



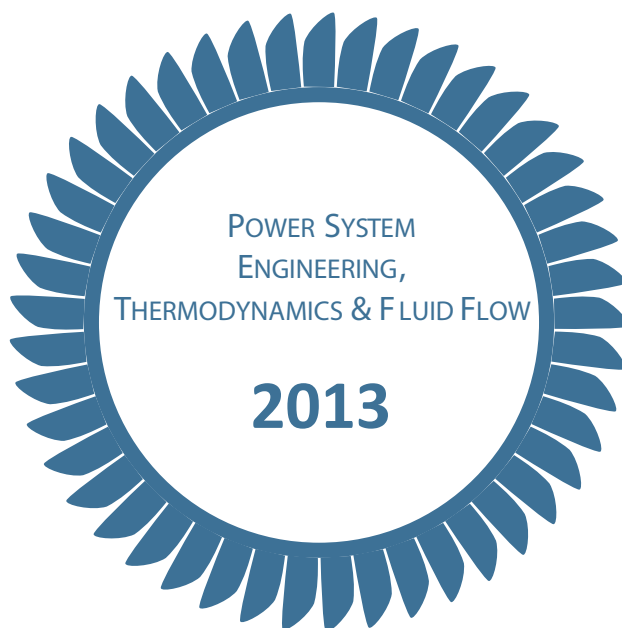
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## Vapor pressure of supercooled water

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*Vapor pressure of supercooled water plays an important role in a great volume of the atmosphere, where water is colder than 0 °C. Meteorology is interested in properties of water at temperatures above -100 °C, but there are only experimental data in the region above -40 °C. We will discuss the selected formulas for vapor pressure of supercooled water and their applicability to extrapolation into the low temperatures region.*

**Keywords:** supercooled water, vapor pressure

### Introduction

There is a number of equations for saturated vapor pressure (over water), examples of which can be found in [3] or [9]. The equations are often based on thermodynamic relations. Some equations fit either experimental data or only table data obtained from other, more complicated equations, or values based on the Maxwell's rule, calculated from a thermodynamic potential.

The equations may also differ in their usage. For technical purposes, the equation for saturated vapor pressure can be used for the calculation of a liquid-vapor interface. The equation for saturated vapor pressure is often used to determine the start value based on the thermodynamic potential and the Maxwell's rule [5-7]. Given the particular usage, the range of validity of these equations for saturated vapor pressure is from 273.16 K to 647.096 K [6].

The relations for vapor pressure over water are used in meteorology and atmospheric physics which commonly operate with temperatures below 273 K. For example, minimum temperatures in the Antarctic winter stratosphere can be below 175 K [9].

Liquid water thus is in a metastable state, and will sooner or later change into ice. A research of thermophysical properties of such 'supercooled' water becomes more difficult with every decrease of the water temperature below 0 °C. In fact, with bulk water, it is not possible to measure properties below 235 K, although some properties, e.g.  $c_p$  dramatically change with the dropping temperature.

### 2. Survey of vapor pressure equations

This short survey presents only some equations used as international institutional benchmarks for calculating saturated vapor pressure. A detailed survey can be found e.g. in [3] and [9]. Many equations are based on the Clausius-Clapeyron equation. Through its integration, we get

$$\ln p = c - \frac{a}{T}, \quad (1)$$

where  $c$ ,  $a$  are constants.

This formula was used by Clausius as early as in 1850 [3], and it has been used in many variations since. One of the generalizations results in the equation

$$\ln p = c - \frac{a}{T + b} . \quad (2)$$

Initially, the  $b$  value was used for the Kelvin-Celsius conversion, deciding on  $b=273.15$ . Nevertheless in order to reach the optimum equation for vapor pressure, it appeared to be suitable to look for the  $b$  value as another parameter using the least squares method.

In 1844, Magnus measured temperatures in the range from  $-7$  °C to  $105$  °C. To fit the data, he used the relation suggested by August in 1828. Magnus obtained the equation

$$p = p_0 \cdot 10^{\left(\frac{7.4475 \cdot t}{234.69 + t}\right)}, \quad (3)$$

where  $t$  is temperature in °C and  $p_0$  is saturated vapor pressure at  $0$  °C in torr ( $p_0 = 4.525$  mm of Hg). It is obvious that the equation (3) corresponds with the equation (2), and using the equation (3) we can easily calculate the coefficients  $a, b, c$ . The relation is:

$$\ln p = c - \frac{a}{T + b} = \frac{cT + bc - a}{T + b} = \frac{cT - e}{T + b}, \quad (4)$$

which is a formula used by Magnus, and where we decided to choose  $e = a - bc$ .

The advantage of (1) and (2) equations is an easy calculation of the inverse relation of the saturated vapor temperature and pressure:

$$T = \frac{a}{c - \ln p} - b . \quad (5)$$

In order to fit the parameters to the larger range of temperatures and to generalize the equation even further, in 1979 Bögel [1], generalized the formula (4) by adding a quadratic component:

$$\ln p = a + \frac{bT + cT^2}{T + d} . \quad (6)$$

This formula generalization (1) contains 4 fitting parameters  $a, b, c, d$ . The form is more complicated but the dependency  $T(p)$  can be calculated. Providing  $z = \ln p - a$ , by solving the quadratic equation we will reach

$$T = \frac{z - b \pm ((b - z)^2 + 4cdz)^{1/2}}{2c} .$$

According to the sign and the temperature range, the physical solution can be chosen out of the two possible ones.

The equation forms (4),(6) are frequently used. To present at least one, we can mention the equations of Buck [2] shown in Tab. 1.

Tab. 1 – Buck's equations [2]

Eq.	Temperature interval	Equations for saturation over water
1w	From -20 °C to 50 °C	$p(T) = 6.1121 \exp\left(\frac{17.502 T}{240.97 + T}\right)$
2w	From 0 °C to 50 °C	$p(T) = 6.1121 \exp\left(\frac{17.368 T}{238.88 + T}\right)$
3w	From -40 °C to 0 °C	$p(T) = 6.1121 \exp\left(\frac{17.966 T}{247.15 + T}\right)$
4w	From -40 °C to 50 °C	$p(T) = 6.1121 \exp\left(\frac{\left(18.729 - \frac{T}{227.3}\right) T}{257.87 + T}\right)$

The meteorological and air-conditioning communities recommend the formulation of Goff and Gratch (1946) [4] who integrated the Clausius-Clapeyron equation considering the departure of water vapor from an ideal gas. They used the state equation in the quasi-virial form:

$$pv = RT - Bp - Cp^2 = RTZ.$$

$B$  and  $C$  are the second and third virial coefficients and  $Z$  is compressibility factor. Goff and Gratch used the temperature dependence  $B$  and  $C$  and got the vapor pressure of pure liquid in the temperature range -50 °C to 102 °C:

$$\log_{10} p = -7.90298 \left( \frac{T_s}{T} - 1 \right) + 5.02808 \cdot \log_{10} \left( \frac{T_s}{T} \right) - 1.3816 \cdot 10^{-7} \left( 10^{11.344 \left( 1 - \frac{T}{T_s} \right)} - 1 \right) + 8.1328 \cdot 10^{-7} \left( 10^{3.49149 \left( \frac{T_s}{T} - 1 \right)} - 1 \right) + \log_{10} p_{ws} \quad (7)$$

$T_s$  is defined as 373.16K – the steam point temperature, and  $p_{ws}$  is the vapor pressure of pure liquid water at the steam-point temperature,  $p_{ws} = 1013.246 \text{ hPa}$ .

The Wagner-Pruss equation [6] is an example of equations fitting experimental data (and data taken from the IAPWS 95 equation of state using the Maxwell's rule), and is an approved IAPWS standard. Its declared validity is for the temperature range from 273.16 K to 647.096 K.

$$\ln \left( \frac{p}{2.2064 \cdot 10^7} \right) = \left( \frac{T_c}{T} \right) \left( -7.85951783 \tau + 1.84408259 \tau^{1.5} - 11.7866497 \tau^3 + 22.6807411 \tau^{3.5} - 15.9618719 \tau^4 + 1.80122502 \tau^{7.5} \right), \quad (8)$$

where  $\tau = 1 - \frac{T}{T_c}$ ,  $T_c = 647,096$ .

### 3. Extrapolation into the supercooled range

In order to calculate the saturated vapor pressure, the Clapeyron equation suggested in 1834 can be used:

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}, \quad (9)$$

where  $\Delta s$  is the change of molar entropy and  $\Delta v = v_g - v_l$  is the change of the molar volume during sublimation,  $v_g$  is the molar volume of gas and  $v_l$  is the molar volume of liquid. Providing the second law of thermodynamics (2) is used, this formula can be written:

$$\frac{dp}{dT} = \frac{L_v(T)}{T \cdot (v_v - v_l)}, \quad (10)$$

where  $L_v(T)$  is the enthalpy of vaporization and  $T$  is temperature in Kelvin. A very frequently used assumption says that the molar volume of water is much smaller than the molar volume of vapor,  $v_v \gg v_l$ . Another approximation can be used for the molar volume of vapor – the molar volume of vapor can be quite reliably taken from the ideal gas equation. We thus get the Clausius-Clapeyron equation [3,9] formulated in 1850:

$$\frac{d \ln p}{dT} = \frac{L_v(T)}{RT^2}, \quad (11)$$

where  $R$  is the molar gas constant,  $R=8.31447 \text{ J mol}^{-1} \text{ K}^{-1}$ . This equation will sometimes be marked with the abbreviation CC in the following text. In order to integrate the Clausius-Clapeyron equation (10), we need to know the temperature dependence  $L_v(T)$ . The equation for  $L_v(T)$  was published in [3,10]:

$$L_v(T) = L_{v,0} + \int_{T_0}^T \Delta c_p(T') dT' + \int_{T_0}^T \frac{dp}{dT'} \left[ (v_v - v_l) - T' \left( \frac{\partial(v_v - v_l)}{\partial T'} \right)_p \right] dT', \quad (12)$$

where  $L_{v,0}$  is the enthalpy of vaporization in the triple point,  $T_0$  is the temperature of the triple point,  $\Delta c_p(T)$  is the difference between molar heat capacities,  $v_v$  and  $v_l$  are molar volumes of vapor and liquid. Since the second integral in (12) is very small, even zero for a gas meeting the conditions of the ideal gas equation, we can approximately write

$$L_v(T) = 45054.7 + \int_{T_t}^T \Delta c_p(T') dT', \quad (13)$$

where  $\Delta c_p(T) = c_{p,v} - c_{p,l}$ .

In [9] the relation for  $c_{p,v}$  (in  $\text{J mol}^{-1} \text{K}^{-1}$ ) is stated as follows:

$$c_{p,v} = 33.2618 + 0.00187T - 0.06165T \exp(-(T/129.85)^2) + 0.06163T \exp(-(T/125.1)^2) \quad (14)$$

Combining (11) and (13) gradually results in:

$$L_v(T) = RT^2 \frac{d}{dT} \ln p \quad (15)$$

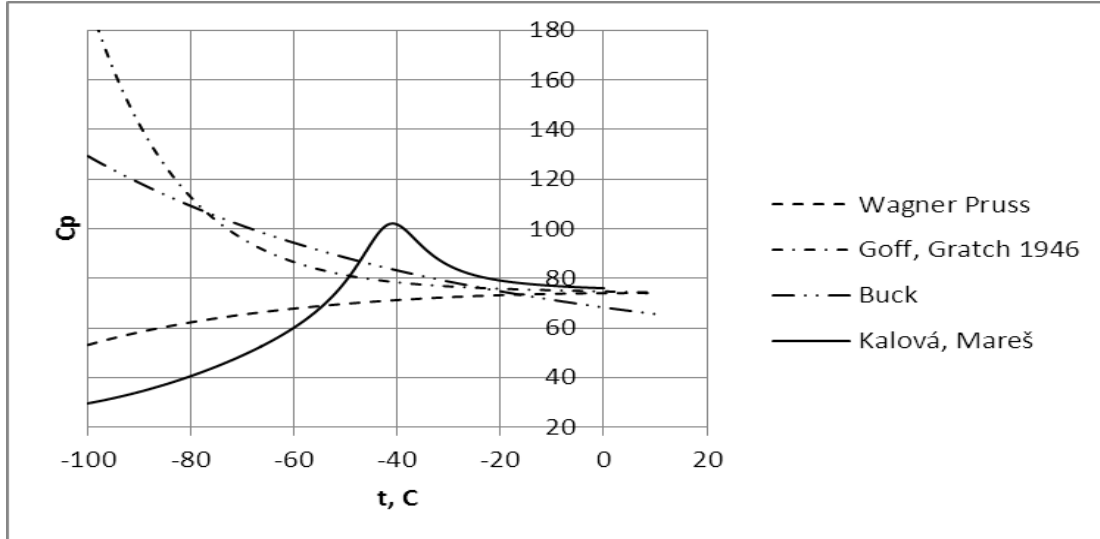
$$\frac{d L_v(T)}{dT} = 2RT \frac{d}{dT} \ln p + RT^2 \frac{d^2}{dT^2} \ln p$$

$$\Delta c_p(T) = 2RT \frac{d}{dT} \ln p + RT^2 \frac{d^2}{dT^2} \ln p \quad (16)$$

Using this and the formula (14),  $c_{p,l}$  can be calculated:

$$c_{p,l} = c_{p,v} - 2RT \frac{d}{dT} \ln p - RT^2 \frac{d^2}{dT^2} \ln p$$

The calculation was run for the Goff and Gratch equation (7), the Buck equation 3w (Tab. 1), and the Wagner-Pruss equation (8). The graph shows the results and the course of  $c_p$  based on the theory of the second critical point [8].



**Fig. 1:** Calculated heat capacities  $c_p$  based on the vapor pressure equations.

## Conclusion

The graph clearly shows that equations used in meteorology (usually down to -100 °C) describe the course of  $c_p$  very inadequately. Thus using them for very low temperatures is very improper. The Wagner-Pruss equation shows better results, although its validity is declared only for temperatures above 273.16 K, its extrapolation into minus temperatures brings sufficiently good results (see also [8]). There are new equations that present a better model of the  $c_p$  course in the supercooled range [8, 9], but they are not commonly used yet mainly because they are complicated and meteorologists stand their ground concerning the traditional equations.

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