Boiling Point Elevation and Boiling Point Elevation Constant

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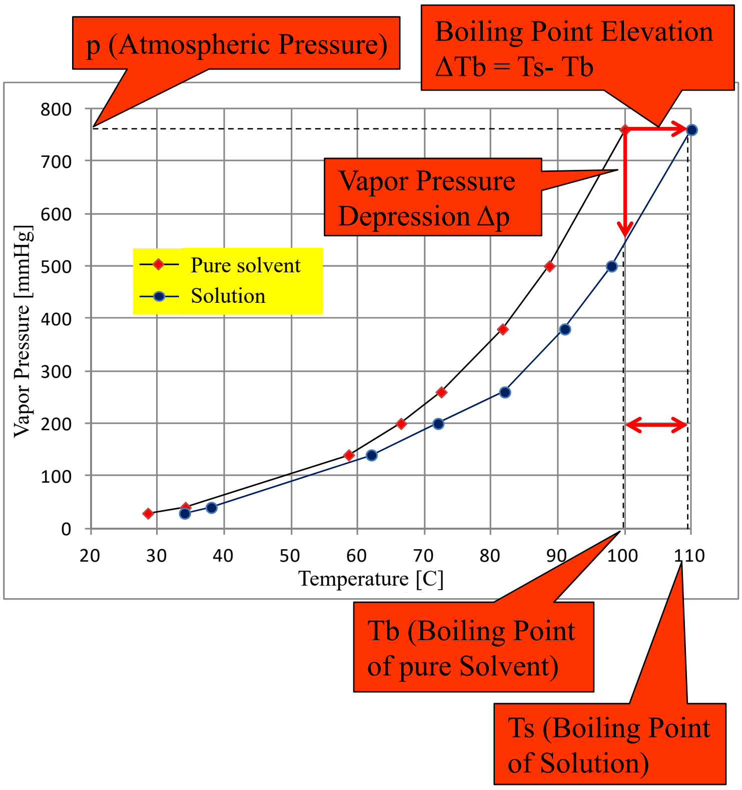
Introduction

- It is known that dissolving a nonvolatile solute such as sugar in a solvent increases the boiling point of the solution compared to that of the pure solvent. This is called boiling point elevation or vapor pressure depression.
- The degree of the boiling point elevation is determined by the boiling point elevation constant, which is a constant specific to the solvent. For this reason, it is possible to experimentally determine the molecular weight of the solute dissolved in the solvent by making use of the boiling point elevation constant.
- Here, we will derive the boiling point elevation constant and examine its range of applicability.

Vapor Pressure Depression and Boiling Point Elevation

- In a pure solvent at its boiling point, the number of molecules evaporating is constant. On the other hand, in a solution in which a solute is dissolved, the solute impedes the evaporation, so the number of solvent molecules evaporating is reduced and the vapor pressure decreases by Δp. This phenomenon is a vapor pressure depression.
- If the vapor pressure is lowered, the boiling point of the solution rises by ΔTb.
- This is called the boiling point elevation.



p (Atmospheric Pressure)

Boiling Point Elevation
ΔTb = Ts- Tb

Vapor Pressure
Depression Δp

Tb (Boiling Point
of pure Solvent)

Ts (Boiling Point
of Solution)

Derivation of Boiling Point Elevation Constant

Assume that an ideal dilute solution and the vapor of a pure solvent are in equilibrium in constant temperature and pressure conditions. In the equilibrium conditions, the chemical potential of the solvent component is equal in the vapor and the liquid phases, so the following equations hold.

$$\mu_1^{(l)} = \mu_1^{*\,(g)}$$

$$\mu_1^{(l)} = \mu_1^{*\,(l)} + RT\ln(x_1) = \mu_1^{*\,(g)}$$

$$\therefore \ln(x_1) = \frac{\mu_1^{*\,(g)} - \mu_1^{*\,(l)}}{RT} \qquad \dots (1)$$

μ : Chemical potential [J/mol]
x : Liquid phase molar fraction [mol/mol]
R : Gas constant [J/mol/K]
T : System temperature [K]

l, g : Subscript l: Liquid, g: Gas
1,2 : Subscript 1: Solvent, 2: Solute
$*$: Subscript Pure solvent

Derivation of Boiling Point Elevation Constant

The chemical potential of Eq. 1 is arranged using the molar Gibbs energy.

$$\ln(x_1) = \frac{\mu_1^{*\,(g)} - \mu_1^{*\,(l)}}{RT} = \frac{G_1^{(g)} - G_1^{(l)}}{RT} \quad \dots (2)$$

Under constant pressure conditions, Eq. 2 is differentiated by temperature.

$$\left[\frac{\partial}{\partial T}\ln(x_1)\right]_P = \frac{\partial}{\partial T}\left(\frac{G_1^{(g)} - G_1^{(l)}}{RT}\right)_P \quad \dots (3)$$

The Gibbs-Helmholtz equation (Eq. 4) is substituted into Eq. 3.

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = \frac{-\Delta H}{T^2} \quad \dots (4)$$

G : Molar Gibbs energy [J/mol]

ΔH : Molar enthalpy change [J/mol]

P : System pressure [Pa]

Derivation of Boiling Point Elevation Constant

$$\left[\frac{\partial}{\partial T}\ln(x_1)\right]_P = \frac{-\Delta H_1}{RT^2} = \frac{-(H_1^{(g)} - H_1^{(l)})}{RT^2} = \frac{-\lambda_1}{RT^2} \quad \dots (5)$$

Eq. 5 is integrated from the boiling point Tb [K] of the pure solvent to the boiling point Ts [K] of the ideal dilute solution.
At this time, for an ideal dilute solution, $x_2 \ll 1,\ T \cong Tb$, and the latent heat of vaporization (λ) can be considered to be constant.

$$\int_{Tb}^{Ts}\left[\frac{\partial}{\partial T}\ln(x_1)\right]_P dT = \int_{Tb}^{Ts}\frac{-\lambda_1}{RT^2}dT \cong \frac{-\lambda_1}{R}\int_{Tb}^{Ts}\frac{1}{T^2}dT$$

$$\therefore \ln(x_1) \cong \frac{\lambda_1}{R}\left(\frac{1}{Ts} - \frac{1}{Tb}\right) \quad \dots (6)$$

λ : Molar latent heat of vaporization [J/mol]

Tb : Boiling point of pure solvent [K]

Ts : Boiling point of solution [K]

Derivation of Boiling Point Elevation Constant

Eq. 6 can be modified as follows since $x_2 \ll 1,\ T \cong Tb$.

$$\ln(x_1) = \ln(1 - x_2) \cong -x_2$$

$$= \frac{\lambda}{R}\left(\frac{Tb - Ts}{Ts \cdot Tb}\right) = \frac{-\lambda}{R}\left(\frac{Ts - Tb}{Ts \cdot Tb}\right) \cong \frac{-\lambda}{R}\left(\frac{\Delta Tb}{Tb^2}\right)$$

$$\therefore \Delta Tb \cong \frac{R \cdot Tb^2}{\lambda} \cdot x_2$$

Since $x_2 = \dfrac{n_2}{n_1 + n_2} \cong \dfrac{n_2}{n_1} = \dfrac{w_2 \cdot M_{W1}}{w_1 \cdot M_{W2}}$

$$\Delta Tb \cong \frac{R \cdot Tb^2 \cdot M_{W1}}{\lambda} \cdot \frac{w_2}{w_1 \cdot M_{W2}}$$

$$\boxed{= Kb \cdot \frac{w_2}{w_1 \cdot M_{W2}}}$$

ΔTb : (Ts-Tb) Boiling point elevation [K]

n : Number of moles [mol]

w : Mass [g]

M_W : Molecular weight [g/mol]

K_b : Boiling point elevation constant [K·g/mol]

Boiling Point Elevation Constant (Kb) of Inorganic and Organic Compounds

$$\boxed{\Delta\theta_b = \frac{K_b\left(1000 w_2\right)}{M_2 w_1}}, \quad \Delta\theta_f = \frac{K_f\left(1000 w_2\right)}{M_2 w_1}$$

Here, $\Delta\theta_b$ and $\Delta\theta_f$ respectively indicate a boiling point elevation and a freezing point depression, and w_1 and w_2 each represent the masses of the solvent and solute that are used. M_2 is the molecular weight of the solute. K_b and K_f are constants determined only by the solvent and are called the molar boiling point elevation constant and the molar freezing point depression constant, respectively.

In the chemical handbook, the physical units of Kb are [K·kg/mol].

Table 9.26 Molar Boiling Point Elevation Constants K_b of Inorganic and Organic Compounds

Solvent	θ_b/°C	K_b/K
Water	100	0.515
Acetonitrile	81.60	1.30
Acetone	56.29	1.71
Aniline	184.40	3.22
Ammonia	-33.35	0.34
Ethanol	78.29	1.160
Ethyl-methyl-ketone	79.64	2.28

"Kagaku Binran Kiso-Hen 2 II-142" *in Japanese*: Chemical Handbook Basic Guide

Boiling Point Elevation Constant (Kb) Verification

$$Kb = \frac{R \cdot Tb^2 \cdot M_{W1}}{\lambda}$$

	Normal Boiling Point [K]	Latent Heat of Vaporization @ Normal Boiling Point DIPPR [J/mol]	Molecular Weight [g/mol]	Boiling Point Elevation Constant [K.kg/mol]
H_2O	373.15	40812	18.02	0.511
Acetone	329.44	29557	58.08	1.773
Ethanol	351.44	38935	46.07	1.215

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The values are almost reproduced although there are some deviations because the values of latent heat of vaporization used for the calculations are different.

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Calculation Example of Molecular Weight of Solute

When 67 mg of a nonvolatile solute is dissolved in 10 g of water, a boiling point elevation of 0.1 ºC is observed. In this case, what is the molecular weight of the nonvolatile substance?

Assume that the boiling point elevation constant Kb of water is 0.51 K·kg/mol.

$$\Delta Tb = Kb \cdot \frac{w_2}{w_1 \cdot M_{W2}}$$

$$M_{W2} = \frac{Kb \cdot w_2}{\Delta Tb \cdot w_1} = \frac{(0.51 \times 1000) \times 0.67}{0.1 \times 10} \cong 341.7$$

The molecular weight of the solute is 341.7 g/mol.
It can be inferred that sucrose was dissolved.

Molecular weight of sucrose = 342.3 g/mol.

Conclusion

- The boiling point elevation constant is a constant inherent to the solvent and can be easily obtained if its boiling point, molecular weight, and latent heat of vaporization at the normal boiling point are known.
- Once the boiling point elevation constant is known, it is possible to experimentally determine the molecular weight of the solute.
- However, the boiling point elevation constant is derived assuming an ideal dilute solution. For this reason caution is required, because it can be expected that deviations will increase in solutions with high solute concentrations, and in systems in which solutes react with solvents or in which solutes are associated with each other.