

計算蒸發潛熱的通用公式

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摘 要

著者綜合前人計算蒸發潛熱的經驗公式，誘導出一個新的計算公式如下：

$$\frac{\lambda}{T_c} = -6.7 \log P_r \frac{T_r}{(1-T_r)^{0.63}}$$

任何物質在任何溫度 T 與壓力 P 狀態下的蒸發潛熱 λ ，只要有了該物質臨界溫度與臨界壓力的數據，就可以根據這個公式計算。式中 T_r 為絕對溫度與臨界絕對溫度之比， P_r 為壓力與臨界壓力之比。此公式的錯誤小於百分之五。

A GENERALIZED EQUATION FOR THE LATENT HEAT OF VAPORIZATION

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Introduction

Various empirical equations have been successfully developed to determine the latent heat of vaporization of substances. Trouton's rule and Kistyakowsky's equation may be used to calculate the latent heat of vaporization at normal boiling point. Watson's equation¹ may be used to calculate the latent heat of vaporization at any temperature from one known value. Applying either Gordon's relationship,² or modified Othmer's method,³ we may obtain the latent heat of vaporization of any substance from the known value of a reference substance at the same reduced temperature. Applying Meissner's equation,⁴ we may calculate the latent heat of vaporization from the reduced tempera-

1. Watson, K., I. E. C. (1931) 23, 360.
2. Gordon, D. H., Univ. of Wis. Ph. D. Thesis, (1942).
3. Othmer, D. F., I. E. C. (1942) 34, 1072.
4. Meissner, W., I. E. C. (1941) 33, 1440-1443.

ture and pressure and compressibility factors. Examining the works of Watson, Othmer, Gordon, Meissner and others, it is obvious that the latent heat of vaporization is merely a function of reduced temperature and reduced pressure.

An attempt is made by the writers to formulate a general equation by which we can determine the latent heat of vaporization of any substance at any temperature without a reference value.

Derivation of the equation

According to Watson's relationship⁵

$$\frac{\lambda_1}{\lambda_2} = \left(\frac{1-T_{r1}}{1-T_{r2}} \right)^{0.38} \dots\dots\dots(1)$$

where λ_1, λ_2 , is molal latent heat of vaporization of one substance at different reduced temperature T_{r1}, T_{r2} , respectively.

Rearrange equation (1), we have

$$\frac{\lambda_1}{(1-T_{r1})^{0.38}} = \frac{\lambda_2}{(1-T_{r2})^{0.38}} = K \dots\dots\dots(2)$$

where K =characteristic constant for that substance.

Divide equation (2) by the critical temperature of that substance, T_c , we have

$$\frac{\lambda_1}{T_c(1-T_{r1})^{0.38}} = \frac{\lambda_2}{T_c(1-T_{r2})^{0.38}} = \frac{K}{T_c} = K'$$

or $\frac{\lambda}{T_c} = K'(1-T_r)^{0.38} \dots\dots\dots(3)$

Similarly, for another substance, we have

$$\frac{\lambda'}{T_c'} = K'(1-T_r')^{0.38} \dots\dots\dots(3a)$$

Divide (3) with (3a), and at the same reduced temperature, we have

$$\frac{\lambda}{T_c} / \frac{\lambda'}{T_c'} = \frac{K}{K'} = \text{Constant} \dots\dots\dots(4)$$

this is Gordon's relationship.⁶

According to modified Othmer's relationship⁷

5. Watson, K., *ibid.*

6. Gordon, D. H., *ibid.*

7. Othmer, D. F., *ibid.*

$$\frac{\lambda}{T_o} / \frac{\lambda'}{T_o'} = \frac{\log p_r}{\log p_{r'}} \dots\dots\dots (5)$$

where $p_r, p_{r'}$ is the reduced vapor pressure of two different substances at the same reduced temperature, $T_r = T_{r'}$.

Equalize equation (4) and (5), we have

$$\frac{K}{K'} = \frac{\log p_r}{\log p_{r'}}$$

or $K = K' \frac{\log p_r}{\log p_{r'}} \dots\dots\dots (6)$

Substituting equation (6) into (3), we have

$$\frac{\lambda}{T_o} = K' \frac{\log p_r}{\log p_{r'}} (1 - T_r)^{0.38} \dots\dots\dots (7)$$

where K' is the characteristic constant of reference substance.

$p_{r'}$ is the vapor pressure of reference substance.

According to van der Waal's relationship⁸

$$\log p_{r'} = A' \left(1 - \frac{1}{T_{r'}} \right) \dots\dots\dots (8)$$

where A' is the characteristic constant for the reference substance.

Substituting equation (8) into (7), we have

$$\frac{\lambda}{T_o} = K' \frac{\log p_r}{A' \left(1 - \frac{1}{T_{r'}} \right)} (1 - T_r)^{0.38} \dots\dots\dots (9)$$

or $\log p_r = \frac{A' \lambda}{K' T_o (1 - T_r)^{0.38}} \left(1 - \frac{1}{T_{r'}} \right) \dots\dots\dots (10)$

this equation is corresponding to Meissner's relationship⁹

$$\log p_r = \frac{\lambda}{T_o (Z_o - Z_l) R} \left(1 - \frac{1}{T_{r'}} \right) \dots\dots\dots (11)$$

where Z_o, Z_l are compressibility factors of gas and liquid.

Simplifying the equation (9), As $T_{r'} = T_r$, we have

$$\frac{\lambda}{T_o} = - \frac{K'}{A'} \log p_r \frac{T_r}{(1 - T_r)^{0.38}} \dots\dots\dots (12)$$

8. Glasstone, S., "Textbook of Physical Chemistry" P. 454. D. Van Nostrand Company, Inc., New York, (1946).

9. Meissner, W., *ibid.*

For any two substances, we have $K/K' = \log p_r / \log p_r'$ as shown by equation (6)

According to Van der Waal's relationship, $\log p_r' = A' \left(1 - \frac{1}{T_r}\right)$, and $\log p_r = A \left(1 - \frac{1}{T_r}\right)$. We have $\log p_r / \log p_r' = A/A'$, so $A/A' = K/K'$ or $K'/A' = K/A = \text{constant}$

Therefore, the ratio of K'/A' will be the same for all substances.

The value of K'/A' has been found to be 6.7 when the molal latent heat of vaporization is in cal. per gm-mole, and the critical temperature is in degree Kelvin. The generalized equation for latent heat of vaporization is

$$\frac{\lambda}{T_c} = -6.7 \log p_r \frac{T_r}{(1 - T_r)^{0.38}} \dots\dots\dots (13)$$

Applicability of the equation

The following data are taken from the International Critical Tables and used to testify the validity of above equation.

For convenience of comparison, the value of both calculated from the empirical equations and taken from the literature are tabulated in the following table.

Watson's value is calculated from the equation

$$\left(\frac{\lambda}{T_c}\right) / \left(\frac{\lambda}{T_c}\right)_b = \frac{(1 - T_r)^{0.38}}{(1 - T_{rb})^{0.38}}$$

where $\left(\frac{\lambda}{T_c}\right)_b$ is taken from the literature.

In the calculation of modified Othmer's and Gordon's values, water is taken as reference substance.

Substance	Formula	$T_c, ^\circ K$	$p_c, atm.$	$T_r = \frac{T}{T_c}$	$p_r = \frac{p}{p_c}$	$\frac{\lambda}{T_c}$ (Calc.)	$\frac{\lambda}{T_c}$ (Literature)	$\frac{\lambda}{T_c}$ (Watson)	$\frac{\lambda}{T_c}$ (Othmer)	$\frac{\lambda}{T_c}$ (Gordon)
Water	H ₂ O	647	217.7	0.421	0.0000276	17.98	16.58	16.89		
				0.438	0.0000555	17.82	16.40	16.68		
				0.454	0.000106	17.60	16.25	16.52		
				0.469	0.000192	17.29	16.10	16.31		
				0.485	0.000335	16.98	15.95	16.14		
				0.499	0.00056	16.70	15.82	15.96		
				0.515	0.00090	16.40	15.65	15.76		
				0.530	0.00144	16.11	15.51	15.61		

				0.546	0.00215	15.90	15.32	15.39		
				0.561	0.00317	15.60	15.16	15.20		
				0.576	0.0046	15.31	15.02	15.02		
				0.592	0.00648	15.10	14.84	14.78		
				0.608	0.0090	14.87	14.62	14.55		
				0.622	0.0122	14.55	14.44	14.35		
				0.639	0.0164	14.38	14.20	14.10		
				0.653	0.0216	14.01	14.00	13.89		
				0.670	0.0279	13.50	13.76	13.64		
				0.685	0.0358	13.59	13.45	13.38		
				0.700	0.0454	13.29	13.33	13.14		
				0.717	0.0570	13.07	13.15	12.86		
				0.732	0.0706	12.78	12.90	12.58		
				0.748	0.0866	12.51	12.61	12.30		
				0.763	0.1052	12.21	12.35	12.02		
				0.778	0.127	11.89	12.07	11.72		
				0.795	0.152	11.63	11.72	11.37		
				0.810	0.180	11.66	11.40	10.82		
				0.825	0.213	10.90	11.05	10.55		
				0.840	0.250	10.50	10.65	10.36		
				0.856	0.290	10.18	10.24	9.94		
				0.872	0.338	9.59	9.79	9.52		
				0.886	0.390	9.25	9.32	9.11		
				0.902	0.448	8.76	8.80	8.58		
				0.917	0.512	8.25	8.22	8.07		
				0.933	0.584	7.75	7.52	7.45		
				0.948	0.633	7.02	6.80	6.76		
				0.965	0.751	6.46	5.91	5.82		
				0.980	0.847	5.45	4.80	4.72		
				0.995	0.955	3.51	2.88	2.76		
				1.000	1.000	0.0	0.0	0.0		
Carbon dioxide	CO ₂	304.1	73.0	0.610	0.014	15.02	10.94	10.94	14.8	12.4
				0.800	0.193	10.61	10.78	16.00	10.43	10.12
				0.899	0.470	7.82	8.08	12.31	8.30	7.66
				0.965	0.772	5.80	5.07	8.20	5.28	5.15
				0.996	0.975	2.26	1.73	3.59	1.58	2.51
Sulfur dioxide	SO ₂	430.2	77.7	0.495		15.72	19.55	15.61	15.30	15.05
				0.670	0.013	13.91	14.72	14.72	13.55	13.80
				0.750	0.105	11.60	10.98	11.95	11.60	11.96
Carbon disulfide	CS ₂	546.0	76.9	0.500		13.60	12.50	11.86	12.95	13.30
				0.584	0.013	12.70	11.77	11.77	12.45	12.50
				0.645	0.035	11.91	11.00	11.10	11.85	11.86
				0.720	0.091	11.01	10.00	10.15	11.50	10.90

Benzene	C_6H_6	561.5	47.7	0.480		14.51	14.90	14.90	14.20	14.68
				0.557		14.20	13.92	14.02	13.90	14.03
				0.628	0.021	13.02	13.70	13.70	12.55	13.24
				0.771	0.146	10.81	10.90	10.91	10.89	11.27
				0.877	0.400	8.61	8.62	8.55	8.65	8.90
				0.950	0.700	6.30	6.07	6.10	5.92	6.28
Toluene	C_7H_8	593.6	41.6	0.642	0.024	13.21	13.43		12.90	13.55
Bromo-benzene	C_6H_5Br	670.0	44.6	0.640	0.022	13.51	13.50		13.31	
Chloro-benzene	C_6H_5Cl	632.0	44.6	0.638	0.022	13.42	13.70		13.20	13.25
Aniline	C_6H_7N	669.0	52.4	0.650	0.019	14.30	13.80		14.45	
Methyl aniline	C_7H_9N	702.0	51.3	0.663	0.019	15.01	14.62		14.82	
m-Cresol	C_7H_8O	705.0	45.0	0.672	0.022	15.02	15.40		14.65	
Benzonitrile	C_7H_5N	699.0	41.6	0.662	0.024	13.91	12.93		13.92	
Pyridine	C_5H_5N	617.0	60.0	0.626	0.016	13.70	13.70		13.40	10.51
Methane	CH_4	190.5	45.8	0.599	0.022	11.90	11.62		11.70	12.73
n-Butane	C_4H_{10}	426.0	36.0	0.640	0.028	12.51	12.50		12.41	12.42
iso-Butane	C_4H_{10}	407.0	37.0	0.646	0.027	12.90	12.51		12.82	
n-Hexane	C_6H_{14}	507.8	29.5	0.672	0.034	13.22	13.45		13.01	
n-Heptane	C_7H_{16}	539.8	26.8	0.685	0.037	13.43	14.10		13.30	
Methyl alcohol	CH_4O	513.0	78.7	0.532	0.0006	18.40	17.75	18.61	17.60	18.33
				0.658	0.013	16.15	16.40	16.40	16.55	16.40
				0.765	0.080	13.83	14.20	14.22	13.90	14.56
				0.885	0.335	10.82	10.91	10.80	10.85	10.90
				0.961	0.715	7.00	6.85	7.21	6.09	7.25
Ethyl alcohol	C_2H_5O	516.1	63.1	0.529	0.000285	20.00	19.62	21.22	19.40	19.92
				0.645	0.00729	17.54	18.80	19.03	17.45	18.10
				0.680	0.016	16.63	18.30	18.30	16.41	17.15
				0.761	0.067	14.64	16.21	16.41	14.80	15.80
				0.877	0.308	11.05	12.13	12.72	11.10	12.35
				0.955	0.671	7.60	7.68	8.68	7.02	8.32
				0.995	0.949	4.04	3.41	3.76	3.26	3.69
Propyl alcohol	C_3H_7O	536.7	49.95	0.690	0.020	16.34	18.40	18.40	15.80	17.50
				0.806	0.138	12.94	14.38	15.40	13.11	14.90
				0.919	0.490	9.13	9.50	11.03	8.79	10.71
				0.955	0.690	7.06	7.06	8.86	6.54	8.47
				0.993	0.945	3.52	3.72	4.33	3.54	3.75
n-Butyl alcohol	C_4H_9O	560.0	48.4	0.698	0.021	16.73	18.70		15.70	17.65

Methyl chloride	CH ₃ Cl	416.1	65.8	0.598	0.015	12.80	12.44		12.30	12.43
Chloroform	CHCl ₃	536.0	48.0	0.508	0.00174	14.50	14.42	14.51	14.01	14.40
				0.623	0.021	12.83	13.12	13.12	12.60	13.22
				0.695	0.067	11.40	12.26	12.10	11.61	12.23
Carbon tetrachloride	CCl ₄	556.1	45.0	0.490	0.00115	14.70	14.38	14.45	13.50	13.82
				0.628	0.022	12.80	12.82	12.82	12.80	12.45
				0.706	0.070	11.70	11.67	11.72	12.33	11.54
				0.815	0.231	9.90	9.82	9.83	10.00	9.81
				0.922	0.573	7.18	7.06	7.07	7.09	6.95
				0.995	0.960	3.16	2.88	2.46	2.60	2.51
Ethyl chloride	C ₂ H ₅ Cl	460.2	52.0	0.620	0.019	13.00	13.01		12.90	12.74
Hydrocyanic acid	HCN	456.5	50.0	0.641	0.020	13.80	12.53		13.52	
Acetonitrile	C ₂ H ₃ N	457.7	47.7	0.614	0.021	13.80	13.05		13.74	
Ethyl amine	C ₂ H ₇ N	456.2	55.5	0.632	0.018	13.73	14.40		13.50	
Di-n-Propyl amine	C ₆ H ₁₅ N	550.0	31.0	0.691	0.032	14.20	13.92		14.32	
Acetic acid	C ₂ H ₄ O ₂	594.6	57.2	0.658	0.017	15.00	8.78	8.78	14.82	
				0.762	0.088	13.11	8.92	8.52	13.35	
				0.830	0.199	11.80	8.20	7.48	11.95	
n-Propionic acid	C ₃ H ₆ O ₂	612.5	53.0	0.675	0.019	15.60	11.95		15.55	
Methyl formate	C ₂ H ₄ O ₂	487.0	59.15	0.625	0.017	13.64	13.90		13.34	
Methyl acetate	C ₃ H ₆ O ₂	506.7	46.3	0.651	0.022	14.03	14.40		14.01	
Ethyl n-butyrate	C ₆ H ₁₂ O ₂	566.0	30.0	0.691	0.033	14.04	15.31		14.20	
Ethyl Propionate	C ₅ H ₁₀ O ₂	545.9	33.0	0.677	0.030	13.94	15.00		13.81	
Ethyl ether	C ₄ H ₁₀ O	466.8	35.5	0.584	0.00668	14.70	14.70	14.34	14.35	14.20
				0.657	0.028	13.22	13.82	13.82	13.10	13.31
				0.755	0.111	11.50	11.50	11.70	11.71	11.80
				0.841	0.277	9.75	9.75	9.95	9.87	10.14
				0.926	0.585	7.88	7.04	7.45	6.95	7.48
				0.970	0.813	5.18	4.74	5.28	4.62	5.27
Acetone	C ₃ H ₆ O	508.0	47.0	0.537	0.002	15.60	15.43	14.44	15.10	
				0.648	0.021	14.02	14.22	14.22	13.80	
				0.734	0.078	12.45	12.90	12.80	12.50	
Ammonia	NH ₃	405.4	111.5	0.561	0.00485	14.50	14.07		14.00	14.15
				0.672	0.038	12.78	12.68		12.55	12.84

				0.795	0.179	10.63	10.54	10.71	10.95
Nitrous oxide	N ₂ O	309.5	71.7	0.786	0.185	10.00	9.68	10.20	
				0.882	0.436	8.03	8.36	8.59	
				0.890	0.874	4.32	3.28	3.82	
Carbon monoxide	CO	134.0	35.0	0.604	0.029	11.10	10.53	11.04	
Hydrogen sulfide	H ₂ S	373.4	88.9	0.566	0.011	12.40	12.08	12.00	
Hydrogen chloride	HCl	324.4	81.6	0.580	0.012	12.62	11.93	12.35	
Tin chloride	SnCl ₄	591.7	37.0	0.650	0.027	13.12	13.35	13.20	

Discussion and Conclusion

Above table shows that the error of this equation is generally less than 5%, and the accuracy is not less than that given by any previous method. This equation also possesses several advantages: (1) It can be used to determine the molal latent heat of vaporization of any substance at any temperature without a reference value. (2) Without referring to any chart in order to obtain S_v or compressibility factors, etc. (3) Watson's, Gordon's, Othmer's and Meissner's relationship may be included in this simple equation.

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ABSTRACT

A generalized equation, $\frac{\lambda}{T_c} = -6.7 \log p_r \frac{T_r}{(1-T_r)^{0.62}}$ is derived to calculate the molal latent heat of vaporization, λ , of any substance at any reduced temperature, T_r , and reduced pressure, p_r , with an error generally less than 5%.