

APPLICATION OF LAWS OF THERMODYNAMICS FOR FAST EVALUATION OF WATER ACTIVITY IN BIOLOGICAL SYSTEMS

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INTRODUCTION: Many publications relating to moisture condition in foods have common opinion, that most objectively moisture condition can be evaluated by analysis of thermodynamic processes that are taking place on the borderline of wet material and environment (WM-E).

That's true as far as the study into water desorption in biological systems ensures deeper understanding of the essence of this important physico-chemical process. Besides, knowledge of moisture desorption mechanism of biological systems is vital for understanding of biochemical reaction mechanism (Izmailova et al., 1988).

Constant temperature of products surface during desorption ensures constancy of such thermodynamic parameters as: partial pressure of vapour above the product, enthalpy, mass-transfer potential and so on. Here it is worth to note that WM-E system acquires thermodynamic equilibrium with parameters, depending upon energy and forms of moisture bond with dry frame of the product.

If we change at least one of the equilibrium parameters, the system will react in such a way, as to minimize this introduced change (Edsoll and Gutfriend, 1986). Upon consideration of thermodynamic equilibrium its dynamic character is usually taken into consideration according to 3 main aspects: mechanical and thermal aspects as well as equality of chemical potentials or of water activity. Consequently, under equilibrium conditions (WM-E), to avoid processes of moisture or vapour transfer under effect of mechanical factors, mechanical equilibrium must be established. To do this one has to create equilibrium of forces, emerging on the borderline of phases, coming into contact. Along with the above-mentioned equilibrium thermal equilibrium should be provided as well. Temperature of enthalpy of wet material surface layers is equal to environmental temperature. One can judge about stability of WM-E equilibrium condition not only by mechanical and thermal equilibrium, but also if equality of chemical potentials of liquid and gaseous phases is provided, i.e. $\mu_l = \mu_g$. Chemical potential depends on substances concentration in the phase, and that is on water activity (a_w). This statement is true if we consider change of the wet air chemical potential above the product when its pressure is changed. If, during isothermal process, pressure is changed from P_A to P_B , the change of chemical potential will be equal to:

$$(1) (\mu_i)_B - (\mu_i)_A = \int_{P_A}^{P_B} V dP = \int_{P_A}^{P_B} RT d(\ln P) = RT \ln \frac{P_B}{P_A} = RT \ln \frac{C_B}{C_A}$$

As far as $P=RTc$, where c - is vapour concentration above the product in moles, then validity of the equality (1) is evident (Edsoll and Gutfriend, 1986). It's absolutely clear that in stable equalized condition in WM-E system, mechanical, thermal equilibrium and chemical potentials equality should be provided (Landau and Lifshits, 1986), (Sazhin, 1984).

Assuming, that air, situated close to wet products surface, is in saturated state and in equilibrium with the product, one can interrelate products parameters in continuously thin surface layer with parameters of equal air layer contacting the surface of material at a certain temperature ($T_{air} = \theta$) (Mushtayev et al., 1984).

MATERIALS AND METHODS: Let's consider a model shown in fig. 1, representing a system with three tanks: A - containing wet product; B - distilled water; C - wet air. The system is equipped with mobile sealing dampers 1 and 2.

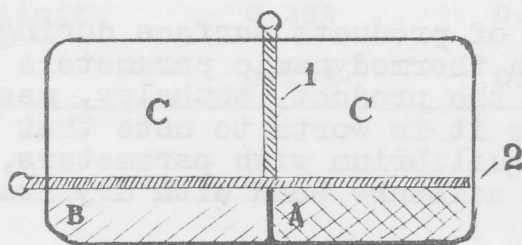


Fig. 1

When damper 2 is opened, thermodynamics of the system will be disturbed and then, after some time, according to Le Chatelier principle (1888), system will acquire thermodynamic equilibrium again, however, now possessing different parameters.

On the phases borderline, for the product, having definite thickness δ in the close to border layer, equation of enthalpy balance may be expressed as follows:

$$I_{v\theta} \cdot d_v + I_{da\theta} = I_{mTe} \cdot d_{mc} + I_{daTe} \quad (2)$$

where I_v - is enthalpy of the vapour above the product in upper part of δ -layer;

T_e - temperature of environment;

d - moisture content of vapour;

$I_{da\theta}$ - enthalpy of dry air

- temperature of products surface;

I_m - enthalpy of moisture vapour in wet air;

d_{mc} - moisture content of wet air,

for δ -layer above distilled water:

$$I_{mTw} \cdot d_{mc} + I_{daw} = I_{mTe} \cdot d_{mc} + I_{daTe} \quad (3)$$

where T_w - is temperature of wet thermometer.

Then,

$$I_{v\theta} \cdot d_v + I_{da\theta} = I_{mTw} \cdot d_{mc} + I_{daTe} \quad (4)$$

or:

$$0,622 \frac{P_{pr\theta}}{P_{da\theta}} (r_{o\theta} + C_{v\theta}) + C_{da\theta} = 0,622 \frac{P_w}{P_{daTw}} (r_{oTw} + C_v \cdot T_w) + C_{da} \cdot T_w \quad (5)$$

where: P_{pr} - partial pressure of vapour above the product;
 P_{da} - partial pressure of dry air
 r_o - specific heat of evaporation
 C_v - specific heat capacity of vapour
 C_{da} - specific heat capacity of dry air.

From this equation (5) we determine $P_{pr\theta}$ and, dividing by $P_{s\theta}$, we find water activity:

$$a_w = \frac{P_{pr\theta}}{P_{s\theta}} = \left[\frac{P_{sTw} - \frac{C_{da}(\theta - T_w) \cdot P_{daTw}}{0,622 \cdot I_{waTw}}}{P_{s\theta}} \right] \frac{P_{da} \cdot I_{waTw}}{P_{daTw} \cdot I_{wa\theta}} \quad (6)$$

where P_s - is pressure of saturated vapour;
 I_{wa} - is wet air enthalpy

In accordance with formula (6) water activity represents ratio of vapour enthalpy above the product to the enthalpy of saturated vapour when temperature of environment is equal to that of product.

One can notice that in case of thermodynamic equilibrium partial pressure of vapour, which is contained in δ -layer becomes equal to partial pressure of environment, involving equalizing of products and environmental temperatures (θ , T_e); formula (6) is transformed into formula for relative humidity determination ψ . However, we should bear in mind, that a_w - calculation according to (6) gives most significant results in case when measurement is taken in the product, containing capillary moisture, which corresponds to the period of continuous drying.

If deepening of evaporation zone occurs (corresponding to the second period - lowering of drying speed (Lykov, 1968)), then, due to convection speed decrease intensity of heat and mass-exchange decreases too. This factor doubtlessly influences accuracy of temperature measurements of products surface when moisture is evaporated from it. The above-said moisture should be taken into consideration when value of water activity is determined.

Investigation, done by O.Krischer into the processes of heat- and mass-exchange between the wet product and air at its laminar and turbulent moving regimes, made it possible to con-

clude that disagreement between results of thermal and mass-transfer coefficients ratio for two extreme variants of air move is not significant (O.Krischer, 1956).

This conclusion proves that for calculation purposes temperature measurement of the products surface in various regimes is found to be within permissible levels.

Let's return to the above-driven model, shown in fig. 1. When dampers 1 and 2 are opened after a definite period of time, system WM-E acquires stable equilibrium which is expressed through equality of enthalpy and moisture temperature on products surface with temperature of environment and enthalpy. In this case enthalpies of systems can be expressed in such a way:

$$\sum I_I = I_M \cdot d_{mc} + I_{da} = (r_o + C_{wa} \cdot T_e) \cdot 0,622 \frac{P_{pr}}{P_{da}} + C_{da} \cdot T_e \quad (7)$$

where C_{wa} - is specific heat capacity of wet air;

$$\sum I_{II} = I_M \cdot d_s + I_{da} = (r_o + C_v \cdot T_e) \cdot 0,622 \frac{P_v}{P_{da}} + C_{da} \cdot T_e \quad (8)$$

the latter being for water, situated in a bordering -layer.

In an equilibrium state the following equation can be used:

$$a_w = \frac{P_{pr}}{P_s} = \frac{I_I - I_{da}}{I_{II} - I_{da}} = \frac{I_{prod} - I_o}{I_w - I_o} \quad (9)$$

where I_{prod} - is enthalpy of the product;

I_w - is water enthalpy,

I_o - enthalpy of products moisture upon equilibrium with environment having enthalpy I_{da} .

RESULTS AND DISCUSSION: Thus, water activity is directly proportional to difference of moisture enthalpy on the products surface and residual enthalpy and inversely proportional to enthalpy of distilled water and to difference of the same residual enthalpy.

Residual enthalpy means enthalpy of the products moisture, which is numerically equal to the enthalpy of absolutely dry air (I_{da}) at a given temperature.

As it can be seen from equation (9), all parameters, included in it, are dependent on temperature, consequently, during determination of water activity, it is necessary to maintain definite temperature in the measuring system, or to use recalculation formulae, otherwise, at the same degree of product wetness, different values of water activity may be received. This fact was affirmed by many investigators (Duckworth, 1974; Davies et al., 1980; Lewicki et al., 1978).

The proposed method for measuring a_w is solved technically, that is, in form of an electronic digital computer.

CONCLUSION: Multiple research into meat raw material a_w showed high reproductivity level of experimental data with standard deviations $\pm 0,5\%$ from arithmetic mean.

Accuracy of measurement was tested on a vacuum-adsorption manometer unit and standard error did not exceed $1,5 - 20\%$. The offered method differs from the existing ones by its high rapidity. Thus, time needed to measure a_w in meat in general, without preliminary operations, did not exceed $1,5 - 5$ minutes.

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