

1. Capillary rise method

This is the oldest method used for surface tension determination.

A consequence of the surface tension appearance at the liquid/gas interface is moving up of the liquid into a thin tube, that is capillary, which is usually made of glass.

This phenomenon was applied for determination of the liquid surface tension.

For this purpose, a thin circular capillary is dipped into the tested liquid.

If the interaction forces of the liquid with the capillary walls (adhesion) are stronger than those between the liquid molecules (cohesion), the liquid wets the walls and rises in the capillary to a defined level and the meniscus is hemispherically concave.

In the opposite situation the forces cause decrease of the liquid level in the capillary below that in the chamber and the meniscus is semispherically convex. Both cases are illustrated in Fig. 11.1

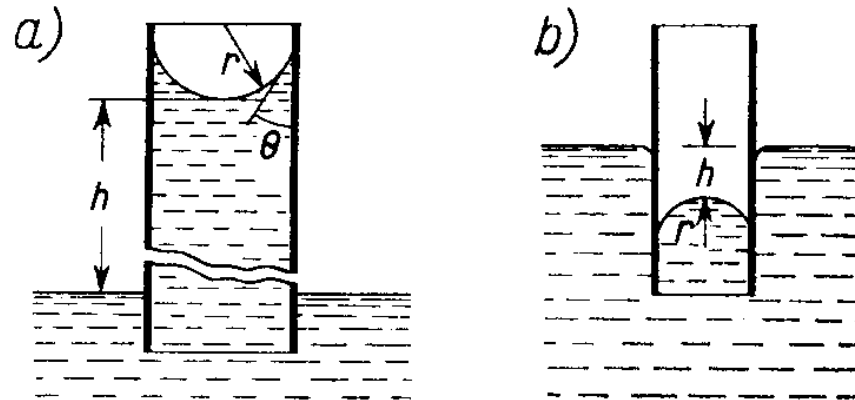


Fig. 12.1. Schematic representation of the capillary rise method.

If the cross-section area of the capillary is circular and its radius is sufficiently small, then the meniscus is semispherical. Along the perimeter of the meniscus there acts a force due to the surface tension presence.

$$f_1 = 2 \pi r \gamma \cos \theta \quad (1)$$

Where: r – the capillary radius, γ – the liquid surface tension, θ – the wetting contact angle.

The force f_1 in Eq.(1) is equilibrated by the mass of the liquid raised in the capillary to the height h , that is the gravity force f_2 . In the case of non-wetting liquid – it is lowered to a distance $-h$.

$$f_2 = \pi r^2 h d g \quad (2)$$

where: d – the liquid density (g/cm^3) (actually the difference between the liquid and the gas densities), g – the acceleration of gravity.

In equilibrium (the liquid does not moves in the capillary) $f_1 = f_2$, and hence

$$2\pi r \gamma \cos \theta = \pi r^2 h d g \quad (3)$$

or

$$\gamma = \frac{r h d g}{2 \cos \theta} \quad (4)$$

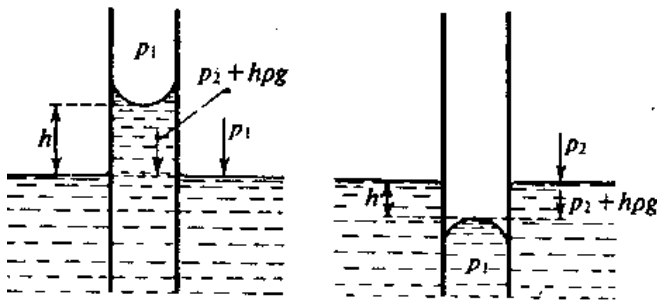
If the liquid completely wets the capillary walls the contact angle $\theta = 0^\circ$, and $\cos \theta = 1$. In such a case the surface tension can be determined from Eq. (5).

$$\gamma = \frac{r h d g}{2} \quad (5)$$

If the liquid does not wet the walls (e.g. mercury in a glass capillary), then it can be assumed that $\theta = 180^\circ$, and $\cos\theta = -1$. As the meniscus is lowered by the distance $-h$, Eq. (5) gives a correct result.

Eq. (5) can be also derived using the Young-Laplace equation, $\Delta P = \frac{2\gamma}{r}$, from which it results that there exists the pressure difference across a curved surface, which is called capillary pressure and this is illustrated in Fig. 12.2.

On the concave side of the meniscus the pressure is p_1 . The mechanical equilibrium is attained when the pressure values are the same in the capillary and over the flat surface. In the case of wetting liquid, the pressure in the capillary is lower than outside it, ($p_2 < p_1$). Therefore the meniscus is shifted to a height h when the pressure difference $\Delta p = p_2 - p_1$ is balanced by the hydrostatic pressure caused by the liquid raised in the capillary.



$$\Delta P = P_1 - P_2 = \Delta d g h \quad (6)$$

Fig. 12.2. The balanced pressures on both sides of the meniscus.

$$\frac{2\gamma}{r} = \Delta d g h \quad (7)$$

$$\gamma = \frac{r h d g}{2} \quad (8)$$

Similar considerations can be made for the case of convex meniscus (Fig. 12.2).

2. Drop volume method – stalagmometric method

The **stalagmometric method** is one of the most common methods used for the surface tension determination.

For this purpose the several drops of the liquid leaked out of the glass capillary of the **stalagmometer** are weighed.

If the weight of each drop of the liquid is known, we can also count the number of drops which leaked out to determine the surface tension.

The drops are formed slowly at the tip of the glass capillary placed in a vertical direction.

The pendant drop at the tip starts to detach when its weight (volume) reaches the magnitude balancing the surface tension of the liquid.

The weight (volume) is dependent on the characteristics of the liquid.

The stalagmometric method

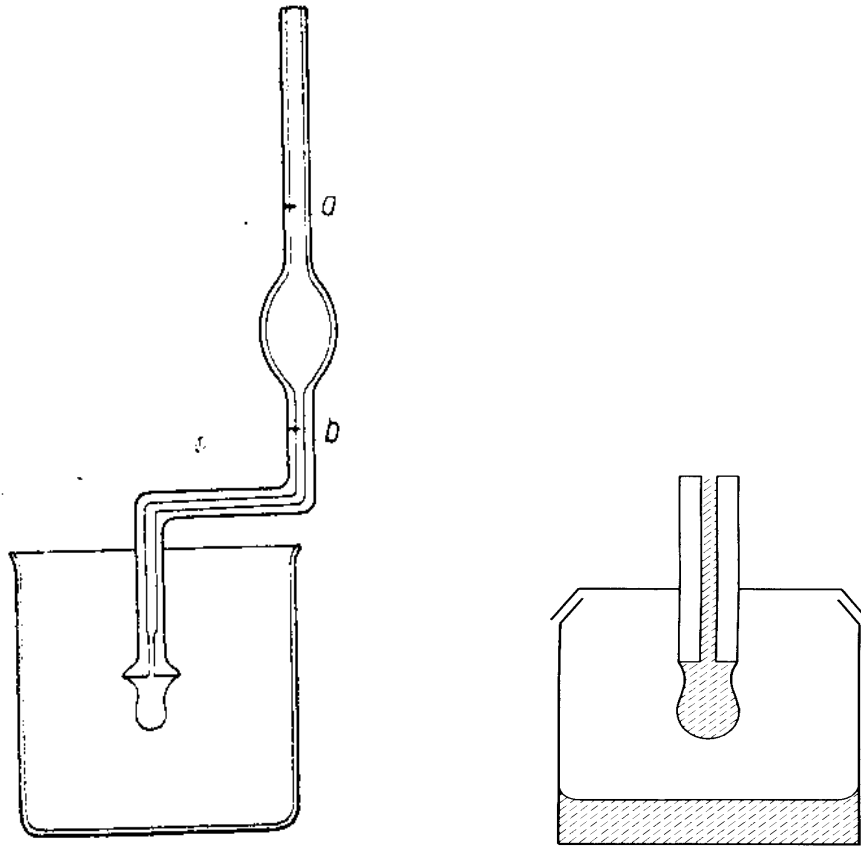


Fig. 12.2. Stalagmometer and the stalagmometer tip.

This method was first time described by Tate in 1864 who formed an equation, which is now called the Tate's law.

$$W = 2\pi r\gamma \quad (9)$$

Where: W is the drop weight, r is the capillary radius, and γ is the surface tension of the liquid.

The drop starts to fall down when its weight g is equal to the circumference ($2\pi r$) multiplied by the surface tension γ .

In the case of a liquid which wets the stalagmometer's tip the r value is that of the outer radius of the capillary and if the liquid does not wet – the r value is that of the inner radius of the capillary (Fig. 12.3).



Fig. 12.3. The drops wetting area corresponding to the outer and inner radii of the stalagmometer's tip.

In fact, the weight of the falling drop W' is lower than W expressed in Eq.(9). This is a result of drop formation, as shown in Fig.12.4.

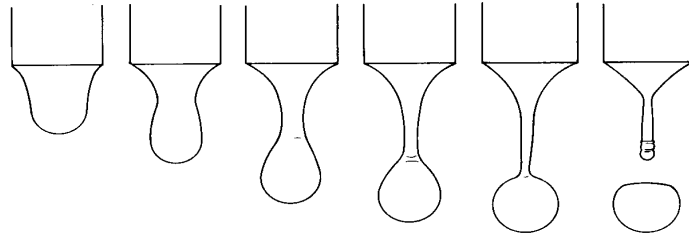


Fig. 12.4. Subsequent steps of the detaching drop

Up to 40% of the drop volume may be left on the stalagmometer tip. Therefore a correction f has to be introduced to the original Tate's equation.

$$W' = 2\pi r \gamma f \quad (10)$$

Where: f expresses the ratio of W'/W .

Harkins and Brown found that the factor f is a function of the stalagmometer tip radius, volume of the drop v , and a constant, which is characteristic of a given stalagmometer, $f = f(r, a, v)$

$$f = f\left(\frac{r}{a}\right) = f\left(\frac{r}{v^{1/3}}\right) \quad (11)$$

The f values for different tip radii were determined experimentally using water and benzene, whose surface tensions were determined by the capillary rise method. They are shown in Table 1.

Table 1. Values of the factor f

$r/v^{1/3}$	f	$r/v^{1/3}$	f	$r/v^{1/3}$	f
0.00	(1.000)	0.70	0.6093	1.15	0.6407
0.30	0.7256	0.75	0.6032	1.20	0.6535
0.35	0.7011	0.80	0.6000	1.25	0.6520
0.40	0.6828	0.85	0.5992	1.30	0.6400
0.45	0.6669	0.90	0.5998	1.35	0.6230
0.50	0.6515	0.95	0.6034	1.40	0.6030
0.55	0.6362	1.00	0.6098	1.45	0.5830
0.60	0.6250	1.05	0.6179	1.50	0.5670
0.65	0.6171	1.10	0.6280	1.55	0.5510

It appeared that the factor f changes the least if:

$$0.6 < r / v^{1/3} < 1.2$$

In practice, after having determined the mean weight m of the liquid drop calculated from several drops weighed, one can calculate its volume at the measurement temperature if the liquid density is known, and then the value of $r/v^{1/3}$. Next the f value can be found in the table. Finally, the surface tension can be calculated from Eq. (10) where $W' = m g$.

$$\gamma = \frac{m g}{2\pi r f} \quad (12)$$

The f value depends also on the kind of liquid tested.

Therefore the relative measurements (in comparison to another liquid of known surface tension) can not be applied here, that is, γ can not be calculated from the ratio of the weights of two drops of two liquids and known surface tension of one of them.

However, such measurement can be done with 0.1 % accuracy if the shape of the stalagmometer tip is like that shown in figure 12.5.

$$\text{Then: } \frac{\gamma_1}{\gamma_2} = \left(\frac{m_1}{m_2} \right)^{2/3} \left(\frac{d_1}{d_2} \right)^{1/3} \quad (13)$$

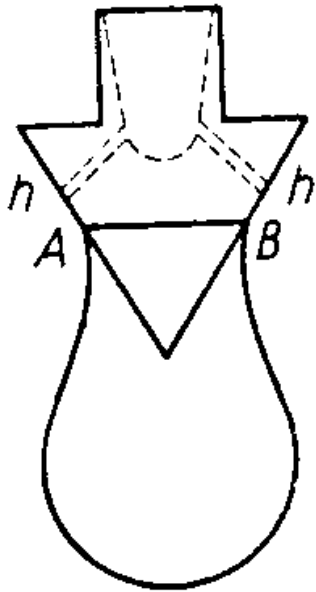


Fig. 12.5. Shape of the stalagmometer tip for relative surface tension measurements.

$$\text{Then: } \frac{\gamma_1}{\gamma_2} = \left(\frac{m_1}{m_2} \right)^{2/3} \left(\frac{d_1}{d_2} \right)^{1/3} \quad (13)$$

Having known the drop volume the surface tension can be calculated from Eq. (14).

$$\gamma = \frac{m g}{2 \pi r f} = \frac{m g}{k} = \frac{v d g}{k} \quad (14)$$

$$\gamma = \frac{V d g}{n k} \quad (15)$$