

## The effect of humidity and temperature on the equilibrium moisture content of powders

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The equilibrium moisture content of maize, wheat and potato starches, alginic acid, tragacanth, acacia, lactose, dextrose, sucrose and hexamine has been determined at different relative humidities and temperatures. Samples were exposed to an atmosphere of controlled temperature and humidity until equilibrium was attained. The moisture content was determined by drying. The moisture content of each powder at equilibrium was dependent on the relative humidity.

**A**LTHOUGH water vapour is usually considered to be one of the minor constituents of the atmosphere, it can be of great importance in the manufacture and storage of materials.

Moisture gained by a solid material can be held in different ways and stages (Geary, 1956). It can be simply acquired by the physical process of sorption and is known as “free water”, or it can be held by a chemical bond and is termed “bound water” (Briggs, 1932).

The sorption of water vapour by powders has been examined by many workers. Edgar & Swan (1922) found that sorption of moisture varies with the specific nature of the material, the exposed surface area of the solid, the temperature and the velocity of the movement of the moist air.

The uptake of moisture by starch was determined by Browne (1922), who found that anhydrous starch reached its saturation point after about 12 days and contained 24.37% moisture. Hellmann & Melvin (1948) found that moisture sorption by 10 corn starches was not affected by origin, condition, preparatory procedure, drying procedure and time of storage.

The sorption of water by maize and potato starches has been studied by Sair & Fetzer (1944). These authors agree with Katz (1917) that starches of different origin vary markedly in sorptive capacity and that water was held by physical sorption between relative humidities of 20 and 90%. This opinion differs from that of Freeman (1942), who stated that water in starch was in the bound form. Ulmann (1957) declared that water sorbed by starch was held by adsorption, by binding, and by two unspecified kinds of association.

Craik & Miller (1958) showed that sucrose deliquesced when exposed above a relative humidity of approximately 80% at 30°. Browne (1922) found the equilibrium moisture contents of dried samples of sucrose, dextrose, and lactose exposed at a relative humidity of 60% to be 0.03, 0.07 and 1.23% respectively, equilibrium being attained after 9 days.

### Experimental

#### EQUILIBRIUM MOISTURE CONTENTS

*Apparatus.* A thermostatically controlled humidity cabinet was constructed so that air could be circulated over suitably chosen saturated

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solutions to attain a given humidity and then over the samples of powders. The humidity was checked with a wet and dry bulb hygrometer (Harb, 1963).

*Materials.* The materials examined were maize, wheat and potato starches, alginic acid, tragacanth, acacia, lactose, anhydrous dextrose, sucrose and hexamine.

*Method.* Samples were spread in a uniform layer about 3 to 5 mm thick in Petri dishes 10 cm diameter and placed in the humidity cabinet. At 1, 2, 3 and 4 hr after exposure to the humidified air each sample was mixed thoroughly. After 24 hr the powders were well mixed and the

TABLE 1. EQUILIBRIUM MOISTURE CONTENTS OF THE POWDERS AT DIFFERENT HUMIDITIES AND TEMPERATURES

(Expressed as a percentage of the dry weight)

| Temp. °C | Relative humidity | Maize starch | Wheat starch | Potato starch | Tragac. | Acacia | Alginic acid | Lactose | Dextrose | Sucrose |
|----------|-------------------|--------------|--------------|---------------|---------|--------|--------------|---------|----------|---------|
| 25       | 34                | 10.8         | 10.9         | 13.5          | 8.5     | 8.2    | 8.7          | —       | —        | —       |
|          | 55                | 13.2         | 13.0         | 16.4          | 13.7    | 12.2   | 10.9         | —       | —        | —       |
|          | 66                | 15.2         | 15.3         | 19.2          | 19.5    | 15.4   | 12.3         | —       | —        | —       |
|          | 87                | 19.8         | 19.4         | 26.4          | 32.4    | 28.9   | 18.9         | —       | 9.6      | —       |
|          | 100               | 27.4         | 28.0         | 35.6          | gel     | gel    | 30.3         | 0.1     | soln.    | soln.   |
| 30       | 33                | 10.9         | 10.4         | 13.7          | 9.6     | 8.9    | 9.0          | —       | —        | —       |
|          | 44                | 12.7         | 12.7         | 16.1          | 12.8    | 11.3   | 11.3         | —       | —        | —       |
|          | 65                | 15.4         | 15.4         | 19.4          | 19.9    | 15.7   | 12.9         | —       | —        | —       |
|          | 80                | 19.1         | 18.9         | 24.1          | 27.7    | 25.9   | 16.2         | —       | 10.0     | —       |
|          | 86                | 19.6         | 20.7         | 26.9          | 31.8    | —      | 19.2         | —       | 10.0     | —       |
|          | 92.5              | 24.8         | 25.9         | 33.0          | 42.5    | gel    | 25.1         | —       | soln.    | soln.   |
| 100      | 26.8              | 29.6         | 35.6         | gel           | soln.   | 30.5   | 0.1          | soln.   | soln.    |         |
| 40       | 32                | 8.07         | 9.6          | 13.1          | 10.8    | 9.8    | 9.2          | —       | —        | —       |
|          | 50                | 12.9         | 12.6         | 16.0          | 14.9    | 12.9   | 11.6         | —       | —        | —       |
|          | 63                | 15.3         | 14.8         | 18.9          | 19.9    | 16.2   | 13.6         | —       | —        | —       |
|          | 75.5              | 17.1         | 16.7         | 21.5          | 25.2    | 20.4   | 15.9         | —       | 3.7      | 0.05    |
|          | 89.5              | 20.1         | 19.9         | 26.2          | 32.7    | gel    | 22.3         | —       | soln.    | 0.2     |
|          | 100               | 30.5         | 29.2         | 36.3          | gel     | soln.  | 31.4         | 0.2     | soln.    | soln.   |
| 50       | 32                | 9.3          | 9.2          | 12.5          | 9.8     | 9.3    | 8.1          | —       | —        | —       |
|          | 47                | 11.5         | 11.5         | 15.2          | 12.5    | 11.1   | 9.8          | —       | —        | —       |
|          | 67                | 15.3         | 15.2         | 19.1          | 19.7    | 15.5   | 13.8         | —       | —        | —       |
|          | 76                | 17.6         | 17.3         | 22.9          | 24.1    | 24.3   | 15.6         | —       | 10.2     | —       |
|          | 87                | 21.1         | 20.9         | 26.3          | 34.2    | gel    | 20.1         | 0.3     | soln.    | soln.   |
|          | 100               | 30.3         | 30.9         | 37.7          | gel     | soln.  | 31.6         | 0.6     | soln.    | soln.   |

moisture content determined. This was repeated at 24 hr intervals until equilibrium was attained as shown by a constant moisture content. Temperatures of 25°, 30°, 40° and 50° were used with relative humidities between 30 and 100% at each temperature.

The moisture content of the starches was determined by drying in a hot air oven at 105° for 3 hr. Samples of tragacanth, acacia, alginic acid, and the sugar samples were dried in a vacuum oven at 10 mm Hg and 70° to constant weight (approximately 2 hr).

### VAPOUR-PRESSURE OF SATURATED SOLUTIONS

*Apparatus.* The apparatus used was essentially that of Smith & Menzies (1910) except that a larger bulb was used. Values were obtained at 25°, 30°, 40° and 50° for lactose, dextrose, sucrose and hexamine.

## Results

Equilibrium moisture contents of the powders at different humidities and temperatures are given in Table 1. The results are expressed as percentage of the dry weight.

On exposing the samples to relative humidities from 32 to 67% at the different temperatures, all the powders kept their normal characteristics, showing little or no agglomeration and caking.

At a relative humidity of 75% the starches and acacia began to cake whereas the other materials remained powdery and free-flowing.

At a relative humidity of 80% potato starch caked slightly but maize and wheat starches showed no change. Acacia and tragacanth swelled and caked. The sugars remained powdery.

TABLE 2. HYGROSCOPICITY DATA OF SUGARS AND HEXAMINE

| °C | Vapour pressure of distilled water (Lange) | Lactose   |  | Dextrose  |  | Sucrose   |  | Hexamine  |  |
|----|--|---|--|---|--|---|--|---|--|
|    |  | Vapour pressure of saturated solution mm Hg 0°C | Relative humidity of air in equil. with saturated solution | Vapour pressure of saturated solution mm Hg 0°C | Relative humidity of air in equil. with saturated solution | Vapour pressure of saturated solution mm Hg 0°C | Relative humidity of air in equil. with saturated solution | Vapour pressure of saturated solution mm Hg 0°C | Relative humidity of air in equil. with saturated solution |
| 25 | 23.756                                     | 22.27   | 93.1   | 19.29   | 81.1   | 18.37   | 77.41  | 17.12   | 72.1   |
| 30 | 31.824                                     | 29.50   | 92.7   | 25.75   | 80.6   | 24.57   | 77.1   | 22.47   | 70.6   |
| 40 | 55.324                                     | 50.25   | 90.8   | 43.98   | 79.5   | 42.77   | 77.3   | 39.37   | 71.2   |
| 50 | 92.51                                      | 83.29   | 90.4   | 71.12   | 77.2   | 70.33   | 76.0   | 69.56   | 75.2   |

Between relative humidities of 86 to 89.5% the starches caked. Acacia changed from its powdery form to a thick sticky paste and tragacanth caked. Hexamine, sucrose and dextrose started to deliquesce and form solutions while lactose showed no change.

The caked starches showed mould growth on the surface of the samples within a few days at a relative humidity of 92.5%; lactose became moist and alginic acid darkened in colour.

As the absolute humidity increases with rise of temperature at a constant relative humidity, this work was carried out at approximately the same relative humidity at each temperature.

There is a linear relationship between the logarithm of the moisture content and the relative humidities for the starches and alginic acid. Tragacanth and acacia behave similarly at the lower relative humidity values but at higher values they pass into solution. The moisture sorption for most of the materials is not materially affected by temperature. Table 2 gives the hygroscopicity data for the sugars and hexamine. The relative humidity of air in equilibrium with the saturated solution of the substance was calculated since it is at this relative humidity that the substance should commence to deliquesce.

## Discussion

Equilibrium was reached when the vapour pressure of water at each relative humidity and temperature equalled the equilibrium vapour pressure of the substance under the stated conditions. Air circulation accelerated the rate of moisture sorption as in the work of Yee & Davis (1944). Lactose did not form a solution even at a relative humidity of 100%; this may be because of its rate of solution or because this degree of relative humidity was not actually attained.

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With rise of relative humidity the sorptive capacity of potato starch and maize and wheat starches showed a clear divergence. Potato starch was more hygroscopic than either maize or wheat starches, which had similar sorption properties. The values of equilibrium moisture content for maize starch are similar to those obtained by Hellman & Melvin (1948).

The results for the sorption of water vapour by starches are similar to those of Sair & Fetzer (1944) above relative humidities of 33%. Desorption isotherms given by these authors suggest that water is retained by starch between relative humidities of 20 and 90% in the adsorbed form only. Further evidence suggesting that starch retains water by adsorptive forces alone is found in heat of adsorption data (Winkler & Geddes, 1931).

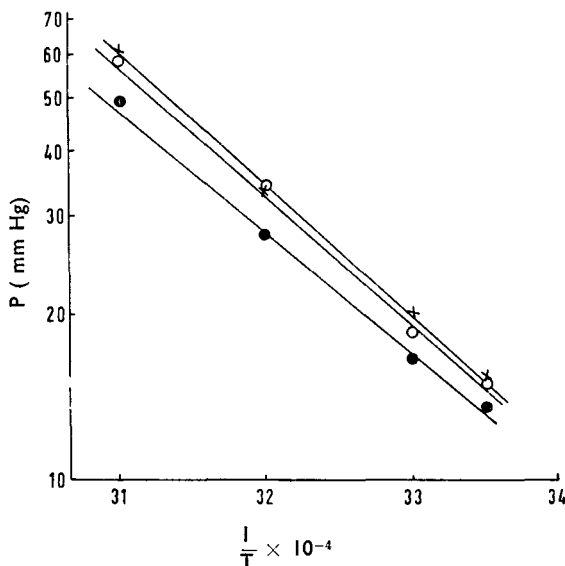


FIG. 1. Relationship between  $\log P$  and  $1/T$  for the moist powders.  $T$  is absolute temperature.  $P$  is the partial pressure of water vapour in equilibrium with the powders containing the moisture content given in Table 3. ○ Maize and wheat starch. × Potato starch. ● Tragacanth, acacia and alginic acid.

The heat of adsorption is a measure of the strength of the bond between the water molecules and the sorbent molecules. The heat sorption was calculated from plots of  $\log P$  against  $1/T$  (Fig. 1) using the Clapeyron equation, where  $T$  is the absolute temperature and  $P$  is the partial pressure of water vapour in equilibrium with the powders containing the moisture content given in Table 3. Using the data from Fig. 1, the heat of sorption of water vapour on the solid was compared with the average latent heat of vaporisation of water from 25 to 50° (Hodgman, 1962-63) (see Table 3).

The values of heat of sorption obtained are little different from the heat of vaporisation of water and this indicates a weak bond is formed which is suggestive of physical adsorption. According to the results, water is retained by the powders by simple adsorption from 32 to 100% relative

humidity. The emulsifying agents showed more avidity for moisture than the starches. This is probably related to their hydrophilic nature and to their water solubility. At relative humidities below that at which they deliquesce, acacia and tragacanth behave similarly to the starches in having values for heat of sorption characteristic of physical adsorption.

TABLE 3. HEAT OF SORPTION OF MOIST POWDER CALCULATED FROM FIG. 1

| Substance                          | Slope from Fig. 1 | Heat of vaporisation kcal/mol. H <sub>2</sub> O | Heat of sorption kcal/mol. H <sub>2</sub> O |
|------------------------------------|-------------------|---|---|
| Maize starch (15% moisture) .. ..  | 2927              | 10.96   | 0.58  |
| Wheat starch (15% moisture) .. ..  | 2927              | 10.96   | 0.58  |
| Potato starch (20% moisture) .. .. | 2417              | 11.06   | 0.68  |
| Tragacanth (15% moisture) .. ..    | 2420              | 11.07   | 0.695                                       |
| Acacia (15% moisture) .. ..        | 2420              | 11.07   | 0.695                                       |
| Alginate acid (15% moisture) .. .. | 2420              | 11.07   | 0.695                                       |

Heat of vaporisation of water = 10.38 kcal/mol. (Hodgman).

Lactose, anhydrous dextrose, sucrose and hexamine at a relative humidity below 65% contained negligible moisture, but absorbed small amounts of moisture between 65 and 85%. Above 85% all except lactose deliquesced. Anhydrous dextrose formed the monohydrate at relative humidities of 87% at 25°, 80% at 30° and 77% at 50°. The sugars and hexamine deliquesced in atmospheres having relative humidities at which the partial pressure of water vapour was equal to the vapour pressure of their saturated solutions.

For a given relative humidity, temperature seemed to have little effect on the equilibrium moisture content for the starches and the emulsifying agents used. For dextrose, the formation of the monohydrate (approximately 10% moisture) occurred at increasingly lower humidities the higher the temperature. The deliquescence of dextrose and sucrose was affected by temperature. At 86–87% relative humidity and 25° and 30° both sugars were still powdery, but at a similar relative humidity at 40° and 50° they formed solutions.

## References

- Briggs, R. D. (1932). *J. phys. Chem.*, **36**, 367.  
 Browne, C. A. (1922). *Industr. Engng Chem.*, **14**, p. 712.  
 Craik, D. & Miller, B. F. (1958). *J. Pharm. Pharmacol.*, **10**, 136T–144T.  
 Edgar, G. & Swan, W. O. (1922). *J. Amer. chem. Soc.*, **44**, 570–577.  
 Freeman, M. E. (1942). *Arch. Biochem.*, **1**, 27–39.  
 Geary, P. J. (1956). British Scientific Inst. Research Assoc. Report 24.  
 Harb, N. (1963). Thesis for Ph.D., London Univ.  
 Hellman, N. N. & Melvin, E. H. (1948). *Cereal Chem.*, **25**, 146–150.  
 Hodgman, C. D. (1962–63). *Handbook of Chemistry and Physics*, 44th Edition, p. 2412–2413.  
 Katz, J. R. (1917). *Kolloidchem. Beitraege*, **9**, 65.  
 Lange, N. A. (1961). *Handbook of Chemistry*, 10th Edition, p. 1415–1422.  
 Sair, L. & Fetzer, W. R. (1944). *Industr. Engng Chem.*, **36**, 205–208.  
 Smith, A. & Menzies, A. W. C. (1910). *J. Amer. chem. Soc.*, **32**, 1412.  
 Ulmann, M. (1957). *Stärke*, **8**, 4–8.  
 Winkler, C. A. & Geddes, W. F. (1931). *Cereal Chem.*, **8**, 409–414.  
 Yee, J. Y. & Davis (1944). *Industr. Engng Chem.*, **36**, 487–490.