pressure may be corrected [15]. However, the error due to air or other gases trapped in the sample and freed during measurement by the vacuum cannot be corrected. Owing to the smallness of values to be measured the errors thus caused may be of consequence and subsequently cannot be corrected. In certain cases, for instance when the ERH values belonging to saturated solutions are measured, the trapped air may be removed through repeated freezing of the sample [20]. In solid samples as stated by SCHANKMAN and GORDON the repeated freezing and evacuation may develop a moisture gradient. This may be the reason for the systematic decrease of ERH values as observed by VAS and PROSZT [15] when repeated measurements were carried out with the same sample. This phenomenon is probably due to the fact that the intensity of moisture conduction within the sample is far too small to permit the equilibration of moisture content within the sample during the 10—20 hours period of measurement. In such cases the last step in the sequence of measurement results in an average moisture content instead of the W_e value of the outer surface of the sample. The greater the evaporating coefficient and the smaller the moisture conductivity factor of the sample, the greater will the error be. No doubt this effect may be reduced by increasing the determination period and the σ factor [23]. No conclusion of general validity can be drawn relating to the determination period, this being among others the function of the material characteristics of the sample.

Vas and Proszt [15] — for unknown reasons — found the measured values dependent on the amount of water placed into the chamber. They state that the tension increased with decreasing water quantities — and vica versa.

The air trapped in the measuring chamber increases the heat-sensitivity. To achieve results of high accuracy the pressure gauge and the whole apparatus has to be air-tight. This has to be controlled by repeated freezing [4].

Since determinations are carried out under vacuum the results are not sufficiently accurate. Various investigations seem to prove that in certain materials the ERH values are affected by the pressure and the presence of air [3, 28].

The method based on the measurement of vapour tension is suitable for use only in desorption tests. The disadvantage of the method is that the ERH values are indirectly calculated with the results of several pressure measurements, and thus, the error inherent in each measurement is added up.

It was proved by experience that the deviation in the measured values is more significant in the range of small moisture contents, therefore to obtain reliable results in this range it is advisable to carry out a greater number of determinations. This is definitely a laboratory method and requires great accuracy, a precision instrument and expert knowledge. In spite of the simple basic principles a great number of factors has to be considered and to attain the desired accuracy great care has to be exercised.

The dynamic method

The difficulties related to the previous method, such as the exact measurement of pressure, the restrictions of use owing to the small volume of samples, further the need of conducting under vacuum may be avoided by the application of the so-called dynamic method. This method was successfully applied in the determination of the ERH values belonging to liquids and composite materials [30].

In the dynamic method the sample is exposed to the continuous flow of air or a gas [38] of known relative vapour pressure. Depending on the desorption or adsorption character of the measurement saturated or dry air is suitable for this purpose. At constant temperature the air streaming through the sample adjusts itself to the ERH value, and thus, in the case of desorption measurements its humidity will increase, whereas in the case of adsorption measurements it will decrease. Thus, the humidity of the air leaving the sample depends on the ERH and in the knowledge of the loss of weight in the desorbent and gain of weight in the absorbent, the initial condition and the amount of air present, by repeated saturation i.e. drying of the air the ERH value may be computed.

The advantage of the dynamic method lies in the fact that it is quick and there are no limitations as regards the size and composition of the sample. For application in powdered substances, however, it is not suitable because of the air streaming through the sample. During a single measurement of a longer test period, by exchanging the desorbent and absorbent, several ERH values may be determined in the same measuring chamber. Of course, the moisture content of the sample has to be determined in each intermediate phase. In the application of the dynamic method various difficulties have to be reckoned with. First of all the air, while streaming through the sample has to approximate the ERH value of the sample to a practically acceptable degree. By choosing a correct size sample and applying the right amount of air, this may be ascertained; however, it is very difficult to verify this. Further it is advisable to check whether a moisture gradient has not developed in the direction of the air stream. This may be checked by determining, at the end of the test period, the moisture content at both the ingoing and outcoming side of the sample. When ERH values belonging to liquids are determined, the adjustment of ERH may be ascertained by the agitation of the liquid.

Since the ERH value is calculated on the basis of very small changes in the weight of the material losing or gaining moisture, weighings have to be carried out with extreme precision. The precision requirements grow with the reduction of both the test period and the amount of air used. On the other hand the more air is streaming through the sample of given size during unit time, the less likely it is for the air to adjust itself to the ERH of the sample. For the same reason it is also very important to keep the airflow at a constant level.

Since the ERH is determined on the basis of the absolute humidity of the air, and the determination is temperature dependent, the stability of the temperature is of great importance.

The isopiestic (isotonic) method

Bousfield [19] developed de Vries's isotonic method for the determination of ERH values. The modified method is more practicable and was applied by several authors [10, 31—36].

In this method the sample and salt or acid solutions of varied concentration are placed in a closed test chamber having a constant temperature and if possible evacuated. The whole system aspires to attain the state of equilibrium (Fig. 7). This state of equilibrium may be considered equal to the ERH value, provided the mass of the control solutions is sufficiently small as compared to the mass of the sample and σ value is sufficiently high. It is advisable to set the concentration of the control solutions so that the ERH value as expected should fall between the initial ERH values belonging to the various solutions. Thus the value to be measured may be approximated from both sides.

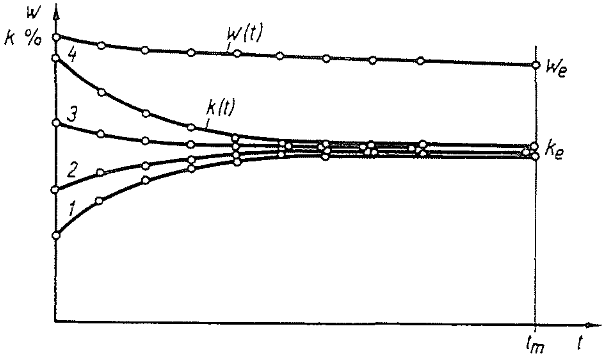

Fig. 7

The progress of the determination may be checked by weighing the control solutions. After opening the measuring chamber weighing has to be carried out with great accuracy.

When the concentration of the solutions as calculated on the basis of the determined weights show good agreement, i.e. further changes of weight may not be observed the measurement is, with the determination of the moisture content of the sample completed. The mean value (k_e) of the ERH values calculated from the final concentration of the respective solutions is accepted as the ERH value of the sample.

Theoretically equilibration takes an infinitely long time. In the practice, however, experience proves that a good aproximation may be attained in a few days. The test period may be shortened by vibrating the solution during measurement, or by bubbling the air through the control solutions in the measuring chamber.

A definitive disadvantage of the method is that the test chamber has to be opened several times during determination. If it is opened cautiously and the solutions are weighed quickly, a significant change of concentration of the control solutions may be prevented, however it is inevitable that the moisture content of the sample should suffer a change. The extent of the change is a function of the number of openings, of the π and σ ratios, and of the humidity of air invading the chamber. The sample has to form a new ERH value in the measuring chamber every time it is opened. (The effect of the control solutions, because of their small volume need not be taken into consideration.) If, however, the moisture content and the moisture distribution in the sample changes during determination, an error occurs, which is dependent on the moisture conduction coefficient of the sample. Since liquids (for instance solutions) are not affected by the changing of moisture distribution the method is more accurate when applied to solutions.

A condition of the application of the isopiestic method is that the ERH as developed by the sample should prevail in the measuring chamber. The initial relative humidity of the air in the test chamber of the determination has to be lower then the ERH value. Thus, the determination of a pair of desorption values becomes possible. If at the closing of the test chamber the relative humidity of the enclosed air is higher then the ERH value, the sample adsorbs moisture and a pair of adsorption values is obtained. To avoid hysteresis it is advisable to establish the change of the sample weight each time the measuring chamber is opened.

A system consisting of control solutions only, without the sample, would also aspire to attain a state of equilibrium which would be reached at a K_{0e} concentration of the solution. If $K_{0e} > K_e$, the average dilution of the solutions is due to the water originating from the sample. If, however, $K_{0e} < K_e$ the average concentration of the solutions will occur only in the case the sample absorbs the amount of water corresponding to the difference. Theoretically this determination would be an adsorption measurement. The effect of K_{0e} is dependent on the proportion of the masses, on the number and conditions of the openings and may be negligible. However, it is easy to take this into consideration in the selection of the initial concentration of the control solutions, particularly when samples are tested in which sorption-hysteresis is apt to cause difficulties.

The result of the measurements in the isopiestic method may be achieved by drawing conclusions from the concentration of the control solutions. In order to obtain results of greater accuracy it is useful to analyse the control solutions at the end of the determination [10]. The ERH values belonging to the average concentration of the solutions is obtainable from tables or diagrams [3, 8—14, 37]. Since data are only available pertaining to a restricted number of temperatures, so in the choice of the control solutions, in measurements at a given temperature, the data available have to be taken into consideration. A certain vagueness in the results is due to the deviations in available data.

The accuracy of the isopiestic measurements greatly depends on the way in which they are carried out. To assure correct measurements a well equipped laboratory, an apparatus of good construction and laboratory workers of special training are essential [31]. Its applicability is restricted by the lengthiness of execution.

Method based on the liquefaction of crystalline salts

As is known, crystalline salts will in an atmosphere of higher humidity than their own ERH value, liquify. From this phenomenon onesided conclusions may be drawn as to the relative humidity of the environmental atmosphere. Based on this phenomenon POUNCY and SUMMERS suggest a method for the determination of ERH [37]. The sample to be tested is placed in a chamber with various crystalline salts of known ERH value at a predetermined temperature. As soon as the sorption equilibrium is reached the liquefaction of some of the crystals may be observed. The mathematical mean of the ERH values belonging to the crystal just liquified and the one next not liquified, is considered the ERH value belonging to the sample. This value is ordered to the moisture content of the sample as determined at the end of the measurement.

The method modified by VAS, CSONTOS and PROSZT was made suitable for the determination of ERH values belonging to powdered substances and liquids [15, 36].

The significance of this method lies in its simplicity. Its applicability is, at least for the time being, restricted by attaining precision in the results. The series of crystals available is incomplete and pertinent data, particularly in relation to temperature, are unreliable [3, 8, 10, 12, 13, 37, 38, 40—45].

Thus it would be desirable to adapt the temperature applied in the determination to the data available, still this is usually predetermined by some external circumstance, such as the technology. However, the data available in relation to temperature are also unreliable and it is somewhat disquieting that in the data produced by various authors very often, and not insignificant deviations, occur. For instance the ERH value belonging to LiCl is 15% at 20°C (HODGMAN, 8), 11,1% at 23°C, 11,2% at 30°C (WINK and SEARS, 38), 13,0% at 25°C (O'BRIEN, 13); the ERH values belonging to $Ca(NO_3)_2 \cdot 4H_2O$ at 20°C are as follows: 54,4% (KAESS, 42), 55,4% (ADAMS and MERZ, 43), 55,8% and 56,0% (O'BRIEN, 13), at 18,5°C 56,0% (LIKOV, 3). There are other values to be found for the same material as follows: at 23°C 51,8%; at 25°C 50,5%; at 30°C 47,0% and 51,0% (!); at 40°C 39,9% and 46,0%.

Thus it seems that this method, owing to the deviations in data concerning the ERH value of various crystals, as well as the incompletion of the crystal-series, is not sufficiently exact. The calculation of the results on the basis of mathematical means may cause a further deviation of 3—4% in the ERH values.

Vas and Proszt suggest circumspection in relation to the test period as well [15]. They observed in their investigations that the picture as developed in the test chamber changed after a few days. Yet the consolidated state may be judged only by the appearance of the crystals. This effect is probably the result of the circumstance that with the advancement of the measurement the equilibration of the moisture content within the sample require as more and more time and during this period the relative humidity of the chamber increases. This increased relative humidity may become the critical value for one of the crystals present and may cause its liquefaction. In order to achieve satisfactory results it is, therefore, advisable to prolong the last phase of the test.

The method based on the liquefaction of crystals is suitable only for desorption measurements. It requires great care in sampling, in the arrangement of the test, in the selection and observation of the crystals. A good collection of crystals is also desirable. The method is applicable in a wide range and is not particularly cumbersome.

Methods based on the determination of the dew-point temperature

In methods based on the development of equilibrium vapour tension, as described above, the chief task is the determination of atmospheric tension. This may be achieved, among others, by measuring the dew-point temperature. From this value and the test temperature the ERH value may be unambiguously established.

The dew-point temperature may be established with the aid of a dew-point mirror. This is cooled by the evaporation of ether or by brine or cold water [4]. The dew-point mirror is suitable for the observation of the appearance or the disappearance of dew and a thermocouple serves to establish the temperature at the critical moment. However, when applying this method difficulty may be caused by the fact that owing to the heat inertia of the thermometer the temperature of the mirror surface, changing during determination, can not be accurately established. A thermocouple of copper-constantan, fitted to the metal mirror and cooled very slowly proved to be the most suitable for temperature determination. Another cause for error is due to the visual observation of the appearance (or disappearance) of dew in a closed measuring chamber, therefore it is advisable to aim at telemetering. Several methods were worked out for the sensing of the dew point with photo-cell [46, 47]. This and other automatic methods require relatively large sensors [48] and their application in the small measuring chambers used in ERH determinations is found to be difficult.

Another method of great importance is the dew-point temperature determination on the basis of the electric conductivity of a hygroscopic film. The difficulties inherent in the method were overcome — after the efforts of TODD, BOUSFIELD [49], P. ANDERSON [50], MCKELVY and TAYLOR [51], WEAVER and LEDIG [52] —, by DUNMORE. He succeeded in developing this practicable method by producing a sensing cell impregnated with LiCl and coated with a hygroscopic film (Dewcel, Hygrocel). After several modifications the method became suitable for application in ERH determinations [54—60] and apparatuses of this kind are now available.

The basic principle underlying this method is the electric conductivity of salt solutions as a function of the changing concentration of the solution. The film of the sensing cell is impregnated with LiCl solution, and bifilar platinum or silver wires are wound around it. As soon as the cell is dried out the ends of the cable are connected to the poles of a low voltage (for instance 25 V) supply unit. The LiCl coating of the sensing element is placed in the measuring chamber, and, owing to the low equilibrium vapour tension, absorbs moisture. In the turns of the coil current begins to flow and in turn generates heat causing electrolysis. The LiOH and HCl forming in the process neutralize each other, thus the coating of the cell continuously regenerates. The so developed heat warms the coating, the vapour tension grows and the coating starts to dry. The process of drying in its turn reduces the heating current and so the temperature of the coating, and the process is repeated with limits getting continuously narrower and the temperature of the coating aproximates the value at which the vapour pressure of the cell solution equals the partial vapour pressure in the measuring chamber. Thus, from the surface temperature belonging to the cell, the partial vapour pressure of the chamber may be established and this equals the vapour pressure belonging to the dew-point temperature. Knowing this and in the knowledge of the temperature of the chamber, the ERH value may be established. The surface temperature of the cell may be determined with a resistance thermometer and the scale of the instrument may be calibrated to directly show the relative humidity. The advantage of this method lies in the fact that it is suitable for distant control, however its accuracy at low temperatures (below 6°C) is not satisfactory. At low temperatures the difference between the pressure belonging to the saturated LiCl solution and the vapour pressures belonging to the water is small and thus to a relatively large difference in the humidity values belongs a small difference in the surface temperatures of the cell. This is rather disconcerting because the temperature of the cell fluctuates anyway and this fluctuation causes, at low temperatures, significant want of precision. The measurement being indirect the inacuracy of temperature measurement enlarges the error.

To eliminate the disadvantages of the method SZALAY [60] developed, by transforming the sensor, an electrolitic humidity measurement method. To eliminate polarisation effects the detector voltage is restricted and a stabilized current supply is applied. The sensing element is a small ceramic tube impregnated with LiCl and not coiled, with metallic terminals. The resistance of the sensing element depends on the humidity of the atmosphere, thus by measuring the resistance the ERH value may be established.

When LiCl sensor is used in ERH measurements, two processes have to become stationary. One of the processes is the development of the ERH in the measuring chamber. The time necessary for this process is a function of the drying characteristics and the σ value [23] belonging to the sample. The second process is the equilibration of the measurement of the sensing cell. The time needed is a function of the formation of the sensor and of the method of determination. The time-constant of the sensor is small compared to the sorption time-constant and so the determination is not affected by the change in the moisture absorption of the cell during determination.

In small measuring chambers the thermal equilibration is to a certain extent affected by the significant difference in the temperature of the cell and the chamber (for example: in the condition of 5°C and 75% relative humidity the cell equilibrates at 36,5°C).

Each of the sensing elements possesses an optimal range of measurement dependent on the LiCl concentration. In other words they are not equally accurate in all ranges of relative humidity. Thus each sensor is suitable to be used at a certain range and each apparatus has to be fitted with several sensors. The construction of this apparatus is rather complicated. It may be used under vacuum and at atmospheric pressure equally well. It is suitable for the determination of desoprtion isotherms. However, when the determination is carried out at atmospheric pressure its desorption or adsorption character is dependent on the initial relative humidity of the atmosphere. An advantage of the method as modified by SZALAY [60], lies in its applicability at very low temperatures (for instance in cold storage) for the investigation of samples of high moisture content.

The bi-sorption method

The majority of the methods previously described is suitable only for desorption measurements. Yet in the solution of various drying technical problems the knowledge of the ASI is also necessary. The aim for working out the bi-sorption method was to have a method for determining both DSI as well as ASI.

Most of the methods are suitable only for laboratory tests and cannot be carried out by an unqualified person. In the majority of the methods samples of small weights are used, thus the investigation of composite materials or coated individual samples is not possible. In some of the methods, the long test period causes problems and this is disadvantageous in the investigation of perishables.

In view of all these difficulties the bi-sorption method was worked out to be used for the determination of the isotherms of meat products such as sausages. This method may be applied to samples removed from the batch during processing in the aging rooms of a factory. The moisture distribution in individual samples is not uniform, therefore, the determination has to produce results within a short time (a few hours) in which the inside moisture equilibration is negligible. Since the drying-technical requirements are strict, and ERH values, particularly at high moisture contents, change very little, a high accuracy of measurement is desirable.

The bi-sorption process is carried out in a closed measuring chamber having controllable temperature [61]. The sample placed in the chamber may be large (0,5 kp) thus the σ value is favourable. However, it may be made even more optimal by reducing the amount of air trapped in the chamber with blocks of non hygroscopic character inserted into the chamber.

Thus a $\sigma > 10^3$ value, incomparably more favourable than in any of the methods based on vapour tension equilibration, may be achieved. Hereby the test period is substantially reduced and the change of the surface tension belonging to the sample may be neglected.

To obtain bi-sorption a tube system supplied with an absorbent and a moisture delivering agent is connected to the measuring chamber. By means of passing the air through the system the humidity of the enclosed air may be set, prior to the measurement, at any desirable level. This is in the case of adsorption measurements higher, and in desorption measurement lower than the ERH value expected.

Thereupon the chamber is closed and the development of ERH begins. This may be accelerated by agitating the air with a ventilator.

When equilibration is achieved the ERH value is obtained by psychrometric determination. An aliquot portion of the air enclosed in the chamber is passed through the opening of the wet-dry bulb thermometer pair, simultanously the volume of the chamber is reduced to an adequate rate. Thus the absolute humidity of the atmosphere in the measuring chamber may be established with great accuracy and from this, in the knowledge of the test chamber temperature, the ERH value may be determined.

Thus, for the sole purpose of checking the equilibrated state, a psychrometer of smaller accuracy is adequate.

In the knowledge of the data belonging to the apparatus and the characteristics of the sample, the length of the test period may be controlled by calculation.

In desorption measurements the vapour taken up by the air of the chamber during unit time (the increase in the absolute humidity of the air x) equals the amount of water lost by the sample during unit time. Since the process occurs at constant temperature and at practically constant surface humidity it may be stated that:

$$V \cdot \gamma \cdot \frac{dx}{dt} = B \cdot A \cdot (p_a - p_g) \tag{2}$$

where

V: volume of the measuring chamber
γ: density of the air
t: time
B: evaporation coefficient of the sample
A: evaporating surface of the sample
p_a: partial vapour pressure on the surface of the sample
p_g: momentary partial vapour pressure of the air in the chamber.

Since

$$p_a = \Phi_e \cdot p_{gt} \tag{3}$$

$$p_a = \Phi \cdot p_{gt} \tag{4}$$

where Φ_e is the ERH value, and Φ the momentary relative humidity of the air. Further with satisfactory aproximation

$$p_g \cdot V = \frac{M_g}{\mu_g} RT \tag{5}$$

$$p \cdot V = \frac{M_l}{\mu_l} RT \tag{6}$$

where

M_g: weight of the vapour in the measuring chamber
M_l: weight of the air enclosed in the measuring chamber
R: general gas coefficient
T: (constant) test temperature
μ_g: molecular weight of the water vapour
μ_l: molecular weight of water
p: partial pressure of the air in the measuring chamber.

Since

$$x = \frac{M_g}{M_l} = \frac{\mu_g \cdot p_g}{\mu_l \cdot p} \tag{7}$$

and

$$p = p_b - p_g \tag{8}$$

where

p_b is the initial barometric pressure and as

$\mu_g = 18{,}9;\ \mu_l = 29{,}0;$

$$\frac{\mu_g}{\mu_l} = 0{,}622 \tag{9}$$

thus

$$x = \frac{0{,}622 \cdot p_g}{p_b - p_g} \tag{10}$$

Using

$$a = \frac{p_b}{p_{gt}} \tag{11}$$

notation and on the basis of (3), (4) and (11)

$$x = \frac{0{,}622 \cdot \varphi}{a - \varphi} \tag{12}$$

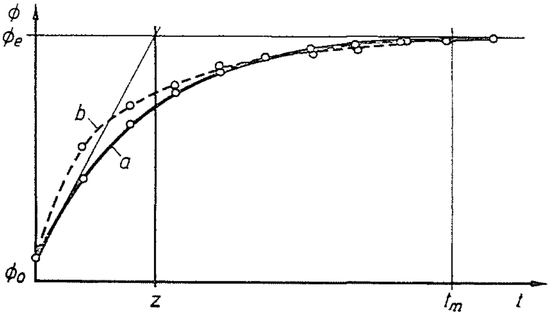

Fig. 8

Substituting (12) into (2), using the following notation:

$$\Theta = \frac{B \cdot A \cdot p_{gt}}{V \cdot \gamma \cdot 0{,}622} \quad \text{and} \tag{13}$$

awaiting the approximation of desired accuracy $(\Phi_e - \Phi)$ during determination, the measuring time needed is:

$$t = \frac{1}{\Theta}\left[\frac{1}{(\Phi - a)(\Phi_e - a)} + \frac{1}{(\Phi_e - a)^2}\ln\frac{|\Phi - \Phi_e|}{|\Phi - a|} + c\right] \tag{14}$$

where

$$c = \frac{-1}{(\Phi_0 - a)(\Phi_e - a)} - \frac{1}{(\Phi_e - a)^2}\ln\frac{|\Phi_0 - \Phi_e|}{|\Phi_0 - a|} \tag{15}$$

and Φ_0 the initial relative humidity of the enclosed air.

As can be seen, in the methods based on the equilibration of the vapour pressure the measuring time — being the function of several factors — has to be determined in each case separately.

In the bisorption method, as proved by detailed investigation, from (z) *relative sorption time-constant* (Fig. 8.) at $t = 3{,}55 \cdot z$ measuring time the error of the deviation from Φ_e does not exceed 0,5%.

Diagram (b) plotted from the data as obtained in the measurement, and diagram (a) as calculated, show a good agreement in the measuring time (Fig. 8.). In the knowledge of the measuring time, accurate determination diagrams permit the calculation with equation (14) and (15) of the evaporation coefficient of a sample.

There are no restrictions as to the applicability of the method. No special qualification is desired in the use of the apparatus.

Other methods

It is known that the adsorption of gases and vapours is a process of exotherm character. In the case of sorption equilibrium the correlation between equilibrium vapour pressure on the one hand, and adsorption temperature on the other, may be unambiguously determined by the Clausius-Clapeyron equation. According to the equation of HENRY and FREUNDLICH the amount absorbed at constant temperature depends on the pressure.

Thus by measuring the adsorption temperature or the amount of water adsorbed, with the aid of the above mentioned equations the points of isotherm may be determined [62].

Methods for quantitative measurements were worked out by PEASE [63], COOLIDGE [64], TAYLOR and STROTHER [65], MARKHAM and BENTON [66] and others [67, 68, 69]. Some of the methods are based on gravimetry, others on the volumetric principle. The adsorption temperature is determined by colorimetric methods [70, 71, 72, 73].

With the aid of the described equations the isotherm determined at a given temperature may be extrapolated at another, provided the constants are determined. However these possibilites may be applied with satisfactory approximation only in the case of the adsorption of gases on clean, homogeneous adsorbents. The main difficulty lies in the circumstance that the constants in the equations may be considered of constant value only with neglection.

In order to explain the adsorption mechanism several theories were worked out and with the aid of these equations were formulated for isotherms of varied shapes [74, 75, 77, 78]. The general multimolecular adsorption theory of BRUNAUER, EMETT and TELLER can be used to advantage for the calculation with good aproximation of the isotherms. The theory is built on LANGMUIR's monomolecular adsorption theory. Several constants needed for the calculation, however, have to be experimentally determined.

Summary

In dealing with drying-technical problems, such as storage, packaging and so on, the knowledge of the sorption isotherms of the moisture containing materials is indispensable.

The determination of the sorption isotherms generally occurs by way of the formation of the state of equilibrium and the establishment of the parameters of the state.

The state of equilibrium is usually achieved tensiometrically or by way of the formation of equilibrium vapour tension. The state of equilibrium may be approximately estimated from the change of weight in atmospheres of various character.

In view of the measuring technical and evaluation aspects, the theoretical and practical problems of the applicability of methods were discussed.

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