



Study Based on Excel and MATLAB Software for Bubble and Dew Point Calculation of Low-Pressure Mixtures

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Abstract. Bubble and dew point calculation is an important part of the chemical thermodynamics course and an essential skill for chemical engineering students in future work research. At present, only the relevant calculation methods of bubble and dew point are introduced in the textbooks of chemical thermodynamics, and there is a lack of specific practice for practical problems. In view of the problems and needs of students in the calculation of bubble and dew point in the course, this article starts from the specific practice of bubble and dew point temperature calculation, and introduces in detail the use of MATLAB and Excel software platform to calculate the bubble point temperature and dew point temperature of mixtures at low pressure. Excel calculations are simple and easy to teach and demonstrate. The MATLAB programming approach is close to modern times and helps to develop students' practical ability. Through specific case applications, it can not only be applied to teachers' teaching demonstrations to help college teaching create high-quality classroom effects, but also guide students' after-class practice, so that students can fully master the calculation of bubble and dew point and solve the actual calculation in engineering.

Keywords: Bubble and dew point calculation · Chemical thermodynamics · MATLAB

1 Introduction

When a liquid is heated, the temperature at which the first bubble begins to be produced is called the bubble point. At this point, the solution is in gas-liquid equilibrium, and as the heating continues, the temperature increases until the temperature at the last droplet is called the dew point. The calculation of bubble dew point is the basis of chemical thermodynamics vapor-liquid phase equilibrium calculation, and is very important for the calculation of multi-component distillation separation in separation engineering.

There are four main types of studies on bubble dew point, namely, bubble point temperature, bubble point pressure, dew point temperature and calculation of dew point pressure. The procedure for calculating bubble dew point pressure is simple and detailed in the textbook. The calculation of bubble and dew point temperature is more tedious

and requires assignment and multiple iterations, but the textbook only talks about the calculation method in general and gives a block diagram [1, 2], where the details of the calculation need to be programmed, calibrated and executed to show. This detailed process is not shown in the book due to the limitation of space and learning time, which may lead to the students' learning of this part of the solidity will be compromised. We have tried to perform complex calculations of chemical thermodynamics using MATLAB software and Excel spreadsheets in our learning inquiry. Based on the understanding of the basic principles, we input the known quantities and calculation formulae into each cell of the spreadsheet, we can easily get the results of certain complicated calculations; We have programmed with MATLAB. We obtain the results and deepen our understanding of the principles and knowledge of the calculations with continuous corrections This process is interesting, full of the joy of inquiry, and the degree of difficulty is suitable for most students, so the teacher can demonstrate and stimulate students' learning initiative, and students can take the initiative to explore and enhance their practical skills and understanding in learning.

In view of the features such as the simplicity of Excel calculation, easy operation and convenient teaching, and the closeness of MATLAB to the times, which can develop students' programming skills, this paper iteratively calculates the bubble dew point temperature of low pressure non-ideal system based on MATLAB and Excel software, which extends the selectivity of the calculation and makes its computational process more flexible.

2 Principle of Calculating Bubble Dew Point Temperature Under Low Pressure

2.1 Calculation of Bubble Point Temperature at Low Pressure

The bubble point is the critical point at which the temperature of the first bubbles separated from the liquid phase. The pressure of the first bubbles separated from the liquid phase at a certain temperature, or the temperature of the first bubbles separated from the liquid phase at a certain pressure. The calculation of the bubble point temperature is detailed in the following equations [1–3], and the block diagram of the calculation procedure is shown in Fig. 1.

$$T_i^s = \frac{B_i}{A_i - \ln p} - C_i \quad (1)$$

$$T = \sum x_i T_i^s \quad (2)$$

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left(-\frac{g_{ij} - g_{ii}}{RT}\right) \quad (3)$$

$$\ln \gamma_i = 1 - \ln \sum_j x_j \Lambda_{ij} - \sum_{k=1}^N \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \quad (4)$$

$$\lg P_i^S = A_i - \frac{B_i}{t + C_i} \quad (5)$$

$$y_i = \frac{P_i^S \gamma_i x_i}{p} \quad (6)$$

- (i) When T is unknown, use Eq. (1) to calculate the saturation temperature of each component at atmospheric pressure, and then calculate the assumed initial temperature T using Eq. (2);
- (ii) Find the Antoine constants A_i , B_i , C_i from the literature in Appendix 4 of the chemical thermodynamics textbook, and calculate the saturation vapor pressure of the component according to Eq. (5).
- (iii) Knowing T, x_i , an activity coefficient model is chosen (Wilson's equation is used here) and γ_i can be calculated from Eqs. (3) and (4). If the constants of this model are unknown, first find the constants;
- (iv) Knowing p (low pressure), let $\alpha_i = 1$;
- (v) Calculate y_i from Eq. (6) respectively;
- (vi) Calculate $\sum_i y_i$, and determine whether it is close to 1;
- (vii) If the first judgment is "Yes", it means that the temperature is the required one, and the calculated y_i is also the required result, and the calculated value can be output.
- (viii) If the first judgment is "NO", it means that the calculated y_i is not normalized, and the temperature needs to be recalculated and the calculation steps of 1–6 are repeated until it is close to 1.

2.2 Dew Point Temperature Calculation Under Low Pressure

Dew point is the temperature at which the air cools to saturation under the condition that the water vapor content in the air remains unchanged and the air pressure is maintained, called the dew point temperature. Dew point temperature calculation is detailed in the following formula, the calculation procedure shown in Fig. 2.

$$K_i = \gamma_i^* p_i^s / p \quad (7)$$

$$x_i = y_i / K_i \quad (8)$$

$$\sum \frac{y_i}{K_i} \approx 1 \quad (9)$$

- (i) Assume a temperature T and choose any one K component such that each $\gamma_i = 1$;
- (ii) Calculate the saturation vapor pressure of each substance from the Antoine equation, as shown in Eq. (5);
- (iii) Use Eq. (7) to find the vapor-liquid equilibrium ratio K_i of each component, and from Eq. (8) to invert the liquid phase molar fraction x_i of component i ;

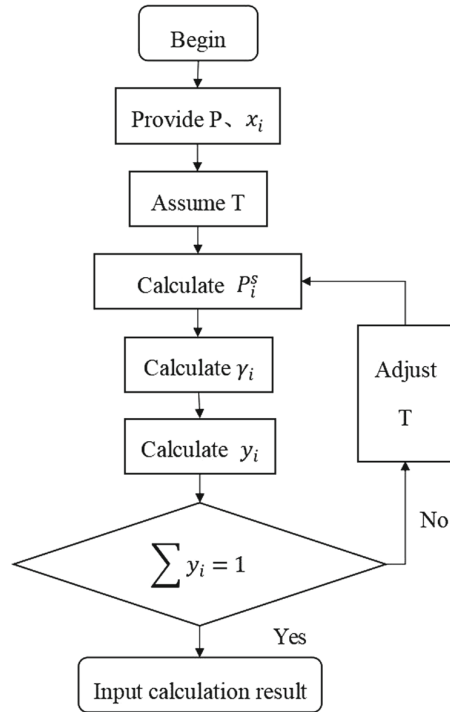


Fig. 1. Block diagram of bubble point temperature calculation procedure

- (iv) Further use the activity calculation equation, Eqs. (3) and (4) to solve for the respective activity coefficients γ_i of the components and use Eq. (7) to calculate the vapor-liquid equilibrium ratio K_i ;
- (v) If $\sum y_i/K_i \approx 1$, the normalization condition is met and the trial difference is over, and the original assumed temperature T is the saturation dew point temperature of the system; If the normalization condition determines that the result is greater than one, the assumed temperature needs to be increased and a new round of trial difference is conducted, and vice versa.

3 Case Analysis

3.1 Calculation of Bubble Point Temperature

For the methanol (1) water (2) binary mixture system at 101.325 kPa and $x_1 = 0.2$, solve for the bubble point temperature and vapor phase composition in this state [4–7].

$$V_1^L = 64.509 - 0.19716T + 3.8738 \times 10^{-4}T^2 \quad (10)$$

$$V_2^L = 22.888 - 0.03642T + 0.6857 \times 10^{-4}T^2 \quad (11)$$

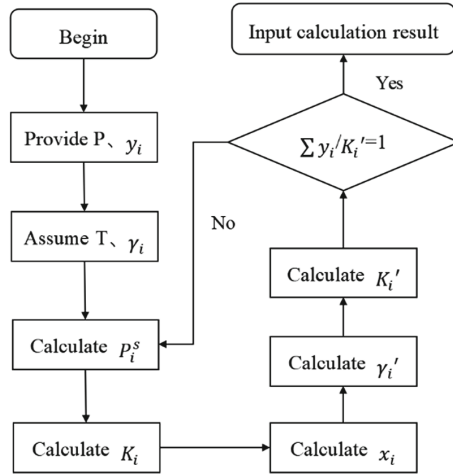


Fig. 2. Block diagram of dew point temperature calculation procedure

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left(-\frac{g_{12} - g_{11}}{RT}\right) \tag{12}$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left(-\frac{g_{21} - g_{22}}{RT}\right) \tag{13}$$

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} + \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \tag{14}$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) - x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \tag{15}$$

3.1.1 Using Excel to Find the Bubble Point Temperature

I. Detailed calculation steps

(i) Find out the Antoine constants of methanol and water and write them into Excel tables B1 to B6, and also write the known total pressure and liquid phase composition into Excel tables B7 to B9.

(ii) Calculate the initial temperature according to Eqs. (1) and (2), and fill it into Excel table E1, and convert the units and fill the resulting temperature into table E2.

(iii) The formula (3) will be translated into the format required by Excel “= B1 – B2/(E1 + B3)” and “= B4 – B5/(E1 + B6)”, fill in the form B10 and B12, respectively, to calculate the logarithmic value of the saturation vapor pressure of the two components.

(iv) Find the relationship between the molar volume of pure methanol and aqueous liquid phase and the temperature of (4) and (5), respectively converted into Excel format

“= 64.509 - 0.19716 * E2 + 3.8738 * 0.0001 * E2 * E2” and “= 22.888 - 0.0364 * E2 + 0.6857 * 0.0001 * E2 * E2”, filled in the table B14 and B15, respectively, to calculate their liquid phase molar volume.

(v) Find the energy interaction coefficients used by the material system to calculate the parameters of Wilson’s equation and fill in cells D16 and D17.

(vi) Translate the formulas (5) and (6) into the format required by Excel “= B15/B14 * EXP(-B16/(8.314 * E2))” and “= B14/B15 * EXP(-B17/(8.314 * E2))” into cells B18, B19, in order to calculate the two components Wilson coefficient.

(vii) Translate (7) and (8) into the format required by Excel into cells B20 and B21, in order to calculate the logarithmic value of the liquid phase activity of the two components, that is, “= -LN(B8 + B9 * B18) + B9 * (B18 / (B8 + B9 * B18) - B19 * B18) - B19 / (B9 + B8 * B19)” and “= -LN(B9 + B8 * B19) - .B8 * (B18 / (B8 + B9 * B18) - B19 / (B9 + B8 * B19))”.

(viii) Calculate the gas phase composition of the two components according to Eq. (9) and fill in the forms B24 and B25, respectively, in the form of specific Excel formulas “=B11*B22*B8/B7” and “=B13*B23*B9/B7”.

Take the deviation between the gas phase composition and 1 as the “target cell”, that is, B26 where the table is located. In the planning solution, make the “target cell” take zero value and select the system temperature E1 for the “variable cell”. Click on the solution button, the result of bubble point temperature is 355.8 K, the gas phase composition of $y_1 = 0.5632$, $y_2 = 0.4369$, at this time $|y_1 + y_2 - 1| = 0.0001$, to meet the accuracy conditions. After normalizing y , $y_1 = 0.5631$ and $y_2 = 0.4369$.

II. Calculation results

The data is substituted into the Excel table to calculate the following results. Through the continuous adjustment of the temperature, we gradually adjust the accuracy from the initial 0.001 to the high accuracy of 0.00001, as shown in Table 1, and finally determine the bubble point temperature of this system is 355.79853 K.

3.1.2 Using Matab Programming to Solve

The bubble point calculation by direct programming of the bubble point equation is actually solving the above system of equations, which has a total of $N + 1$ equations and $N + 1$ variables, so the system of equations has a unique solution. Based on the system of equations, the block diagram of the program shown in Fig. 1 is designed, and the program is written in MATLAB software (see Appendix for MATLAB code details), and the results are run as shown in Fig. 3. Therefore, the bubble point temperature of this binary system is 355.79 K [8, 9].

3.2 Calculation of Dew Point Temperature

For a two-component mixture of ethyl acetate (1)-ethanol (2), we calculate the dew point temperature at 101.325 kPa with known liquid phase composition $x_1 = 0.8$, $\Lambda_{12} = 0.144$, $\Lambda_{21} = 0.170$ for this composition.

Table 1. High-precision Excel calculation results

A ₁	7.1339	V ₁ ¹	43.39920056
B ₁	1541.861	V ₂ ¹	18.61027166
C ₁	236.154	g ₁₂ -g ₁₁	1085.13
A ₂	7.0641	g ₂₁ -g ₂₂	1631.04
B ₂	1650.4	Λ ₁₂	0.297137678
C ₂	226.27	Λ ₂₁	1.343593937
x ₁	0.2	lnγ ₁	0.36351447
x ₂	0.8	lnγ ₂	0.049210437
lgP ₁ ^s	2.297486001	γ ₁	1.43837567
P ₁ ^s	198.3745713	γ ₂	1.050441379
lgP ₂ ^s	1.721591019	y ₁	0.563211758
P ₂ ^s	52.67335956	y ₂	0.436853898
ly₁ + y₂-1l		6.56557E-05	

T:355.27K, y1=0.5535, y2=0.4278
 T:355.31K, y1=0.5542, y2=0.4285
 T:355.35K, y1=0.5549, y2=0.4291
 T:355.39K, y1=0.5557, y2=0.4298
 T:355.43K, y1=0.5564, y2=0.4305
 T:355.47K, y1=0.5571, y2=0.4312
 T:355.51K, y1=0.5579, y2=0.4319
 T:355.55K, y1=0.5586, y2=0.4326
 T:355.59K, y1=0.5594, y2=0.4333
 T:355.63K, y1=0.5601, y2=0.4339
 T:355.67K, y1=0.5608, y2=0.4346
 T:355.71K, y1=0.5616, y2=0.4353
 T:355.75K, y1=0.5623, y2=0.4360
 T:355.79K, y1=0.5631, y2=0.4367
 After iteration T:355.79K, Σyi=0.9998, y1=0.5632, y2=0.4368>>

Fig. 3. MATLAB run results

$$\ln p_1^s = 21.0444 - 2790.50/(T - 57.15) \tag{16}$$

$$\ln p_2^s = 23.8047 - 3803.98/(T - 41.68) \tag{17}$$

$$K_1 = \frac{\gamma_1 P_1^s}{P} \tag{18}$$

$$K_2 = \frac{\gamma_2 P_2^s}{P} \tag{19}$$

$$x_1 = \frac{y_1}{K_1} \quad (20)$$

$$x_2 = \frac{y_2}{K_2} \quad (21)$$

$$\ln \gamma_1' = \frac{\Lambda_{12}}{\left(1 + \frac{\Lambda_{12}x_1}{\Lambda_{21}x_2}\right)^2} \quad (22)$$

$$\ln \gamma_2' = \frac{\Lambda_{21}}{\left(1 + \frac{\Lambda_{21}x_2}{\Lambda_{12}x_1}\right)^2} \quad (23)$$

$$K_1' = \frac{\gamma_1' P_1^S}{P} \quad (24)$$

$$K_2' = \frac{\gamma_2' P_2^S}{P} \quad (25)$$

$$\sum \frac{y_i}{K_i'} = \frac{y_1}{K_1'} + \frac{y_2}{K_2'} \quad (26)$$

3.2.1 Using Excel to Find the Dew Point Temperature

I. Detailed calculation steps

(i) Assume the system temperature T , the activity coefficients γ_1 and γ_2 of the liquid phase of ethyl acetate and ethanol are written into cells B2–B4 of the Excel table, and the known Van Laar parameters, system pressure and molar fraction y_1 and y_2 of the two substances are filled into the Excel table B7–B11.

(ii) The Antonii equation, i.e., Eqs. (16), (17), is filled in B20 and B21 in the form required by Excel to obtain the saturation vapor pressure p_1^s and p_2^s of ethyl acetate and ethanol at the assumed temperature. e.g., Eq. (16) is filled in: “=21.0444–2790.50/(T-57.15)” in B20.

(iii) Translate (18)–(21) into the format required by Excel and fill in the corresponding cells to obtain the vapor-liquid equilibrium ratio K_i of the two components and the molar fraction x_i in the liquid phase, such as ethyl acetate K_1 and x_1 are translated as: “=B3*B22/B9” and “=B10/B24”, respectively, into cell B24, B26.

(iv) Using the formula (22)–(25), it will be coded into the Excel cell according to the corresponding algorithm to calculate the activity coefficient γ_1' , γ_2' of the liquid phase of the two substances, and further deduce the vapor-liquid equilibrium ratio K_i' . Taking ethanol as an example, its $\ln \gamma_2'$, γ_2' and K_2' are translated in order according to the algorithm as “=B8/(1 + (B8*B27/B7/B26))^2”, “=EXP(B29)” and “=31*B23/B9”, fill in the cells B29, B31 and B33.

Table 2. Excel final calculation results

Assump T/k	349.8412	K_1	0.983853236
Assump γ_1	1	K_2	0.936587882
Assump γ_2	1	x_1	0.813129409
Λ_{12}	0.144	x_2	0.213541093
Λ_{21}	0.17	$\ln\gamma_1$	0.008065185
Pressure p/pa	101325	$\ln\gamma_2$	0.099056803
y_1	0.8	γ_1'	1.008097796
y_2	0.2	γ_2'	1.104129016
$\ln p_1^s$	11.50980991	K_1'	0.991820279
$\ln p_2^s$	11.46057653	K_2'	1.034113856
p_1^s /pa	99688.92914	p_2^s /pa	94899.76713
$\Sigma y_i/K_i'$	1.000000046		

(v) Verify the assumed temperature by normalization. Normalization conditions are shown in Eq. (26), which is translated as: “=B10/B32 + B11/B33” as needed. Fill in cell B34 If the calculation result is 1, the original assumed temperature T is the dew point temperature of the system; If the calculation result is greater than 1, it is necessary to select a temperature higher than the original assumed temperature T for a new round of trial and error and vice versa.

II. The calculation results

For this two-component system, the normalized result from the room temperature of 298.15 K starts with a large deviation from 1, and the assumed temperature is increased for each trial. After several trial differences, when the assumed temperature is taken as 349.8412 K, as shown in Table 2, the normalized result is 1.000000046 \approx 1, so the dew point temperature of this two-component system is 349.841208 K.

When $\Sigma y_i/K_i' \approx 1$, it means that the temperature is dew point temperature.

3.2.2 Using MATLAB Programming to Solve

We have written the calculation method in 1.2 in MATLAB software as a program language according to the program block diagram shown in Fig. 2, and then run it as shown in Fig. 4. The temperature after iteration is 349.9 K, and the comparison with the Excel calculation shows that the two are basically equal. Therefore, the two methods corroborate each other and are in the same way.

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T:348.3 K,  $\Sigma y_i/k_i = 1.053569$   
T:348.4 K,  $\Sigma y_i/k_i = 1.049954$   
T:348.5 K,  $\Sigma y_i/k_i = 1.046354$   
T:348.6 K,  $\Sigma y_i/k_i = 1.042768$   
T:348.7 K,  $\Sigma y_i/k_i = 1.039197$   
T:348.8 K,  $\Sigma y_i/k_i = 1.035641$   
T:348.9 K,  $\Sigma y_i/k_i = 1.032100$   
T:349.0 K,  $\Sigma y_i/k_i = 1.028573$   
T:349.1 K,  $\Sigma y_i/k_i = 1.025061$   
T:349.2 K,  $\Sigma y_i/k_i = 1.021563$   
T:349.3 K,  $\Sigma y_i/k_i = 1.018080$   
T:349.4 K,  $\Sigma y_i/k_i = 1.014611$   
T:349.5 K,  $\Sigma y_i/k_i = 1.011156$   
T:349.6 K,  $\Sigma y_i/k_i = 1.007715$   
T:349.7 K,  $\Sigma y_i/k_i = 1.004289$   
T:349.8 K,  $\Sigma y_i/k_i = 1.000876$   
T:349.9 K,  $\Sigma y_i/k_i = 0.997478$   
after iteration T:349.9 K,  $\Sigma y_i/k_i = 0.997478$ 
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Fig. 4. Dew point temperature calculation results

4 Conclusion

The current chemical thermodynamics textbooks on bubble dew point calculation lack specific practice for practical problems. In this paper, starting from the specific practice of bubble dew point calculation, we introduce in detail the use of MATLAB software and Microsoft spreadsheet Excel to calculate the bubble temperature, bubble pressure and dew point temperature of mixtures at low pressure [10–12]. In view of the advantages that Excel calculation is simple and clear, convenient for teaching and demonstration, and MATLAB programming method is close to the times and good for students' practical ability cultivation, this paper uses two methods for calculation. The steps are well organized, simple and easy to understand not only for teachers' teaching demonstration and students' practice after class, but also for practical calculations in engineering.

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