On the B Value of the Antoine Equation

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PreFEED Corporation

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Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

The Clapeyron equation indicates that the temperature dependence of the system pressure is the ratio of the change of entropy (ΔS) to the change of volume (ΔV) due to a phase change.

$$\Delta S = \frac{\Delta H_v}{T}$$

The change of entropy (ΔS) is defined as the ratio of the amount of heat entering and leaving the system (in this case the latent heat of vaporization) and the temperature (boiling point) at that time.

$$\Delta V = V_V - V_L$$

The change of volume (ΔV) due to the phase change is the volumetric difference per mole between the gas and the liquid.

$$\therefore \frac{dP}{dT} = \frac{\Delta H_v}{T(V_V - V_L)}$$

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Clausius-Clapeyron Equation

$$\Delta V \equiv V_V - V_L \cong V_V = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_V - V_L)} = \frac{\Delta H_v}{T\frac{RT}{P}} = \frac{P\Delta H_v}{RT^2}$$

Clausius approximated the Clapeyron equation by using the ideal gas equation of state and assuming that the liquid volume is negligible compared to the gas volume.

$$\therefore \frac{dP}{dT} = \frac{P\Delta H_v}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H_v}{R}\frac{dT}{T^2}$$

$$\int \frac{dP}{P} = \frac{\Delta H_v}{R}\int \frac{dT}{T^2}$$

$$\ln P = \frac{\Delta H_v}{R}\frac{-1}{T} + const = const - \frac{\Delta H_v}{R}\frac{1}{T}$$

$$\therefore \ln P = const - \frac{\Delta H_v}{R}\frac{1}{T}$$

By integrating the obtained differential equation with a constant latent heat of vaporization, an equation related to the temperature change of the vapor pressure is obtained.

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Relationship with Antoine Equation

$$\log_e P = const - \frac{\Delta H_v}{R}\frac{1}{T}$$

$$\frac{\log_{10} P}{\log_{10} e} = const - \frac{\Delta H_v}{R}\frac{1}{T}$$

$$\log_{10} P = const - \log_{10} e\frac{\Delta H_v}{R}\frac{1}{T}$$

$$= const - \log_{10}(2.718)\frac{\Delta H_v}{(1.986)}\frac{1}{T}$$

$$= const - 0.2187\Delta H_v\frac{1}{T}$$

$$cf.Antoine: \log_{10} P = A - \frac{B}{(t+C)}$$

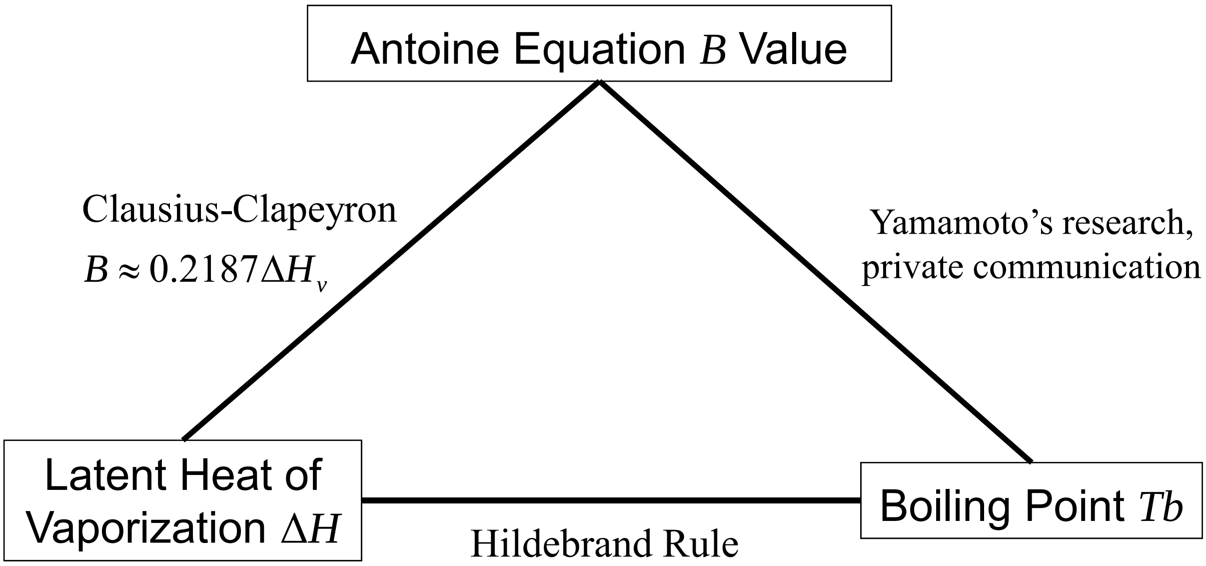
$$\therefore B \approx 0.2187\Delta H_v$$

By converting the base of the logarithmic expression from e to 10, it can be seen that the Clausius-Clapeyron equation is the theoretical basis for the Antoine equation.

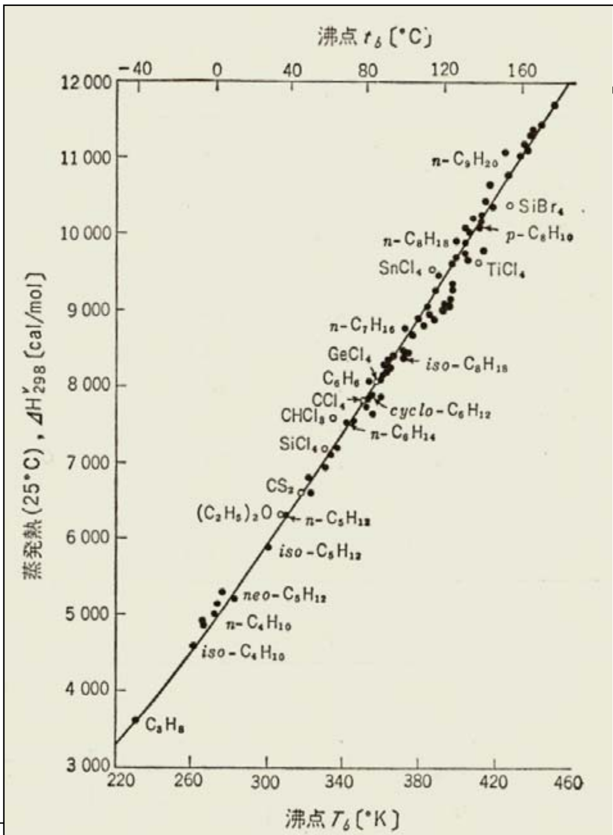
That is, considering the case where *C*=273.15, it can be seen that the *B* value of the Antoine equation is a value proportional to the latent heat of vaporization.

In what follows, we will investigate whether the relation between *B* and the latent heat of vaporization holds quantitatively.

Relationship between Antoine Equation B Value, Latent Heat of Vaporization and Boiling Point



Relationship between Latent Heat of Vaporization and Boiling Point



The relationship between boiling point heat of vaporization and boiling point is known as the Hildebrand rule.

"Yoeki to yokaido" (*in Japanese*: Solutions and Solubility) Hirata Mitsuho, P. 103, Kozo Shinoda

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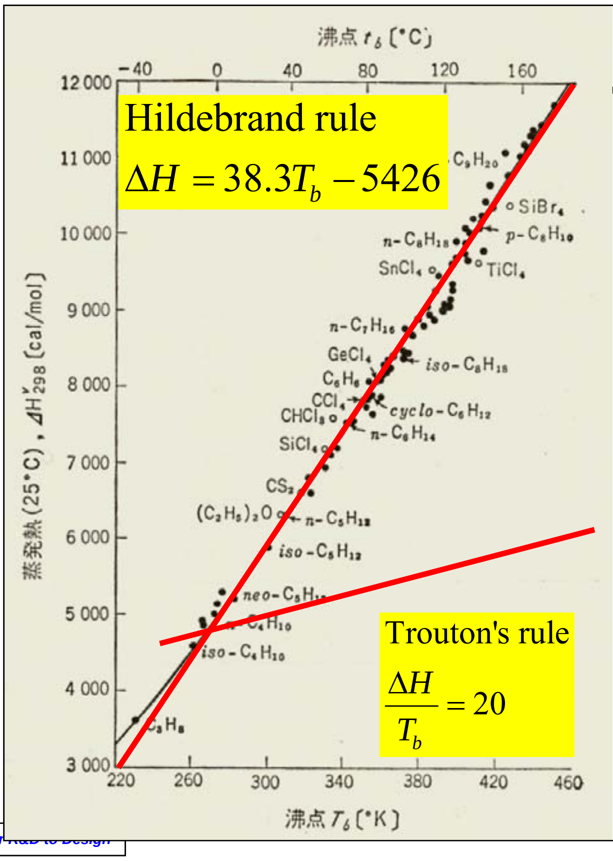
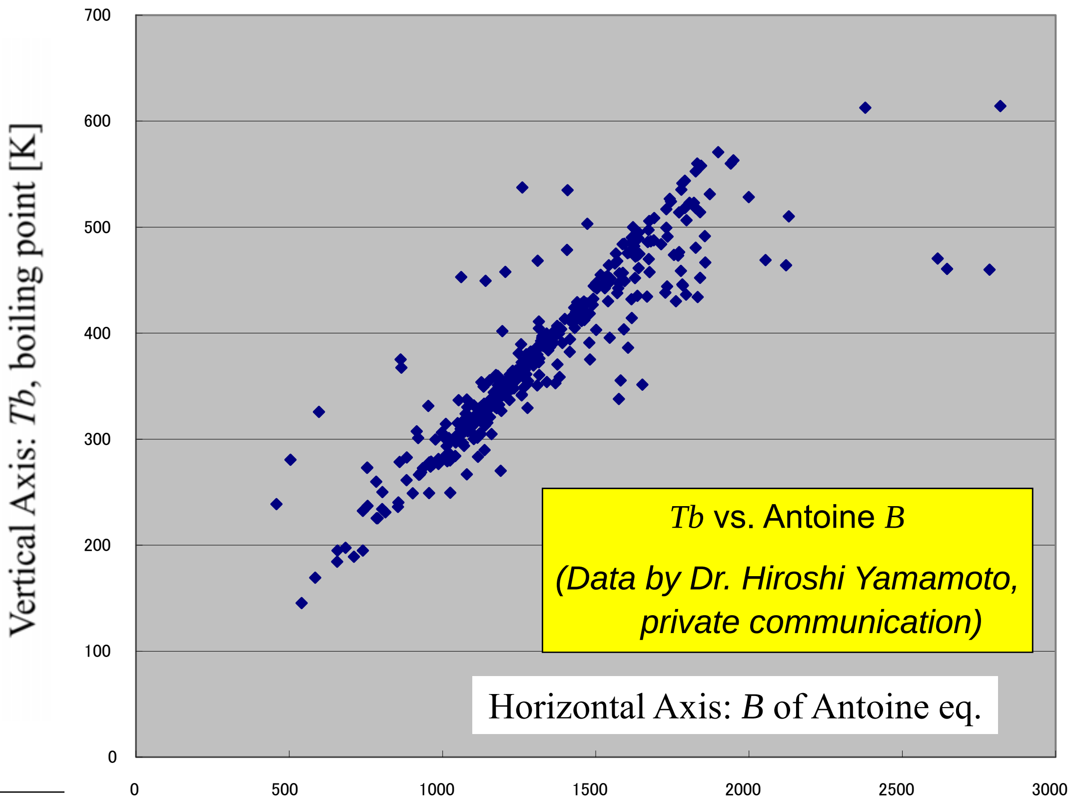
Relationship between Latent Heat of Vaporization and Boiling Point



Comparison of Hildebrand rule and Trouton rule

Relationship between Antoine Equation B Value and Boiling Point



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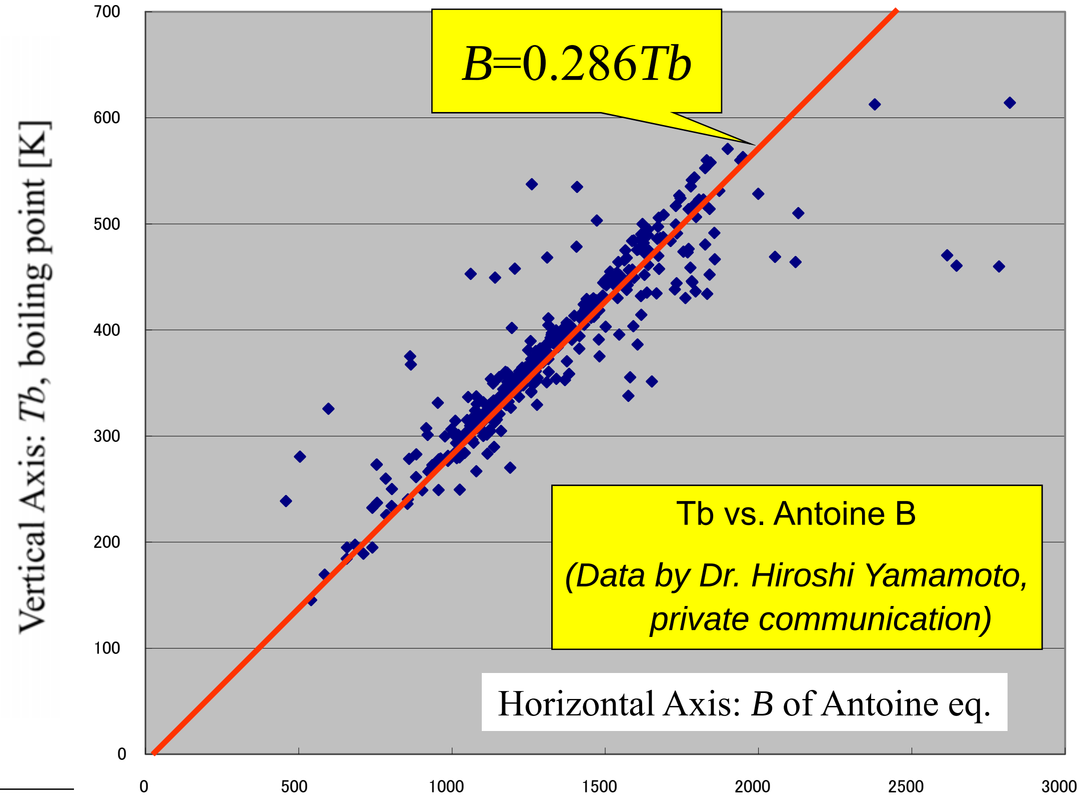

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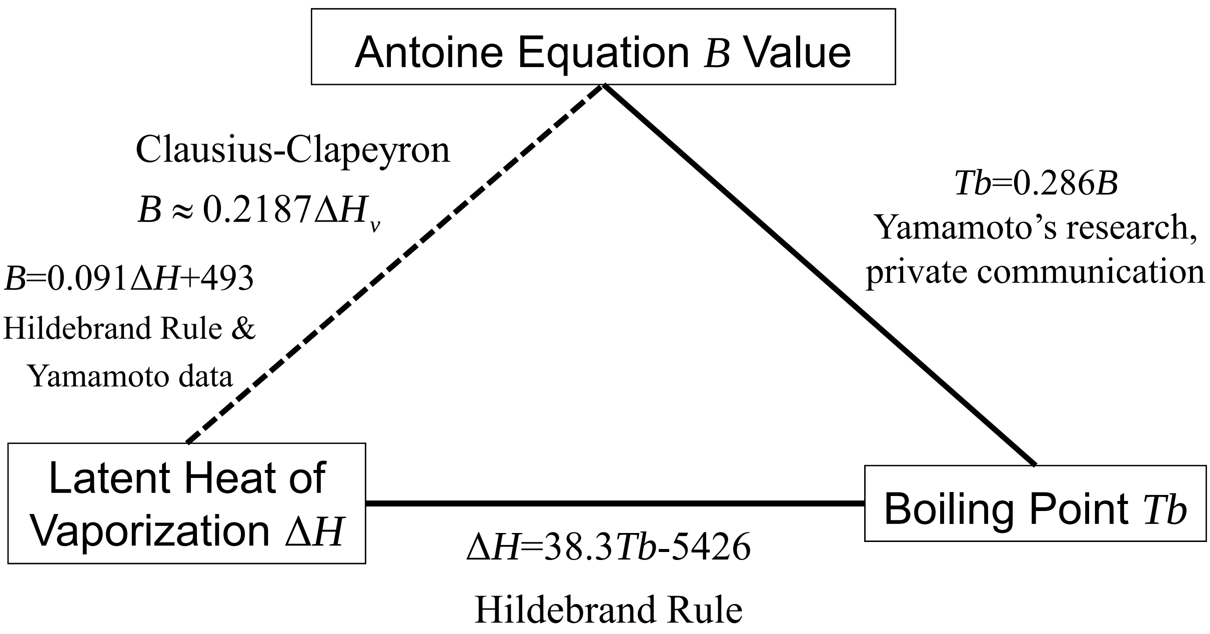

Conclusion

- The Clausius-Clapeyron equation is the theoretical basis for the Antoine equation, and the B value of the Antoine equation is related to the latent heat of vaporization.
- However, the relationship between the B value obtained by the Clausius-Clapeyron equation and the latent heat of vaporization is not quantitatively established.