Calculation of Carbon Dioxide Solubility in Liquefied Natural Gas

Taotao SHEN, Wensheng LIN

Abstract-It is important to evaluate the solubility of solid carbon dioxide in liquefied natural gas for natural gas liquefaction at relatively high temperature. The regular solution method and the equations-of-state (EOS) are used to calculate the solubility of carbon dioxide in saturated liquid methane in this paper. The calculation results are compared with the experiment data, and it certifies that the EOS method can be recommended for this kind of solubility calculation. In addition, nitrogen and ethane are common components in natural gas. In this paper, PR EOS is selected to calculate the solubility of carbon dioxide in CH₄+N₂ and CH₄+C₂H₆ mixtures. Results show that the solubility of carbon dioxide in liquid CH₄+N₂ mixtures increases with the addition of nitrogen content in the relatively low temperature region (lower than 155K). With the temperature increases, the solubility of carbon dioxide decreases with the increase of nitrogen content. While in liquid CH₄+C₂H₆ mixtures, it increases with the increase of ethane content.

Index Terms—carbon dioxide, equation-of-state, liquefied natural gas (LNG), solubility.

I. INTRODUCTION

Oceans are rich in natural gas resources, and the reserves of which are about 1/3 of the Global total quantity. LNG technology is considered the most promising options among the lots of offshore natural gas programs, as the volume of natural gas will reduce to 1/ 600 after liquefaction. However, the high cost of offshore platforms limit the practical application of liquefied natural gas plants. Accordingly, reducing the area of LNG plants will be the key of the maritime LNG plant[1]-[3].

Carbon dioxide is a common impurity in natural gas. When its concentration is too high, it will form solid phases which would cause blockage of pipelines, heat exchangers, etc. As a result, stability and safety of the plants will be threatened. So it is very important to predict the solubility of carbon dioxide in natural gas before designing and operating of the whole system. The greater solubility of carbon dioxide in LNG, the less solid phases will be precipitated. When the solid phase formation amount to zero, it will be possible to cancel the pretreatment plant of CO₂. It will substantially reduce the investment and the area of the whole system[4]-[6] which make the offshore plants practical.

Currently, only a few papers studied about calculating the solubility of carbon dioxide in cryogenic liquids, such as

liquid nitrogen, liquid oxygen or LNG. In 1940, Fedorova calculated the solubility of carbon dioxide in liquid oxygen and in liquid nitrogen according to ideal solution theory. At the same time, he did some experiments and found that the theoretical calculations are more than 100 times larger than the experimental values[7]. In 1962, Davis et al performed a series of experiments on the methane-carbon dioxide system and got the solubility of carbon dioxide in methane at different temperatures[8]. Most of these researchers are experts in the field of chemistry, who were focus on a variety of experimental methods of solubility determination.

Li from Zhejiang University used the regular solution method and modified Scatchard-Hildebrand relation in her PhD thesis to calculate the solubility of carbon dioxide in liquid nitrogen and liquid oxygen, and obtained good results[9]. As liquid methane is a cryogenic non-polar liquid similar with liquid nitrogen and liquid oxygen, similar method has been imitated in the calculation of the solubility of carbon dioxide in the saturated liquid methane in this paper. Additionally, simple cubic equations-of-state has been widely used in non-polar fluid phase equilibria calculations. In 2006, ZareNezhad and Eggeman[10] used PR EOS to predict CO₂ freezing points of hydrocarbon liquid and vapor mixtures at cryogenic conditions of gas plants. The overall average absolute relative deviation between the experimental and predicted CO₂ freezing temperatures for this binary system is 0.26%. So EOS method is selected for the solid-liquid phase equilibria calculation in this paper.

II. CALCULATING METHOD

A. Regular Solution Method

1) Basic principle.

The solubility of solid in cryogenic liquid involves principle of thermodynamics and physical chemistry, and especially at special low temperature, solubility of solute in the solvent also related to the calculation of activity coefficient of actual solution. Firstly, we are concerned with solid-liquid equilibria for which the solid phase is pure solute and the liquid phase is a saturated solution of the solute in the solvent. For such systems the equation of equilibrium is

$$f_2^s = \gamma_2 x_2 f_2^L \tag{1}$$

where subscript 2 refers to the solute, f^s is the fugacity of pure solid, f^L is the fugacity of pure liquid, x is the mole

fraction in solution, and γ is the activity coefficient.

Then, according to the Gibbs free energy relationship, a basic equation can be obtained to estimate the solubility of solids in liquids.

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$$\ln \gamma_2 x_2 = \ln \frac{f_2^s}{f_2^L} = -\frac{\Delta H_m}{RT} \left(1 - \frac{T}{T_m} \right)$$

$$-\frac{1}{RT} \int_{T_m}^T \Delta C_p dT + \frac{1}{R} \int_{T_m}^T \frac{\Delta C_p}{T} dT$$
(2)

where ΔH_m is the fusion heat of solute, T_m is the fusion temperature of solute, and ΔC_p is the molar specific heat of the liquid solute minus that of the solid solute. If we make an assumption that ΔC_p is independent of temperature, Equation (2) becomes

$$\ln \gamma_2 x_2 = -\frac{\Delta H_m}{RT} \left(1 - \frac{T}{T_m} \right)$$

$$-\frac{\Delta C_p}{R} \left[1 - \frac{T_m}{T} + \ln \left(\frac{T_m}{T} \right) \right]$$
(3)

Equation (3) also can be simplified because effect of ΔC_p is very small.

$$\ln \gamma_2 x_2 = -\frac{\Delta H_m}{RT} \left(1 - \frac{T}{T_m} \right) \tag{4}$$

Therefore, in the case of fusion heat and fusion temperature are given, as long as the activity coefficients obtained, we can estimate the mole fraction of solid in liquid solubility.

2) Ideal solution equation.

Solubility in an ideal mixture can be calculated from Equations (4) upon assuming that $\gamma_2 = 1$.

$$x_2 = \exp\left[-\frac{\Delta H_m}{RT} \left(1 - \frac{T}{T_m}\right)\right]$$
(5)

where fusion heat of CO₂, $\Delta H_{m,CO_2} = 8616$ J/mol, and the fusion temperature of solute, $T_{m,CO_2} = 216.58$ K.

Fedorova estimated the solubility of carbon dioxide in liquid oxygen and in liquid nitrogen according to similar ideal solution theory and found that the theoretical calculations are more than 100 times larger than the experimental values. So for many systems of industrial interest, $\gamma_2 = 1$ is a bad assumption, we should find the actual solution formula.

3) Regular solution equation.

For nonpolar systems, an approximate method for obtaining liquid-phase activity coefficients is provided by Scatchard-Hildebrand equation for a binary system[11]:

$$\ln \gamma_2 = \frac{\nu_2^L A_{12} \Phi_1^2}{RT}$$
(6)

where v_2^L is the molar volume of the liquid solute, Φ_1 is the volume fraction of solvent in the solution, and A_{12} is the exchange energy density. The exchange energy density is related to the cohesive energy densities, C_{ii} , by

$$A_{12} = C_{11} + C_{22} - 2C_{12} \tag{7}$$

where C_{11} is the cohesive energy density of the solvent, C_{22} is that of the solute, and C_{12} is a cohesive energy density describing the intermolecular forces between solvent and solute. For C_{12} we use

$$C_{12} = \left(C_{11}C_{22}\right)^{1/2} \tag{8}$$

If we introduce the solubility parameter δ into (6), we obtain

$$\ln \gamma_{2} = \frac{V_{2}^{L} \left(\delta_{1} - \delta_{2}\right)^{2} \Phi_{1}^{2}}{RT}$$
(9)

where $\delta_1 = (C_{11})^{1/2}$ and $\delta_2 = (C_{22})^{1/2}$ are the solubility parameters of liquid solvent and solute respectively. And

$$\delta_i = \left(\frac{\Delta h^{evp} - RT}{v_i^L}\right)^{0.5} \tag{10}$$

where Δh^{evp} is molar evaporation enthalpy of liquid, v_i^L is molar volume of liquid.

Before calculation, we need to estimate liquid molar volumes and solubility parameters for the solute and the solvent.

4) Modified S-H equation.

Preston et al proposed an amendment to the intermolecular forces of the S-H equation[12],[13]:

$$C_{12} = (C_{11}C_{22})^{1/2}(1 - l_{12}) = \delta_1 \delta_2 (1 - l_{12})$$
(11)

where l_{12} is a constant of the order of $10^{(-2)}$, characteristic of a given solute-solvent pair, and, to a close approximation, independent of temperature and composition.

After substituting (1) into (2), we can get the modified S-H equation as follow:

$$\ln \gamma_2 = \frac{\nu_2^L \left[\left(\delta_1 - \delta_2 \right)^2 + 2l_{12} \delta_1 \delta_2 \right] \Phi_1^2}{RT}$$
(12)

Preston gives 25 parameters of the system at low temperature[12], in the calculation, we use his summary data for CO₂+CH₄ system, $l_{12} = -0.02$.

5) Empirical equation.

Equation (12) cannot be used to calculate solubility near the critical temperature of the solvent where the excess volume of mixing is not negligible as assumed by regular solution theory. Nevertheless, solubility in the critical region can be estimated if we make the reasonable assumption[12] that $\ln \gamma_2$ varies inversely with temperature at constant composition.

We first calculate $\ln \gamma_2$ at a lower temperature and then use the 1/T temperature dependence to calculate $\ln \gamma_2$ at other temperatures.

B. EOS Method

Equations-of-state (EOS) are the theoretical basis to estimate fluids' thermodynamic properties, which have many advantages. An EOS usually contains only a few parameters, it is simple in form with high calculation accuracy, and so on. Considering that EOS have been widely applied for both theoretical and engineering calculations, the very popular PR EOS and SRK EOS are selected for the solid-liquid phase equilibria calculation.In order to perform solid-fluid phase equilibria between a ternary fluid phase (species 1, 2 and 3) and a pure solid phase (species 2), one solves the fugacity balance for species 2 between the phases:

$$f_2^L(T, P, x_2) = f_2^s(T, P)$$
(13)

where subscript 1 refers to the solvent CH₄, subscript 2 refers to the solute CO_2 , subscript 3 refers to the solvent N_2 (or C_2H_6), f^s and f^l are the fugacity of pure solid and liquid, Respectively

According to the definition of fugacity coefficient, Equation 1 becomes

$$\phi_{2}^{L}Px_{2} = \phi_{2}^{s}P_{2}^{s} \exp\left(\frac{V_{2}(P - P_{2}^{s})}{RT}\right)$$
(14)

where x_2 is the mole fraction of CO₂ in liquid phase, ϕ_2^L the liquid phase partial fugacity coefficient for CO2, P the system pressure in Pa, P_2^s the saturated vapor pressure of solid CO₂ at system temperature in Pa, ϕ_2^s the fugacity coefficient of pure CO2 at system temperature, V2 the molar volume of solid CO₂.

With the simplification, we can obtain

$$x_{2} = \frac{\phi_{2}^{s} P_{2}^{s} \exp(V_{2} (P - P_{2}^{s}) / RT)}{\phi_{2}^{L} P}$$
(15)

where the fugacity coefficient ϕ can be evaluated using the EOS.

The linear regression analysis of experimental solid CO₂ vapor pressure data[14] in the form of $\ln P_2^s$ versus 1/T with the overall average absolute deviation (AAD) of 0.1% gives

$$P_2^s = 9.44 \times 10^8 \exp(-3108.2/T) \tag{16}$$

1) PR EOS [10]

We chose a standard form of PR EOS[15] for solid-vapor and solid-liquid equilibrium calculations, since it is widely used to model natural gas processing systems. This equation can be written as

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m (V_m + b) + b (V_m - b)}$$
(17)

$$z^{3} - (1-B)z^{2} + (A-3B^{2}-2B)z$$

$$-(AB-B^{2}-B^{3}) = 0$$
where $A = \frac{aP}{R^{2}T^{2}}, B = \frac{bP}{RT}$
(18)

To apply such an EOS to mixtures, mixing rules are used to calculate the values of a and b of the mixtures. Classical mixing rules are used in this study

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) = x_1^2 a_1 + x_2^2 a_2$$

+ $x_3^2 a_3 + 2x_1 x_2 (a_1 a_2)^{0.5} (1 - k_{12}) + 2x_1 x_3 (a_1 a_3)^{0.5}$ (19)
 $\cdot (1 - k_{13}) + 2x_3 x_2 (a_3 a_2)^{0.5} (1 - k_{32})$
$$b = \sum_{i=1}^{N} x_i b_i = x_1 b_1 + x_2 b_2 + x_3 b_3$$
 (20)

where

$$a_{i} = 0.45724 \frac{R^{2} T_{ci}^{2}}{P_{ci}} \left[1 + m_{i} \left(1 - \left(\frac{T}{T_{ci}} \right)^{0.5} \right) \right]^{2} ,$$

$$b_{i} = 0.0778 \frac{RT_{ci}}{P_{ci}} ,$$

$$m_{i} = 0.37464 + 1.5422 \omega_{i} - 0.26992 \omega_{i}^{2} ,$$

The mole fraction of component i is represented by x_i ,

 ω_i is the eccentric factor of component i. k_{ii} is the binary interaction parameter characterizing molecular interactions between molecules i and j, listed in TABLE I. k_{ii} between CH_4 and CO_2 is derived from ZareNezhad et al[10], and the rest data come from the software HYSYS.

CO₂ C₂H k CH₄ N₂ 0.0998+5.4835/T-36.134/T 0.036 CH 0.00224 CO_2 0.0998+5.4835/T-36.134/T² 0.036 N_2 0.00224 C_2H_6

Using the PR equation of state, the fugacity coefficient of a component in the mixture can be evaluated by the following equation:

$$\phi_{2}^{l} = \exp\left(\frac{\frac{b_{2}}{b}(z-1) - \ln(z-B)}{-\frac{A}{2\sqrt{2}B}\left(\frac{\overline{a_{2}}}{a} - \frac{b_{2}}{b}\right) \ln\left(\frac{z+(\sqrt{2}+1)B}{z-(\sqrt{2}-1)B}\right)}\right)$$
(21)

where
$$\frac{a_2 = 2x_1a_{12} + 2x_2a_2 + 2x_3a_{23} = 2x_2a_2}{+2x_1(a_1a_2)^{0.5}(1-k_{12}) + 2x_3(a_2a_3)^{0.5}(1-k_{23})}$$

2) SRK EOS [16]

Calculating solubility by the SRK EOS is similar to PR EOS, just a different form of equations.

The standard form of SRK EOS is

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$$=\frac{1}{V_m-b}-\frac{1}{V_m(V_m+b)}$$
(22)

It can also be written in cubic form

$$z^{3} - z^{2} + (A - B - B^{2})z - AB = 0$$
 (23)
where

hD

аD

$$A = \frac{dI}{R^2 T^2}, B = \frac{dI}{RT}$$

$$a_i = 0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} \left[1 + m_i \left(1 - \left(\frac{T}{T_{ci}} \right)^{0.5} \right) \right]^2,$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}},$$

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$$

So, using the SRK equation of state, the fugacity

coefficient of a component in the mixture can be evaluated by the following equation:

$$\phi_2^{\prime} = \exp\left(\frac{\frac{b_2}{b}(z-1) - \ln(z-B)}{-\frac{A}{B}\left(\frac{\overline{a_2}}{a} - \frac{b_2}{b}\right)\ln\left(1 + \frac{B}{z}\right)}\right)$$
(24)

where $a_2 = 2x_1a_{12} + 2x_2a_2$

And the fugacity coefficient of pure solid CO2 is as follows

$$\phi_2^s = \exp\left(z - 1 - \ln\left(z - B\right) + \frac{A}{B}\ln\left(1 + \frac{B}{z}\right)\right) \tag{25}$$

III. RESULTS AND DISCUSSION

A. Solubility of CO_2 in pure methane

The regular solution method and the equations-of-state are used to calculate the solubility of solid carbon dioxide in saturated liquid methane in this paper, including the results of the regular solution theory, modified S-H equation, an empirical equation, PR EOS and SRK EOS. The calculation results and the experimental data of Davis et al[8] are plotted in Fig. 1.



Fig. 1 Comparison of the solubility of solid carbon dioxide in saturated liquid methane

Firstly, we can draw a conclusion from Fig. 1 that the solubility of solid carbon dioxide in saturated liquid methane increases with temperature increasing.

As shown in the Fig. 1, both of the values by the regular solution method and the EOS method are very close to experimental data in the relatively low temperature region(Less than 130K). With the temperature increase, the results of EOS law are still a high degree of agreement with the experimental data. However, results derived from the regular solution method gradually deviate from the experimental values, which unexpectedly decrease with temperature increasing when the temperature is greater than 165K. At the same time, the empirical equation which is applied near the critical temperature begins to show the superiority as its results are very close to the experimental values.

To predict the solubility of CO_2 in liquid methane by the regular solution method is more accurate than the ideal solution hypothesis. Regular solution theory is fit for non-ideal and non-polar liquids, which is usually used to semi-quantitatively calculate the solubility of the system formed by two non-polar liquids. From the derivation of its definition, there must be some error because the force

between two molecules is replaced by a geometric mean.

Data derived from the modified S-H equation are closer to the experimental results than that by the regular solution method. l_{12} in (11) is a value obtained from the experiments. If we have more precise data, the results will be closer to reality.

It can also be seen from Figure 1 that data calculated by the regular solution method and the modified S-H equation decreased with temperature increasing when the temperature is higher than 165K, which is clearly anomalous. The reason is that when calculating the solubility of the solvent near the critical temperature, the excess volume of mixing is not negligible. Therefore, an empirical equation based the reasonable assumption is used near the critical temperature and a better result is obtained.

The predicted solubility of CO_2 in saturated methane by the PR EOS and SRK EOS are are very close to the experimental data with the average AAD of less than 5%. Obviously, these two widely used cubic equations of state can be recommended for this kind of solubility calculation..

B. Solubility of CO_2 in CH_4+N_2 and $CH_4+C_2H_6$ mixtures

PR EOS is used to calculate the solubility of solid carbon dioxide in liquid CH_4+N_2 and $CH_4+C_2H_6$ mixtures in this paper. The temperature range is 112K-170K, and the ratio of nitrogen or ethane in the mixture range from 0.5% to 20%. It should be noted that, addition of a component may be have a greater impact of the carbon dioxide solubility in pure methane, so more calculation are made in the low concentration of the additional component. The calculation results are shown in TABLE II and TABLE III.

For comparison, part of the representative data of the above two tables are plotted into Fig. 2.

Fig.2 indicates that the solubility of carbon dioxide in mixtures changes tiny with the addition of species 3 in the relatively low temperature region (lower than 130K). With the temperature increase, the existence of nitrogen or ethane in methane has a greater influence on the solubility of carbon dioxide.



Fig.2 Comparison of the solubility of solid carbon dioxide in liquid mixtures

As can be seen from TABLE II, when temperature is low than 155K, addition of nitrogen content in the methane will slightly increase the solubility of carbon dioxide in liquid CH_4+N_2 mixtures. On the contrary, the solubility of solid carbon dioxide decreases with the increase of nitrogen content when the temperature is higher than 155K. TABLE III shows that, in all temperature range, adding ethane in the methane will increase the solubility of carbon dioxide in liquid $CH_4+C_2H_6$ mixtures.

TABLE II SOLUBILITY OF SOLID CARBON DIOXIDE IN LIQUID CH_4+N_2 MIXTURES (MOLE FRACTION, $X_2 \times 10^3$)

Т	$x_{3}/(x_{1}+x_{3})$								
	0	0.005	0.01	0.02	0.03	0.05	0.1	0.2	
112	0.2138	0.2154	0.2170	0.2202	0.2235	0.2301	0.2465	0.2785	
116	0.3465	0.3487	0.3511	0.3558	0.3605	0.3699	0.3932	0.4368	
120	0.5443	0.5475	0.5508	0.5574	0.5639	0.5770	0.6086	0.6659	
124	0.8318	0.8361	0.8405	0.8494	0.8582	0.8756	0.9172	0.9889	
130	1.452	1.458	1.465	1.477	1.490	1.515	1.572	1.662	
135	2.409	2.417	2.425	2.442	2.459	2.491	2.563	2.660	
140	3.451	3.460	3.471	3.491	3.511	3.548	3.626	3.712	
145	5.202	5.212	5.224	5.247	5.269	5.309	5.386	5.423	
150	8.063	8.074	8.086	8.109	8.129	8.164	8.210	8.109	
155	11.19	11.20	11.21	11.22	11.24	11.25	11.24	10.93	
158	13.72	13.72	13.73	13.74	13.74	13.74	13.66	13.13	
160	15.66	15.66	15.67	15.67	15.66	15.64	15.50	14.80	
162	17.88	17.87	17.87	17.86	17.85	17.80	17.58	16.66	
165	21.56	21.55	21.54	21.51	21.47	21.38	21.01	19.68	
168	25.95	25.91	25.89	25.83	25.76	25.60	25.03	23.16	
170	29.03	29.00	28.96	28.87	28.78	28.57	27.85	25.56	

TABLE III SOLUBILITY OF SOLID CARBON DIOXIDE IN LIQUID $CH_4+C_2H_6$ mixtures (mole fraction, $x_2 \times 10^3$)

Т	x3/(x1+x3)								
	0	0.005	0.01	0.02	0.03	0.05	0.1	0.2	
112	0.2138	0.2159	0.2181	0.2224	0.2267	0.2353	0.2566	0.2981	
116	0.3465	0.3497	0.3531	0.3597	0.3664	0.3797	0.4125	0.4755	
120	0.5443	0.5493	0.5543	0.5645	0.5746	0.5946	0.6437	0.7370	
124	0.8318	0.8391	0.8467	0.8617	0.8767	0.9062	0.9782	1.114	
130	1.452	1.464	1.477	1.503	1.528	1.577	1.697	1.919	
135	2.409	2.429	2.450	2.491	2.532	2.612	2.805	3.155	
140	3.451	3.480	3.510	3.569	3.627	3.741	4.012	4.499	
145	5.202	5.246	5.291	5.380	5.468	5.639	6.044	6.760	
150	8.063	8.134	8.206	8.348	8.486	8.756	9.385	10.48	
155	11.19	11.29	11.39	11.60	11.79	12.18	13.06	14.58	
158	13.72	13.84	13.98	14.23	14.48	14.96	16.07	17.93	
160	15.66	15.81	15.97	16.26	16.55	17.11	18.39	20.53	
162	17.88	18.05	18.24	18.58	18.92	19.57	21.06	23.52	
165	21.56	21.79	22.02	22.45	22.88	23.69	25.53	28.55	
168	25.95	26.23	26.51	27.07	27.60	28.62	30.91	34.61	
170	29.03	29.37	29.70	30.34	30.96	32.13	34.75	38.97	

IV. CONCLUSION

The regular solution method and the equations-of-state method are adopted to calculate the solubility of carbon dioxide in saturated liquid methane in this paper, and the results are compared with the experiment data from Davis. Additionally, The PR equations-of-state are adopted to calculate the solubility of carbon dioxide in liquid CH_4+N_2 and $CH_4+C_2H_6$ mixtures in this paper. The following conclusions are drawn from the results.

1) The solubility of carbon dioxide in LNG increases with temperature increasing. The increase becomes significant only when the temperature is higher than 130K. This means that a natural gas liquefaction process running at 145K may allow CO_2 content as high as 0.5%, much higher than the usual value of 50ppm for conventional process at 111K. Consequently, the CO_2 removal unit in an LNG plant may be minimized or even cancelled.

2) Results by the regular solution theory and the modified S-H equation are very close to experimental data when the temperature is lower than 130K. But this method will result in a great error in the relatively high temperature. So it is not suitable for solubility calculation of carbon dioxide in saturated liquid methane.

3) Results obtained from PR and SRK EOS are consistent with the experimental values in the whole temperature region, so these two EOS can be recommended for calculating the solubility. 4) The solubility of solid carbon dioxide in liquid CH_4+N_2 mixtures increases with the addition of nitrogen content in the relatively low temperature region (lower than 155K). But, when the temperature increases, the solubility of solid carbon dioxide decreases with the increase of nitrogen content.

5) The solubility of solid carbon dioxide in liquid $CH_4+C_2H_6$ mixtures increases with the increase of ethane content.

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