

## EFFECT OF TEMPERATURE AND WATER ACTIVITY ON HEAT TRANSFER IN PARSLEY LEAVES IN THE RANGE OF TEMPERATURES 10–30 °C

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### Abstract

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The equilibrium moisture contents of parsley leaves were measured by the gravimetric dynamic method with continuous recording of changes in sample weight. Consequently water activity values were determined. Henderson equation was found to be a good model both for moisture adsorption and desorption. Isothermic heat of sorption was defined and determined in the temperature range of 10–30 °C. Clausius-Clapeyron equation was used to calculate the isothermic heat of sorption since no dependence on temperature in the analysed range was observed. The isothermic heats of sorption ( $q_n^{st}$ ) were indicated graphic in the form  $q_n^{st}$  versus moisture content. Values for isothermic heat of sorption ranged from 54.41 to 46.85 kJ/mol.

moisture content, Clausius-Clapeyron equation, Henderson model, isothermic heat of sorption

Design of effective drying, storage and package systems for agricultural products requires knowledge of hygrothermal properties of wet biological materials, because their moisture content is usually changed during processing. In general, drying is a coupled heat and mass transfer process, in which product temperature rises from initial level, usually room temperature, and approaches the drying air temperature. In drying, packaging or storing modelling the coupling of heat and mass transfer is done mathematically via the equilibrium relationship – equilibrium moisture content (EMC), for example Moreira and Bakker-Arkema (1989), Štencl (2004):

$$\frac{dw}{dt} = -k(w - w_e) \quad (1)$$

where  $w_e$  is EMC of the sample,  $w$  is the moisture content of the sample at the time  $t$ , and  $k$  is the drying constant. Even for a qualitative discussion of these processes there is to need to know, how sensitive the EMC is to temperature change. In addition,

these equilibrium data are used to predict storage stability and package conditions. EMC and thermodynamic properties of wet materials are readily calculated from water sorption isotherm (WSI) equations (Iglesias and Chirife, 1982). WSI's help to establish the final moisture content and to compute net energy requirements of drying (Fasina, 2006; Vitáček, 2004), it means to determine the heat transfer between wet material and environment at specific temperature differences. Clapeyron equation plays the principal role in these thermal analyses, because it describes direct or indirect changes in specific entropy, internal energy and enthalpy of the thermodynamic system. Basically, using Clapeyron equation, it is possible to evaluate the change in enthalpy  $h$  during vaporization, sublimation or melting from state values pressure  $p$ , specific volume  $v$  and temperature  $T$  (p-v-T).

Clapeyron equation is usually expressed as follows (Moran and Shapiro, 1992)

$$\left( \frac{dp}{dT} \right)_{sat} = \frac{h_g - h_f}{T(v_g - v_f)} \quad (2)$$

In particular, the Clapeyron equation would take the form

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h'' - h'}{T(v'' - v')} \quad (3),$$

where superscript " or ' and subscript  $g$  or  $f$  denote respective phases, and  $\left(\frac{dp}{dT}\right)_{sat}$  is the slope of the relevant saturation pressure – temperature curve.

An approximate form of equation (2) can be derived when the following two idealizations are justified:  $v_f$  is negligible in comparisons to  $v_g$  and the pressure is low enough that  $v_g$  can be evaluated from the ideal gas equation of state as

$$v_g = \frac{RT}{p} \quad (4).$$

With these, equation (2) becomes

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{\frac{RT^2}{p}} \quad (5),$$

which is usually rearranged to the form

$$\left(\frac{d \ln p}{dT}\right)_{sat} = \frac{h_g - h_f}{RT^2} \quad (6).$$

Expression (6) is called the Clausius-Clapeyron equation;  $T$  is temperature,  $R$  – gas constant,  $p$  – pressure,  $h$  – enthalpy, and subscripts  $g$  – property of saturated vapour, and  $f$  – property of saturated liquid.

The purpose of the investigation was to obtain data on adsorption and desorption isotherms of parsley leaves in the temperature range of 10–30 °C and water activity ( $a_w$ ) from 0.3 to 0.99 (Štencl, 2005) and further energetic analyses of the process. The aim of the paper is to interpret received sorption data in energy aspects of sorption processes measured and to determine the isosteric heat of sorption for particular moisture content of parsley leaves samples at the specific near ambient air conditions.

## MATERIAL AND METHODS

One of the ways to analyse the energy aspects of the sorption processes is to consider it from a thermodynamic standpoint, calculating the heat of sorption  $Q^{st}$ , (Rao and Rizvi, 1985). Since several different heats of sorption have been defined, it seems useful to clarify, which one is being considered. The reason for confusion stems from the fact, that the gas phase

is characterized by three out of four variables  $p$ ,  $V_g$ ,  $T$  and number of moles  $n_g$  (Enenkl *et al.*, 1981). Depending of which variables are kept constant during the experiment or a theoretical derivation it results different heat of sorption. For example, there are two isothermal heats of sorption:

The first corresponds to adsorption at constant  $V_g$  and  $V_f$ . The experimental set up could be represented by a constant volume calorimeter with a specified amount of adsorbent, the whole in a constant temperature bath. The case is to describe by the first law of thermodynamics as it applies to closed system:

$$Q^{st} = \Delta U - A \quad (7).$$

No work  $A$  is exchanged with the surroundings. The heat of sorption  $Q^{st}$  is then equal internal energy  $\Delta U$ .

The second isothermal heat of sorption corresponds to adsorption at constant  $T$ ,  $p$  and  $n_f$ . It involves a calorimeter, in which pressure is kept constant through a movable piston. For such system is valid (Moran and Shapiro, 1992):

$$Q^{st} = \Delta U + p\Delta V = \Delta H_p \quad (8).$$

In this case the heat evolved is called isosteric heat of sorption:

$$Q^{st} = \Delta H_p = n_f(H_g - H_f) \quad (9).$$

$H_g$  and  $H_f$  are enthalpy of gas and adsorbed phase, respectively.

The interest of this paper is focused in the isosteric heat of sorption  $q_n^{st}$ , because it explains the energy relationships as a function of moisture content or water activity, and it could be important for energy consumption optimization in praxis. For a system in equilibrium made up of adsorbed and unadsorbed gas, on the bases of equal chemical potential (Moran and Shapiro, 1992; Štencl and Komprda, 2004) in both phases the Clausius-Clapeyron equation, see (6), is valid in general. It is possible to express it as follows:

$$\frac{d \ln \frac{p}{p_0}}{dT} = \frac{d \ln a_w}{dT} = \frac{q_n^{st}}{RT^2} \quad (10),$$

$$q_n^{st} = h_g - h_f \quad (11).$$

It is obvious, that water activity  $a_w$  is a function of partial pressures, e.g. Štencl and Komprda (2004):

$$a_w = \frac{p}{p_0} \quad (12),$$

where  $p$  is vapour pressure of water in foodstuffs and  $p_0$  is saturated water vapour pressure. The application of this method requires the measurement of sorption isotherms at least at three temperatures (Sanches *et al.*, 1997). On the other hand, the integration of equation (10) allows theoretically calculation of  $q_n^{st}$  by taking measurements at only two temperatures:

$$\frac{\ln a_{w2} - \ln a_{w1}}{T_2 - T_1} = \frac{q_n^{st}}{RT_1 T_2} \quad (13).$$

It is possible to express using equation (13):

$$q_n^{st} = \frac{RT_1 T_2 \ln \frac{a_{w2}}{a_{w1}}}{T_2 - T_1} \quad (14)$$

or

$$q_n^{st} = R \left[ \frac{T_1 T_2}{T_2 - T_1} \right] \left[ \ln \frac{a_{w2}}{a_{w1}} \right] \quad (15).$$

Integrating equation (10), assuming that the net isosteric heat of sorption is temperature independent, gives the following equation:

$$\ln a_w = - \left( \frac{q_n^{st}}{R} \right) \frac{1}{T} + K \quad (16).$$

Heat of sorption can be determined from calorimetric measurements or from moisture sorption data. The second method is more convenient, given that sorption isotherms are determined routinely. The usual

procedure to evaluate isosteric heat of sorption consists in plotting the sorption isostere as  $a_w$  vs.  $\frac{1}{T}$  and determining the slope, which is equal to  $\frac{q_n^{st}}{R}$ .

The gravimetric dynamic method with continuous registration of sample weight changes was used for determining the sorption characteristics of parsley leaves (Štencl, 2004; Štencl, 2005). The procedure of each test was as follows: after reaching the equilibrium moisture content of the sample at a certain relative air humidity (at a constant air temperature, velocity and pressure), the relative humidity was automatically increased (adsorption) or decreased (desorption) and the new equilibrium was obtained under these conditions. Each test was repeated three times. The experimental EMC data were processed using specially developed software and analysed using the non-linear regression procedure of UNISTAT (1995). Equations (Halsey, Henderson, Chung-Pfost, Oswin, and GAB), which model the dependence of EMC of leaves of parsley on  $a_w$  in the temperature range of 10–40 °C were investigated and reviewed. The statistical values showed (Tab. I), that Henderson's model (Štencl, 2005)

$$w_e = \left( \frac{\ln(1 - a_w)}{a(t + b)} \right)^c \quad (17)$$

for leaves of parsley, both for water adsorption and desorption, has the smallest standard error of estimate (s.e.e.) and the smallest mean relative percentage deviation (P). The standardized residuals of these models are uncorrelated (Durbin-Watson test, d) and normally distributed (Chi-square test). Coefficient of determination ( $R^2$ ) has been also done.

I: Statistical values for Henderson's model

Model	s.e.e.	P	d	Chi-square-test	$R^2$
Henderson adsorp.	0.3482	3.3633	1.8999	0.171	0.9897
Henderson desorp.	0.3540	3.3460	1.8810	0.176	0.9888

## RESULTS AND DISCUSSION

In accordance with hypothesis, the EMC of parsley leaves increased with increase in water activity. An increase in temperature caused an increase in water activity for the same moisture content and, if water

activity was kept constant, an increase in temperature caused a decrease in the amount of absorbed water (Štencl, 2005). Tab. II and III present dependence of EMC ( $w_e$ ) of parsley leaves on  $a_w$  at temperatures 10, 20 and 30 °C in accordance with the Henderson's model, equation (17).

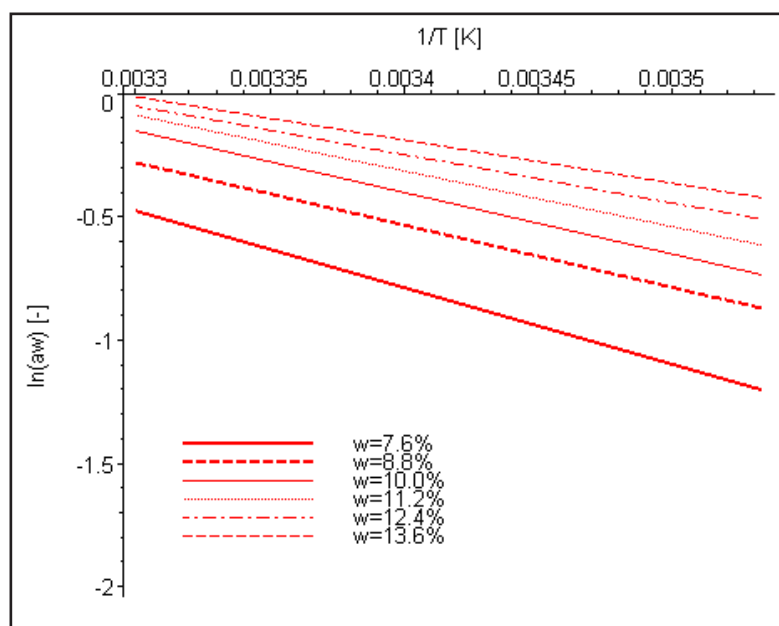
II: Dependence of  $w_e$  of parsley leaves on  $a_w$  at temperatures 10, 20 and 30 °C for desorption

$a_w$ [-]	$w_e$ [% w.b.]		
	$t_1 = 10$ [°C]	$t_2 = 20$ [°C]	$t_3 = 30$ [°C]
0,3	7.65	5.12	4.81
0,4	8.52	6.04	5.69
0,5	10.41	6.98	6.53
0,6	12.38	7.81	7.48
0,7	14.51	8.77	8.31
0,8	16.94	10.04	9.28
0,9	19.86	12.29	10.76
0,99	23.45	16.98	13.67

III: Dependence of  $w_e$  of parsley leaves on  $a_w$  at temperatures 10, 20 and 30 °C for adsorption

$a_w$ [-]	$w_e$ [% w.b.]		
	$t_1 = 10$ [°C]	$t_2 = 20$ [°C]	$t_3 = 30$ [°C]
0,3	8.14	5.97	4.98
0,4	9.22	6.89	5.89
0,5	10.91	7.81	6.77
0,6	13.32	8.61	7.58
0,7	15.11	9.62	8.45
0,8	17.54	10.74	9.38
0,9	20.37	12.89	10.96
0,99	23.45	16.98	13.67

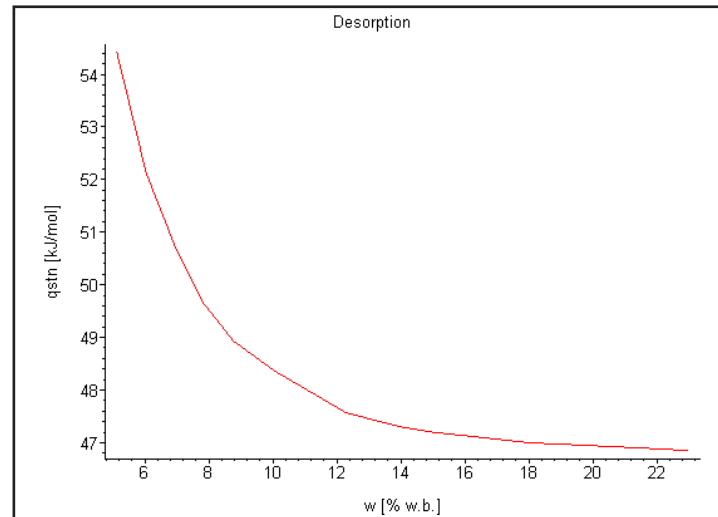
Fig. 1 shows the plot of  $\ln a_w$  versus  $\frac{1}{T}$  for parsley leaves at different moisture content [% w.b.]



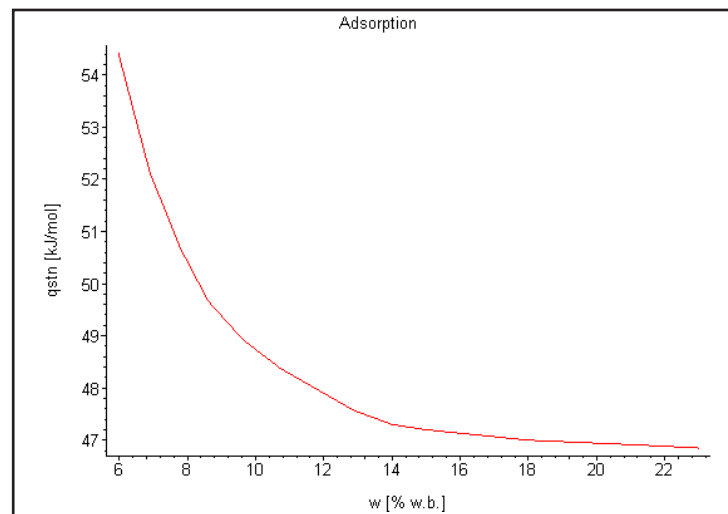
1: Natural logarithmic of  $a_w$  versus  $\frac{1}{T}$  at different moisture  $w$

Since no dependence on temperature was observed in this relation, except for the lowest moisture content, which are not important in praxis, the Clausius-Clapeyron equation, version (15), was used to calcu-

late the isosteric heat of sorption. These values are indicated for 20 °C in Fig. 2 and 3 in the form of  $q_n^{st}$  [kJ/mol] plot versus  $w$  [% w.b.] both for water desorption and adsorption, respectively.



2: Isosteric heat of desorption vs. moisture content for parsley leaves at the temperature 20 °C



3: Isosteric heat of adsorption vs. moisture content for parsley leaves at the temperature 20 °C

The isosteric heat of sorption decreased rapidly with an increase of moisture content in the area of bounded water in samples tested both for desorption and adsorption. For moisture content > 16% (w.b.), the isosteric heat tends to the value of latent heat of evaporation, considered 44.17 kJ/mol. Iglesias and Chirife (1976) explained that the level of moisture content at which the heat of sorption approaches

the heat of vaporization of water is indicative of water existing in free form in the product. Values of isosteric heat of sorption are from 54.41 kJ/mol at 5.6% (w.b.) for water desorption and 54.41 kJ/mol at 6.0% (w.b.) for water adsorption. The bottom value 46.85 kJ/mol at 22.4% (w.b.), both for desorption and adsorption, approaches to the heat of vaporization of pure water.

## SOUHRN

Vliv teploty a vodní aktivity na sdílení tepla u lístků  
petrželové natě v rozsahu teplot 10–30 °C

Návrh a tvorba efektivních sušicích, skladovacích a balicích systémů pro zemědělské produkty vyžaduje znalosti hygrotermických vlastností biologických materiálů, protože obsah vody zásadně mění jejich kvalitu a také určuje používané technologické postupy. Rovnovážná vlhkost (EMC) je jedním ze základních sledovaných parametrů. Hodnoty EMC lístků petrželové natě byly měřeny gravimetrickou dynamickou metodou s kontinuálním zaznamenáváním změn hmotnosti vzorku. Následně byly stanovovány hodnoty vodních aktivit. Pro popis EMC při desorpci i adsorpci vlhkosti v rozsahu vodních aktivit 0,3 až 0,99 byla stanovena rovnice podle Hendersona jako vhodný matematický model. V článku je definováno isosterické teplo sorpcí ( $q_n^{st}$ ) a jsou stanoveny jeho hodnoty v rozsahu teplot 10–30 °C. Pro výpočet byla použita Clausius-Clapeyronova rovnice. Hodnoty  $q_n^{st}$  byly znázorněny graficky v diagramu isosterické sorpční teplo vs obsah vlhkosti. Vypočtené hodnoty pro  $q_n^{st}$  byly od 54,41 kJ/mol do 46,85 kJ/mol. Nejnižší stanovená hodnota isosterického tepla sorpcí pro lístky petrželové natě v rozsahu teplot 10–30 °C byla 46,85 kJ/mol. Její hodnota se blíží latentnímu teplu vypařování čisté vody, 44,17 kJ/mol.

obsah vlhkosti, Clausius-Clapeyronova rovnice, Hendersonův model, isosterické sorpční teplo

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