

Prediction Method of Vapor Pressure for Pure Substances

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Abstract

Prediction of vapor pressure from boiling point data or one vapor pressure data is almost impossible with the conventional prediction method, and even if it can be calculated, the prediction result is not accurate. A method is presented to accurately predict the vapor pressure of the organic compound only from the boiling point data or one point of vapor pressure data. The fundamental equation of the vapor pressure is the Clausius-Clapeyron equation, and the logarithmic value of vapor pressure ($\log P$) is linearly related to the reciprocal of absolute temperature (T). This equation has two constants A and B , but the constant B is a constant related to latent heat of vaporization. Since the molar evaporation latent heat of homologous is almost the same, the constant B of homologous can be almost the same. Therefore, the constant B of a substance whose vapor pressure is unknown can be set to be a constant B of a substance having a known vapor pressure close to the boiling point in the homologue. Find a substance with a vapor pressure close to boiling in the homologue as a reference substance with unknown vapor pressure, and let the constant B be a constant B of vapor pressure unknown substance. There is a similar relationship also in the three constants Antoine equation, and it is possible to more accurately predict by using the two constants B and C of the homologous substance. The method can be widely used without limitation, and was applied to organic compounds in the previous report (Ohe, 2019), but this time we will report the possibility of application to inorganic compounds.

Keywords

vapor pressure, prediction, Antoine equation

Introduction

The vapor pressure data is not only essential for the design of chemical equipment but also important physical property constants indispensable for the calculation of vapor-liquid equilibrium. In the chemical industry, due to the development of new products and the appearance of new chemical processes, one needs to handle substances whose vapor pressure has not been observed. Engineers and Scientists refer to the well-known book (Poling, Prausnitz, et al. 2001) for finding methods of predicting vapor pressure, however, most of the methods in the book are based on the corresponding state principle in which critical constants not observed for the substances with no vapor pressure data. The book has no method to predict from one observed value.

A method of estimating the vapor pressure from data with boiling point etc. has already been reported, but most methods are difficult to estimate accurately. The method presented uses the existing vapor pressure data of organic compounds. By using single boiling point or a set of vapor pressure data can accurately estimate the vapor pressure of an organic compound.

1. Conventional Prediction Method

The vapor pressure equation is derived from the concept of the equilibrium state of thermodynamics.

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (1)$$

Where, ΔH is the enthalpy change accompanying evaporation, which is equal to the latent heat of vaporization L and ΔV is the volume difference between the gas phase and the liquid phase Eq.1 is rewritten using the compressibility factor z .

$$\frac{d(\ln P)}{d(1/T)} = - \frac{\Delta H}{R\Delta z} \quad (2)$$

$$\Delta z = \Delta z_{\text{vapor}} - \Delta z_{\text{liquid}}.$$

Equation 1, the Clausius-Clapeyron equation is derived ignoring the temperature change of the latent heat of the vaporization and the volume of the liquid phase, assuming that the ideal gas law is hold.

$$\ln P = A - \frac{B}{T} \quad (3)$$

Equation 3 can also be applied to solid sublimation pressure.

The Antoine equation (Antoine, 1888) using three constants A, B and C is shown as below.

$$\ln P = A - \frac{B}{T - C} \quad (4)$$

Although it is an empirical equation, the vapor pressure can be expressed accurately by limiting the temperature range. In the temperature relational expression of the vapor pressure, it is possible to express the vapor pressure accurately by increasing the constant. A considerable number of expressions are proposed. There are, for example, the Wagner equation (Wagner, 1973), etc. There are Cox diagram (Cox, 1923) and Nakanishi method (Nakanishi, Kurata, et al.

There is an equation of Sato (Sato, 1954) as a prediction equation from one point of data, and there is a method of obtaining a normal boiling point from a chemical structural formula.

2. Predictions from one point of data

There are many substances whose boiling points are known as one point of data. On the other hand, since there are considerable numbers of substances with known vapor pressure data as well, it is preferable to use the data of vapor pressure known substances for prediction.

2.1. Method by Clausius-Clapeyron equation

The expression equation of the vapor pressure with the least equation constant is the Clausius-Clapeyron equation. In order to determine the two constants of A and B, two measured values are necessary. If it is a homologous substance, each value of L and ΔV , therefore, the value of $L / \Delta V$ related to the constant B, are considered to be close values. That is, it is possible to use the same value of for the constant B for the two substances between the homologous substances. Therefore, if there is one point data, constant A can be

determined.

An example of the vapor pressure of a homologous substance is shown in Figure 1, 2 and Table 1 (Landolt-Bornstein). Figure 1 and 2 show a plot of the natural logarithm of the vapor pressure P with respect to the reciprocal $1/T$ of absolute temperature. Figure 1 shows the vapor pressure data for inorganic compounds of HoBr_3 , HoI_3 and NdI_3 . From the figure, it is clear that slope of each line is similar. In Figure 2, Substances (7) and (8) and (4) and (5) are substances with similar structures, and the slope of $\ln P$ to $1/T$ is almost the same..

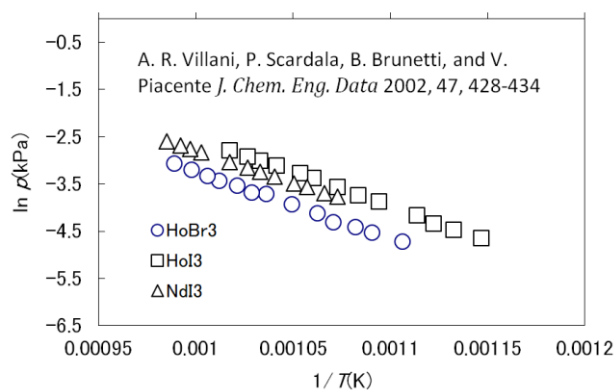


Fig.1 Vapor pressure of homologue in inorganic compound

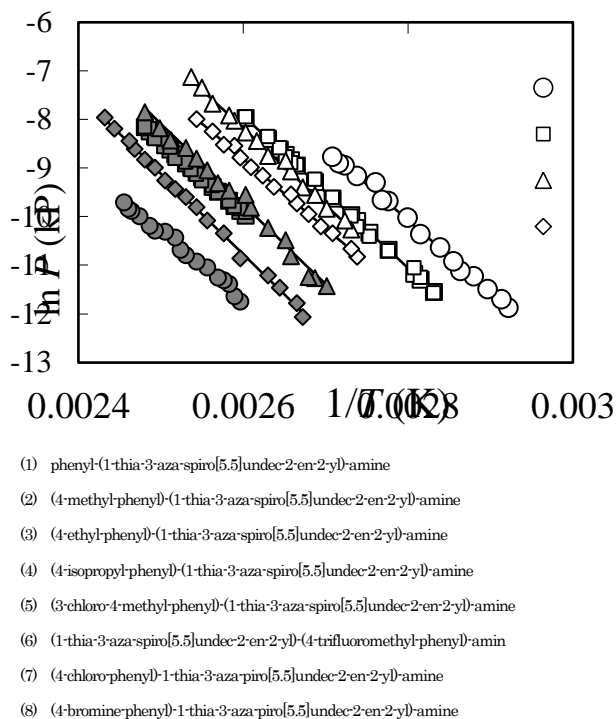


Fig.2 Vapor pressure of homologue in organic compounds

The sets of constant B of inorganic compounds are close to each other as shown in Table 1, for example, the sets of No.1, 2, and 4.

Table 1 Constants of Clausius-Clapeyron Equation
for homologue in inorganic compounds

No.	Substance	State	Constants of Clapeyron Eq.	
			A	B
1	NH ₃	l	25.263	3716.74
	ND ₃	l	25.575	3820.10
2	HCN	s	19.568	4322.73
	DCN	s	19.808	4391.82
3	SO ₃ (α)	s	24.331	6172.04
	SO ₃ (β)	s	25.529	6586.58
	SO ₃ (γ)	s	30.250	8313.83
4	ScCl ₃	s	31.079	32702.60
	ScBr ₃	s	31.033	31781.40
	ScI ₃	s	30.618	30745.05
5	N ₂ O ₄	l	16.340	3544.32
	NO ₂	l	20.946	5195.57
6	TeO ₂	l	21.586	26023.90
	TeF ₄	l	18.927	30340.41
7	Cl ₂ O	l	16.109	3162.02
	ClO ₂	l	17.215	3574.26
	Cl ₂ O ₆	l	14.336	4767.21
	Cl ₂ O ₇	l	16.478	4186.85
8	POF ₂ Cl	l	15.696	3059.07
	POFCl ₂	l	16.049	3726.78
	POF ₂ Br	l	16.331	3569.65
	POFBr ₂	l	14.494	3783.60
9	SiF ₃ Cl	s	15.157	2140.18
	SiF ₂ Cl ₂	s	15.084	2521.79
10	Si ₂ O ₄ F ₄ Cl ₂	l	16.369	3403.83
	Si ₂ OF ₃ Cl ₃	l	16.264	3680.19
11	TiO	–	28.638	67756.56
	TiO ₂	–	30.388	69921.38

2.2. Method by Antoine equation

The constants B and C of the Antoine equation have the following relation (Tezuka, 1957).

$$\frac{\Delta H}{R\Delta z} = B \left(\frac{T}{T-C} \right)^2 \quad (5)$$

Therefore, for homologous substances, the values of B and C are considered to be close to each other.

Vapor pressure constant A can be determined from data of one point by using B and C of substances as is in

the case of Clausius-Clapeyron equation.

Antoine constants of homologous substances shown in Figure 3 are shown in Table 2 (Butrow, Buchanan, et al., 2009).

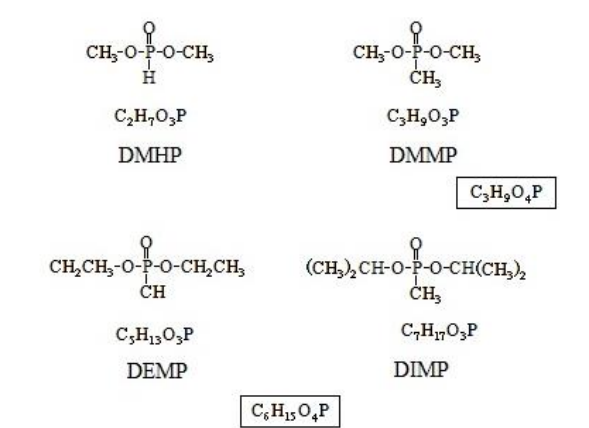


Fig.3 Structures of DMHP, DMMP, DEMP, and DIMP.

Table.2 Constants of Antoine constants for homologue

Compound	A	B	C	AAD (kPa)
DMHP	23.068	4890	20.0	0.084
DMMP	22.319	4340	51.7	0.093
DEMP	22.471	4500	54.2	0.196
DIMP	23.130	4785	50.5	0.999

DMHP (dimethyl phosphonate), Temperature range: 434 ~ 489 K

DMMP (dimethyl methylphosphonate), Temperature range: 258.2 ~ 454.4 K

DEMP (diethyl methylphosphonate), Temperature range: 253.2 ~ 465.9 K

DIMP (diisopropyl methylphosphonate), Temperature range: 253.2 ~ 468 K

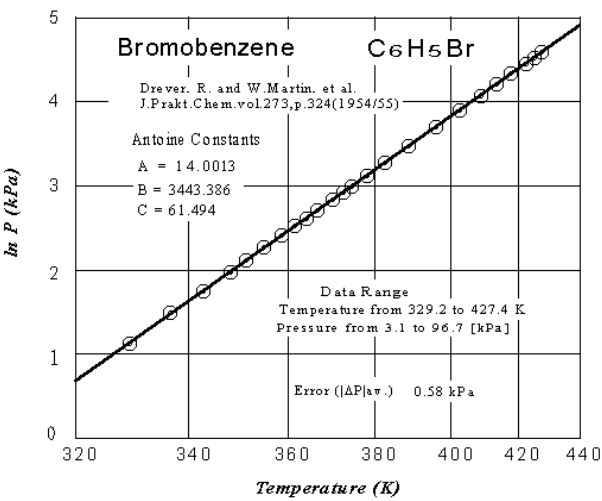


Fig.4 Vapor pressure of bromobenzene

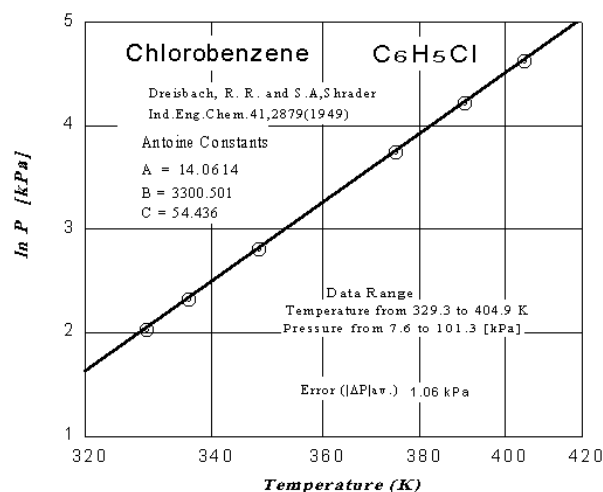


Fig.5 Vapor pressure of chlorobenzene

From Table 2, the Antoine constants B for between DMHP and DIMP, and between DMMP and DEMP show close values. The Antoine constant C shows values close to those of three substances except for DMHP. Especially DMMP and DIMP are almost the same. Figure 4 and Figure 5 show vapor pressure diagrams of bromobenzene and chlorobenzene. The author determined the Antoine constant of both substances (Ohe, 2002). The Antoine constants of both substances are shown below.

	<i>A</i>	<i>B</i>	<i>C</i>
Bromobenzene	14.0013	3443.386	61.694
Chlorobenzene	14.0614	3300.501	54.436

The Antoine constants of both substances are very close.

3. Prediction result and consideration

3.1. Selection of Reference Substance

Figure 6 shows the result of predicted vapor pressure of SO_2Cl_2 from Cl_2SO with AAD: 0.208 using Antoine constants B and C of Cl_2SO . Figure 7 shows vapor pressure data (Marsh, Morris, et al., 2016) of three types of silane compounds dichlorosilane (SiH_2Cl_2), trichlorosilane (SiHCl_3), and silicone (IV) chloride (SiCl_4). As can be seen, the slope of $\ln P$ for $1/T$ is almost the same.

The vapor pressure of chlorodisilane ($\text{Si}_2\text{H}_5\text{Cl}$) (Craig, Urenovitch, et al., 1962) is estimated. The boiling point of this substance is 314.75 K, then $1/T$ is 0.00318 and $\ln P$ is 4.618, it exists close to silicone (IV) chloride (SiCl_4) in Figure 7, so silicone (IV) chloride is used as a reference substance and its constant B is

used. The results are shown in Figure 8. As can be seen from the figure, the prediction results are satisfactory.

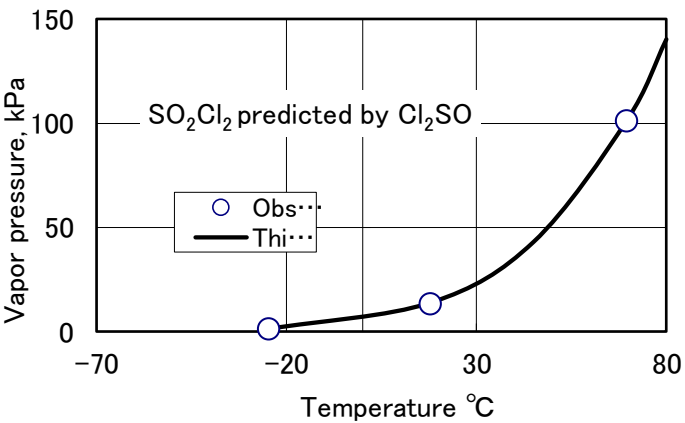


Fig.6 Vapor pressure predicted for inorganic compound

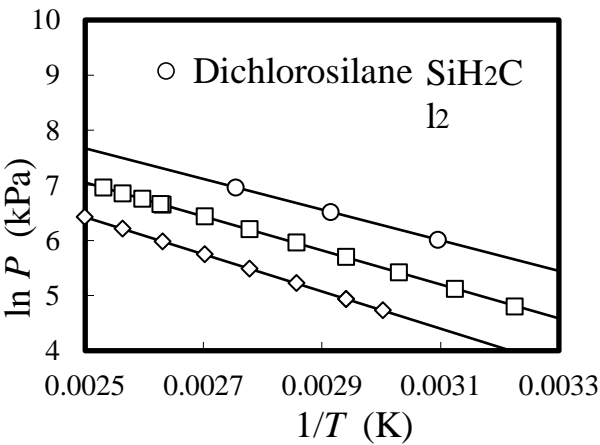


Fig.7 Vapor pressure of silane compound

In the figure, the low temperature part is shown on the right side vapor pressure scale, in which the solid line is the result of the Antoine equation (AAD is 0.076 kPa) and the dotted line is the result of the Clausius-Clapeyron equation (AAD is 0.235 kPa).

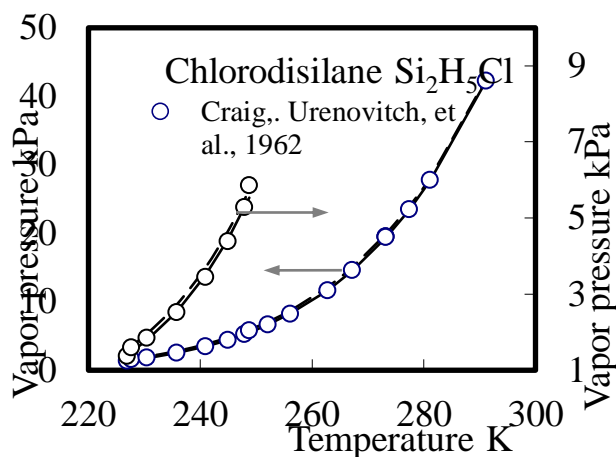


Fig.8 Prediction result of chlorodisilane ($\text{Si}_2\text{H}_5\text{Cl}$) from the data of silicone(IV) chloride (SiCl_4)

The homologues of the four organophosphorus compounds are shown in Figure 3. The molecular formula of the substance predicted in the figure is shown in a square frame. Trimethyl phosphate $\text{C}_3\text{H}_9\text{O}_4\text{P}$ has one oxygen number more than DMMP. Carbon number of triethyl phosphate $\text{C}_6\text{H}_{15}\text{O}_4\text{P}$ is between DEMP and DIMP, and the number of oxygen is 1. The Antoine constant (Butrow, Buchanan, et al., 2009) of this homolog is shown in Table 2. The vapor pressure of trimethyl phosphate $\text{C}_3\text{H}_9\text{O}_4\text{P}$ and triethyl phosphate $\text{C}_6\text{H}_{15}\text{O}_4\text{P}$ (Stull, 1947) was predicted from the Antoine constants of DMMP and DIMP, respectively, and the results are shown in Figure 8 and Table 5. Clausius-Clapeyron equation constant was determined from the vapor pressure data of DMMP and DIMP. As is clear from the figure, the result by Antoine equation is better than the result by Clausius-Clapeyron equation.

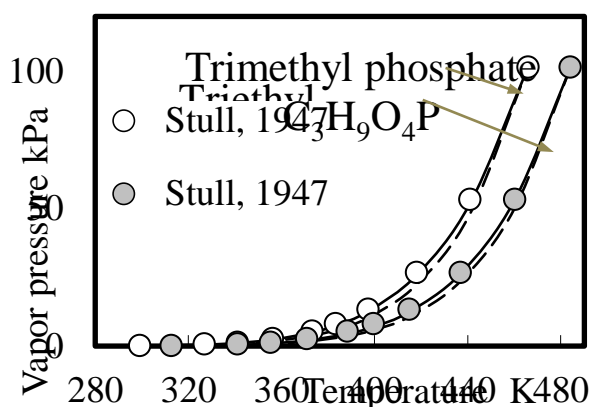


Fig.9 Prediction result of trimethyl phosphate ($\text{C}_3\text{H}_9\text{O}_4\text{P}$) and triethyl phosphate ($\text{C}_6\text{H}_{15}\text{O}_4\text{P}$) from the data of DMMP ($\text{C}_3\text{H}_9\text{O}_3\text{P}$) and DIMP ($\text{C}_7\text{H}_{17}\text{O}_3\text{P}$), respectively

3.2. Effect of Reference Substance on Prediction Accuracy

The Antoine constant (Ambrose, Sprake, 1970) and Clausius-Clapeyron constants of saturated alcohol

are shown in Table 3. To examine the criterion for reference substance selection in this method, the vapor pressure of Hexan-1-ol (temperature range 325.4 to 430.5 K, Herbert, Kreps, 1969) were tried to estimate from the alcohols shown in Table 3 using the straight chain alcohol Antoine constant and Clausius - Clapeyron constant shown in Table 4. The results are shown in Table 4. Prediction results using the Clausius-Clapeyron constant are shown in Figure 10. The mean absolute deviation (AAD) shown in Table 3 is the mean absolute deviation for the representation of the observed values of the Antoine and Clausius-Clapeyron equations. The Clausius-Clapeyron constant in Table 3 is the value determined by the author. Only the value of A of the Antoine equation and Clausius - Clapeyron equation constant used for prediction was shown, and the value of Table 3 is used for B or B, C. As can be seen from Figure 10 and Table 4, the larger the difference in carbon number between the substance to be predicted and the reference substance, the larger the error. In the figure, the point with the highest temperature (430.45 K, 100.97 kPa) is the point used for determining the constant A as the observed value, so it agrees with the observed value. The prediction result by the Antoine constant also shows the similar result as in Figure 10 .

Table 3 Constants of Antoine and Clausius - Clapeyron equation for alcohols

No.	Alcohols	Observed Temperature	
		Range (K)	
		Tmin	Tmax
1	Methanol	288.0	356.8
2	Ethanol	292.8	366.6
3	Propan-1-ol	338.7	377.7
4	Propan-2-ol	329.9	362.4
5	Butan-1-ol	351.7	398.8
6	Butan-2-ol	340.9	380.3
7	2-Methylpropan-1-ol	348.6	388.8
8	2-Methylpropan-2-ol	329.9	362.7
9	Pentan-1-ol	356.7	429.1
10	Octan-1-ol	390.9	479.3
11	Decan-1-ol	400.4	528.3
12	Dodecan-1-ol	425.7	549.7

No.	Antoine equation			
	Constants			Error
	A	B	C	AAD
1	16.5450	3614.54	34.613	0.057
2	16.5097	3575.64	50.731	0.068
3	15.5312	3144.93	82.093	0.065
4	15.5198	2971.66	82.778	0.064
5	14.7722	2908.15	104.445	0.070
6	14.4364	2594.71	108.361	0.064
7	14.6329	2751.23	106.291	0.066
8	14.3724	2416.58	107.724	0.066
9	14.1357	2741.52	123.055	0.097
10	13.3439	2782.32	149.407	0.050
11	13.6887	3304.24	139.888	0.093
12	13.7917	3632.68	141.679	0.074

No.	Clausius-Clapeyron Equation		
	Constants		Error
	A	B	AAD
1	18.0740	4544.62	0.394
2	18.8600	5004.99	0.479
3	18.8869	5283.81	0.213
4	19.0377	5124.78	0.213
5	18.8709	5570.89	0.408
6	18.8277	5295.54	0.381
7	18.8493	5422.77	0.354
8	18.9118	5081.72	0.308
9	18.8135	5837.58	1.073
10	18.5528	6516.33	1.098
11	18.4228	6951.55	2.166
12	18.3754	7376.57	1.321

As shown in Table 4, the average absolute deviation of the prediction result was slightly larger than that of the Clausius-Clapeyron equation.

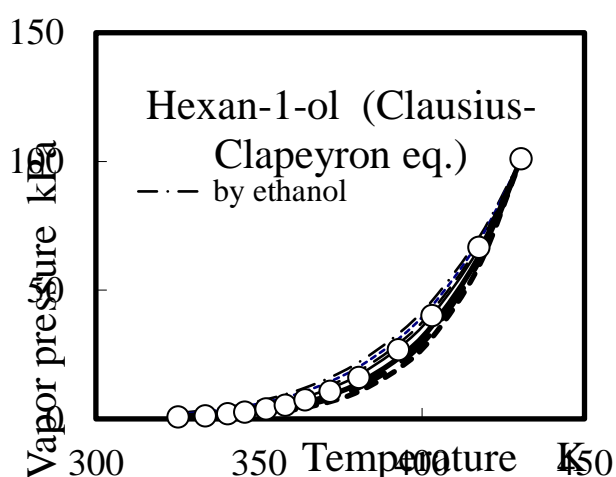


Fig. 10 Prediction result of hexan-1-ol ($C_6H_{14}O$) by Antoine equation from the data of alcohols shown in Table 4

Table 4 Prediction result of vapor pressure for hexan-1-ol

No.	Reference compounds	Antoine equation		Clausius-Clapeyron Equation	
		Constant	Error	Constant	Error
		A	AAD	A	AAD
2	Ethanol	14.031	5.270	16.2421	3.851
3	Propan-1-ol	13.643	3.941	16.8899	2.704
5	Butan-1-ol	13.535	2.539	17.5568	1.634
9	Pentan-1-ol	13.533	1.169	18.1764	0.735
10	Octan-1-ol	14.515	2.409	19.7532	1.243
11	Decan-1-ol	15.987	3.818	20.7643	2.304
12	Dodecan-1-ol	17.195	5.199	21.7517	3.215

3.3. Selection of temperature range

Similarly, the vapor pressure of 2-Methyl-1-pentanol was predicted using pentan-1-ol as a reference substance and the results are shown in Figure 11 and Table 5. In the figure, Thomas, Meatyard, et al. (1979). The data in the observed temperature range is 261.4 to 294.1 K and outside the measurement range 356.70 to 429.13 K of the reference material pentan-1-ol. In the figure, the result by the Antoine equation

is better than the result of the Clausius - Clapeyron equation. The reason of the result of the Antoine equation is better, because the expression of the change of the vapor pressure with respect to the temperature is superior than that of the Clausius - Clapeyron equation. The observed temperature range of the data of Hovorka and Lankelma, et al., (1938) is 298.2 ~ 423.2 K. A considerable part is contained within the observed temperature range of pentan-1-ol. As can be seen from the figure and table, both the prediction result is satisfactory, and the Antoine equation gives better results.

3.4. Scope of application

Table 5 shows the prediction results of the following types of substances.

- (1) pinenes 1 and 2 (substance numbers in the table, the same shall apply hereinafter)
- (2) Alcohols 3, 4, 5
- (3) Ketones 6
- (4) Esters 7
- (5) Acids 8
- (6) Organophosphors 9, 10
- (7) Silanes 11

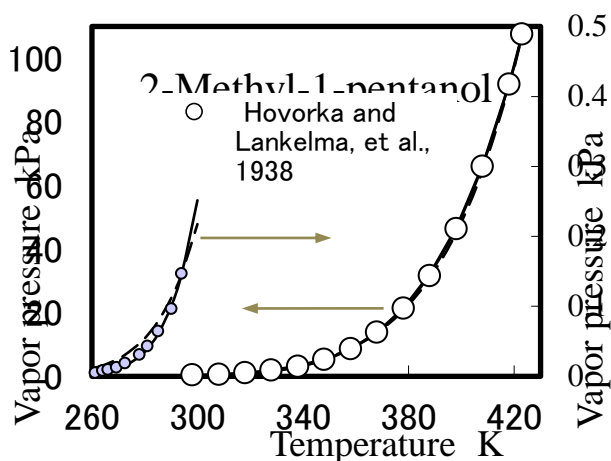


Fig.11 Prediction result of 2-methyl-1-pentanol (C₆H₁₄O) from the data of pentan-1-ol (C₅H₁₂O)

The parentheses after the substance name are the figure numbers shown in the text. The symbols of the

reference substances are shown in the fourth column of the upper table. The reference substances are shown in Table 6. At the bottom of Table 5, the value of A in the Antoine constant and Clausius-Clapeyron constant determined by this method and used for the prediction is shown. The constant B or B, C required for determining the constant A is shown in the middle part of Table 6. This constant B, or, B and C are used for prediction together with the above constant A. The average absolute deviation (AAD) in Table 5 is the mean absolute deviation of the predicted, and the mean absolute deviation (AAD) in Table 6 is the mean absolute deviation of the calculated for the observed value.

Table 5 Prediction result of vapor pressure

No.	Compound (shown in mentioned figure)	Chemical	Symbol
		formula	for reference compound
1	3,3-dimethyl-2-methylidenebicyclo[2.2.1]heptane	C ₁₀ H ₁₆	a
2	4,6,6-trimethylbicyclo[3.1.1]heptane	C ₁₀ H ₁₈	a
3	hexan-1-ol (Fig. 8)	C ₆ H ₁₄ O	b
4	2-methyl-1-pentanol (Fig. 9)	C ₆ H ₁₄ O	b
5	2-methyl-1-pentanol (Fig. 9)	C ₆ H ₁₄ O	b
6	heptan-4-one	C ₆ H ₁₄ O	c
7	propyl butanoate	C ₇ H ₁₄ O ₂	d
8	heptanedioic acid	C ₇ H ₁₂ O ₄	e
9	trimethyl phosphate (Fig.7)	C ₃ H ₉ O ₄ P	f
10	triethyl phosphate (Fig.7)	C ₆ H ₁₅ O ₄ P	g
11	Chlorodisilane (Fig.6)	Si ₂ H ₅ Cl	h

No.	Antoine equation		Clausius-Clapeyron equation		Temperature range (K)	
	Constant	Error (kPa)	Constant	Error (kPa)		
	A	AAD	A	AAD	Tmin	Tmax
1	13.51018	0.079	16.29231	0.530	309.7	407.6
2	13.30531	0.656	16.07184	0.163	330.3	415.0
3	13.53333	1.165	18.17635	0.735	325.4	430.5
4	14.11307	0.003	17.93267	0.011	261.4	294.1
5	13.81310	0.232	18.47313	0.383	298.2	423.2
6	17.08939	1.654	19.53600	0.871	296.2	416.9
7	13.99902	1.849	16.07513	0.809	271.6	415.9
8	17.09393	0.872	20.62386	0.118	436.6	615.2
9	15.09763	0.475	17.83617	1.809	299.2	465.9
10	15.65233	0.485	18.37141	1.754	312.8	484.2
11	14.97244	0.076	15.29165	0.235	227.0	291.2

The Antoine constants and Clausius-Clapeyron constants of the reference materials used for prediction are shown in Table 6. To select the reference substance, substance with the most similar properties to the substance to be predicted is selected. As the substance close to the property of the substance to be predicted, the substance is selected with the difference of carbon number etc. is less than 1. There are cases of one more carbon number, or one less. In this paper, in principle, one less carbon number was chosen. This is

because there will be difficult to find greater carbon number substance with the observed vapor pressure data.

Symbol a is common name α -pinene (Wang, Huang, et al., 2014), c is a common name methyl n-butyl ketone, d is a common name ethyl n-butyrate, e is a common name adipic acid (Stull, 1947). The reference substances b, f, g and h are 1-Pentanol, DMMP, DIMP, Silicon (IV) chloride as already mentioned.

As can be seen from the results in Table 5, an accuracy of prediction does not change by kind of substances. The presented method can be applied to a wide range of substances if substances of similar properties are used as reference substances.

Table 6 Reference compounds for prediction of vapor pressure

symbol	Reference compounds	Chemical formula	Temperature range (K)	
			Tmin	Tmax
a	4,6,6-trimethylbicyclo[3.1.1]hept-3-ene	C ₁₀ H ₁₆	292.6	428.9
b	pentan-1-ol	C ₅ H ₁₂ O	356.7	429.1
c	hexan-2-one	C ₆ H ₁₂ O	280.8	400.7
d	ethyl butanoate	C ₆ H ₁₂ O ₂	254.8	394.2
e	hexanedioic acid	C ₆ H ₁₀ O ₄	432.7	610.7
f	dimethyl methylphosphonate	C ₃ H ₉ O ₃ P	258.2	454.4
g	diisopropyl methylphosphonate	C ₉ H ₁₇ O ₃ P	253.2	465.9
h	Silicon (IV) chloride	SiCl ₄	333.0	400.0

Symbol	Antoine equation constants			Error (kPa)
	A	B	C	AAD
a	13.6380	3251.78	68.807	0.068
b	14.1357	2741.52	123.055	0.097
c	17.6573	4632.79	45.367	0.091
d	14.5820	3476.12	45.289	0.035
e	17.2106	6478.62	95.947	0.137
f	22.3190	4340.00	51.700	0.093
g	23.1300	4785.00	50.500	0.999
h	12.4671	3108.46	14.345	0.044

Symbol	Clausius-Clapeyron Equation Constants		Error (kPa)
	A	B	AAD
a	16.4545	5046.20	0.868
b	18.8135	5837.58	1.073
c	20.1919	6218.43	0.808
d	16.7759	4764.31	1.030
e	20.8260	9847.40	1.225
f	18.3901	6157.53	1.425
g	19.3188	6658.55	0.086
h	12.8299	3368.95	0.049

Conclusions

The accuracy of this prediction method depends on the selection of reference substance and temperature

range to be used for prediction. It is desirable that the property of the reference substance is close to the property of the substance predicted and the temperature range of the substance to be predicted coincides with the observation range of the temperature of the reference substance used for prediction. Although Antoine equation and Clausius-Clapeyron equation can be used, the Antoine equation is generally more accurate to predict. When the temperature range to be predicted coincides with the observed temperature range of the reference material used for prediction, there is almost no difference between the two equations. When these temperature ranges do not coincide, the Antoine equation should be used.

We presented a method of predicting vapor pressure for organic as well as inorganic compounds with single vapor pressure data such as boiling point. Clausius-Clapeyron equation and Antoine equation can be used for prediction. From the point of engineering use, it is a prediction method with satisfactory prediction accuracy.

Nomenclature

AAD : average absolute deviation	kPa
A, B : Constants of Clausius-Clapeyron equation	[-]
A, B, C : Constants of Antoine equation	[-]
H : enthalpy	kJ mol^{-1}
L : latent heat of vaporization	kJ mol^{-1}
P : vapor pressure	kPa
R : gas constant	$\text{J K}^{-1} \text{mol}^{-1}$
T : absolute temperature	K
V : volume	mL mol^{-1}
z : compressibility factor	[-]

min: minimum

max: maximum

Δ : difference

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