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Theory of Non-Calorimetric Methods for the Determination of the Liquid Water Content of Wet Snow

By Henri Bader, New Brunswick, N. J.

Past efforts to determine the liquid water content of wet snow seem to have been based exclusively on calorimetry, consisting in the direct or indirect determination of the quantity of heat necessary to melt the ice in a weighed sample of wet snow. The wetter the snow, the smaller the ratio of ice to water, and the less heat is required for melting. Careful calorimetry in the laboratory gives the liquid water content to within 1 or 2 % absolute, which is sufficient for most purposes.

More accurate determinations may become desirable in the future, and we also lack a good method for use in the field.

Here the theory of three simple field methods and one accurate laboratory method is discussed. The author has had no opportunity for experimental work.

Thanks are extended to Drs. J. F. LANE and F. G. DUNNINGTON, Rutgers University, for suggestions and criticism.

First Field Method

A sample of wet snow is put into a thermos flask precooled to 0° (by wet ice) and weighed in the flask. A determined quantity of equally precooled solution of known concentration is also added to the flask and the semi-liquid mixture gently stirred with a thermometer. The depressed temperature $-t^{\circ}$ is read after a suitable lapse of time.

We will use the following notations:

- b = grams wet snow in the flask, temperature 0°
- a_0 = grams ice in wet snow
- x = grams liquid water in wet snow. Quantity to be determined
- c_0 = grams of solution introduced into the flask

m_0 = molal concentration of solution introduced into the flask
(m_0 gram-mols of solute in 1000 grams solution)

c_1 = grams of solution in phase equilibrium with ice

m_1 = molal concentration of solution in phase equilibrium with ice

a_1 = grams of ice in phase equilibrium with the solution

a_m = grams of ice melted in process of establishment of phase equilibrium

$-t^0$ = temperature of ice-solution mixture at phase equilibrium

t = positive value of temperature interval between 0^0 and $-t^0$

F = grams of flask glass cooled during process

β = molal temperature depression constant of the dissolved substance

γ = specific heat of ice (0,492 calories)

α = heat of fusion of ice (79,7 calories)

δ = specific heat of flask glass (0,16 calories).

The following relations can immediately be stated:

$$b = a_0 + x \quad (1)$$

$$t = \beta m_1 \text{ (freezing point depression law for dilute solutions)} \quad (2)$$

$$a_1 = b + c_0 - c_1 \quad (3)$$

$$c_1 = \frac{m_0}{m_1} \cdot c_0 \quad (4)$$

$$a_m = a_0 - a_1 \quad (5)$$

Eliminating m_1 from (2) and (4), and b from (1) and (3) we obtain:

$$c_1 = \frac{\beta m_0 c_0}{t} \quad (6)$$

$$\text{and} \quad a_1 = a_0 + c_0 - c_1 + x \quad (7)$$

Elimination of c_1 from (6) and (7) gives us:

$$a_1 = a_0 + c_0 - \frac{\beta m_0 c_0}{t} + x \quad (8)$$

Inserting in (5) we get

$$a_m = \frac{\beta m_0 c_0}{t} - c_0 - x \quad (9)$$

A second expression for a_m is obtained by considering the thermal process. Assuming that the dilute solution has unit specific heat, the quantity c_1 , on being cooled from 0^0 to $-t^0$, gives off tc_1 calories, the quantity of ice a_1 gives off γta_1 calories, and the inner

wall of the flask gives off δtF calories. Using equations (3) and (6) we obtain:

$$tc_1 = \beta m_0 c_0 \quad (10)$$

$$\text{and } \gamma ta_1 = \gamma tb + \gamma tc_0 - \gamma \beta m_0 c_0 \quad (11)$$

The total heat given off by solution (10) plus ice (11) plus flask is absorbed in melting a_m grams ice:

$$a_m = \frac{tc_1 + \gamma ta_1 + \delta tF}{\alpha} = \frac{\beta m_0 c_0 + \gamma tb + \gamma tc_0 - \gamma \beta m_0 c_0}{\alpha} + \frac{\delta tF}{\alpha} \quad (12)$$

Equating the two expressions for a_m (9) and (12), and solving for x , we obtain the desired equation:

$$\begin{aligned} x &= \beta m_0 c_0 \left(\frac{1}{t} - \frac{1 - \gamma}{\alpha} \right) - \frac{\gamma}{\alpha} t(b + c_0) - c_0 - \frac{\delta tF}{\alpha} \\ &= \beta m_0 c_0 \left(\frac{1}{t} - 0,0064 \right) - 0,0062 t(b + c_0) - c_0 - 0,002 tF \end{aligned} \quad (13)$$

The value of t has to be kept small in order to maintain near-isothermal conditions, and then the term 0,0064 can be neglected as it becomes very small compared to $1/t$. The correction for the cooling of the flask ($-0,002 tF$) is then also insignificant and can be omitted. We obtain a simplified expression for x .

$$x \cong \frac{\beta m_0 c_0}{t} - 0,0062 t(b + c_0) - c_0 \quad (14)$$

Second Field Method

The alternative to measuring the temperature depression is to determine the concentration of the solution at phase equilibrium. Substituting βm_1 for t in (13) gives us:

$$x = m_0 c_0 \left(\frac{1}{m_1} - \frac{\beta - \beta \gamma}{\alpha} \right) - \frac{\beta \gamma}{\alpha} m_1 (b + c_0) - c_0 - \frac{\beta \delta}{\alpha} m_1 F \quad (15)$$

When $\beta = 1,86$ (molal temperature depression constant for dilute non-electrolytes)

$$x = m_0 c_0 \left(\frac{1}{m_1} - 0,012 \right) - 0,011 m_1 (b + c_0) - c_0 - 0,0037 m_1 F \quad (16)$$

As 0,012 will be very small compared to $1/m_1$ for low concentrations, it can be omitted. The term $0,0037 m_1 F$ is also insignificant, so

$$x \cong \frac{m_0 c_0}{m_1} - 0,011 m_1 (b + c_0) - c_0 \quad (17)$$

A quantity of solution at phase equilibrium can be poured from the flask through a sieve inserted in the neck and titrated on the spot or later in the laboratory. There should be no difficulty in the choice of a salt, acid, base or oxidizable non-electrolyte.

For an interpretation of its terms, equation (13) must be written in less useful form.

$$\frac{\beta m_0 c_0}{t} = x + c_0 + \frac{\beta m_0 c_0}{\alpha} + \frac{\delta t F}{\alpha} + \frac{\gamma}{\alpha} t \left(b + c_0 - \frac{\beta m_0 c_0}{t} \right)$$

or

$$c_1 = x + c_0 + \frac{t c_1}{\alpha} + \frac{\delta t F}{\alpha} + \frac{\gamma t a_1}{\alpha}$$

The six terms state that the quantity of solution in phase equilibrium with ice is equal to the quantity of liquid water originally present in the wet snow, plus the quantity of solution added to the wet snow, plus the quantity of ice melted to cool the solution, plus the quantity of ice melted to cool the container, plus the quantity of ice melted to cool the remaining ice. The limit of validity of the equation is reached when the quantity of remaining ice becomes zero.

$$a_1 = 0 = b + c_0 - \frac{\beta m_0 c_0}{t}$$

and solving for t :
$$t = \frac{\beta m_0 c_0}{b + c_0}$$

If the temperature interval t becomes smaller than the above term, there is no ice phase and no phase equilibrium. In this case we can simply equate the expressions for the heat given off by the solution and the flask, and the heat absorbed by the melting ice:

$t(b + c_0 + \delta F) = \alpha a_0 = \alpha(b - x)$ <p style="text-align: center;">or</p> $x = b - \frac{t}{\alpha} (b + c_0 + \delta F) = b - 0,0125 t(b + c_0 + 0,16 F)$	(18)
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We have here a Third Field Method for the determination of x , in which all the ice must be melted. It is closer to calorimetry than those previously described, and may prove to be less accurate for wet snow which can hardly contain more than 25 % liquid water. It could, however, be useful for determining the ice content of mixtures with a high ratio of water to ice, should that be desirable. The main virtue of this last method lies in the fact that the concentration of the solution need not be known, but must only be high enough to cause melting of all the ice, yet not high enough to produce a noticeable thermal effect on being diluted. The minimum permissible concentration m_0 , derived from $c_1 = b + c_0$ and (4), is:

$$m_0 > \frac{t(b + c_0)}{\beta c_0}$$

Examples for first and second field methods

$b = 100$, (x then is %), $c_0 = 50$, $m_0 = 0,500$, $\beta = 1,86$

$$x \cong \frac{46,5}{t} - 0,93t - 50$$

x	t	Δt	m_1	Δm_1	c_1
0	0,915		0,492		50,9
1	0,898	0,017	0,483	0,009	51,8
2	0,881	0,017	0,474	0,009	52,8
3	0,865	0,016	0,465	0,009	53,8
4	0,849	0,016	0,457	0,008	54,8
5	0,835	0,016	0,449	0,008	55,8
6	0,820	0,015	0,441	0,008	56,8
7	0,805	0,015	0,433	0,008	57,8
8	0,791	0,014	0,425	0,008	58,8
9	0,778	0,013	0,418	0,007	59,8
10	0,765	0,013	0,411	0,007	60,8
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0	0,915		0,492		50,9
10	0,765	0,150	0,411	0,081	60,8
20	0,660	0,105	0,355	0,056	70,6
30	0,578	0,082	0,311	0,044	80,5
40	0,514	0,064	0,276	0,035	90,5
50	0,463	0,051	0,249	0,027	100,4
60	0,421	0,042	0,226	0,023	110,4
70	0,386	0,035	0,208	0,018	120,4
80	0,357	0,029	0,192	0,016	130,3
90	0,332	0,025	0,178	0,014	140,3
99,7	0,310	0,022	0,167	0,011	150,0

Considering that the water content of wet snow rarely exceeds 20 %, and if we choose to depress the temperature to not more than -1° , the figures show that temperatures will have to be measured to hundredths of degrees in order to obtain results accurate to approximately 1 %. This is probably feasible, but if it should not be so, then titration will certainly be applicable, determination of concentration to within a few units of the third decimal being easy.

Example for Third Field Method

$$b = 100, \quad c_0 = 900, \quad F = 200, \quad \text{then } x = 100 - 12,9t$$

$$\begin{aligned} \text{For } x &= 100, & t &= 0 \\ \text{and } x &= 80, & t &= 1,55 \end{aligned}$$

The increment of t for every 1 % of water content is 0,08, which is quite satisfactory. If we limit t to 1,6, ($x > 80$), the concentration m_0 will have to exceed 0,94 as all the ice must be melted.

The disadvantage of this method is that in order to keep t small, c_0 must be made large compared to b , and a_0 must be small compared to x .

Laboratory Method

For greater accuracy in laboratory work, t can be kept very small by the use of a correspondingly dilute solution. Titration being not sufficiently accurate for small concentration differences of such dilute solutions, it is suggested that a highly active sugar such as maltose be used and that the concentration be determined by saccharimetry.

In principle, the water content of wet snow could be determined much more accurately than necessary by this method. Considering the errors introduced by the handling of wet snow, weighing, etc., determination of the water content to better than the nearest $\frac{1}{2}$ % would probably be useless. It is, however, well to note that greater accuracy can be obtained, should the need for it arise.

Example

$$\begin{aligned} b &= 100 \\ c_0 &= 50 \\ F &= 100 \\ m_0 &= 0,02 \text{ (6,844 g anhydrous maltose per 1000g solution)} \\ \beta &= 1,86. \end{aligned}$$

Inserting the above values in equation (16) we get:

$$x = \frac{1}{m_1} - 0,012 - 1,65 m_1 - 50 - 0,37 m_1$$

$$m_1 < m_0, \text{ so inserting } m_0 \text{ for } m_1$$

$$0 \cong 50 - 0,012 - 0,03 - 50 - 0,007$$

This shows that the corrective terms $0,012 m_0 c_0$, $0,011 m_1 (b + c_0)$ and $0,0037 m_1 F$ in (16) are very small and can be omitted. It means that the quantity of ice melted due to the small temperature depression (max. $0,037^\circ$) is negligibly small. We then simply have a dilution of c_0 by x , and (16) reduces to

$$x \cong c_0 \left(\frac{m_0}{m_1} - 1 \right) = \frac{1}{m_1} - 50$$

The angular rotation of a maltose solution for sodium light and 20° is:

$$a_D^{20} = 47,37 L d m_1$$

where L = length of observation tube in decimeters, d = density of the solution and m_1 = molal concentration of solution. For $L = 2$ decimeters and $d = 1$ (actually approximately 1,002)

$$a_D^{20} = 94,7 m_1$$

x	m_1	a_D^{20}	Δa_D^{20}	x	m_1	a_D^{20}	Δa_D^{20}
0	0,0200	1,894		0	0,0200	1,894	
1	0,0196	1,857	0,037	10	0,0167	1,579	0,315
2	0,0192	1,821	0,036	20	0,0143	1,353	0,226
3	0,0189	1,787	0,034	30	0,0125	1,184	0,169
4	0,0185	1,754	0,033	40	0,0111	1,052	0,132
5	0,0182	1,722	0,032	50	0,0100	0,947	0,105
6	0,0179	1,691	0,031	60	0,0091	0,861	0,086
7	0,0175	1,661	0,030	70	0,0083	0,789	0,072
8	0,0172	1,633	0,028	80	0,0077	0,728	0,061
9	0,0169	1,605	0,028	90	0,0071	0,676	0,052
10	0,0167	1,579	0,026	100	0,0067	0,631	0,045

The figures show that a saccharimeter reading to $0,01^\circ$ will be quite satisfactory.

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