

# Experimental and Estimation of Vapor-Liquid Equilibria in Aqueous Electrolyte System: CO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub>-MDEA+DEA-H<sub>2</sub>O

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## Abstract

Absorption with chemical reaction process of CO<sub>2</sub> gas using K<sub>2</sub>CO<sub>3</sub> solution or known as hot potassium carbonate promoted with amine was widely used in many chemical industries. DEA and MDEA mixture was proposed as promoter. Vapor-liquid equilibrium (VLE) data of CO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub>-MDEA+DEA-H<sub>2</sub>O system are needed for rational design and optimal operation of CO<sub>2</sub> removal unit. The purpose of this research is to determine solubility data of CO<sub>2</sub> gas in aqueous solution of potassium carbonate with DEA and MDEA as a promoter at various temperatures of 30-50°C with 30% K<sub>2</sub>CO<sub>3</sub>, 1-3% MDEA and 1-3% DEA. The CO<sub>2</sub> solubility is very important property when establishing thermodynamics models for the VLE. In order to obtain the CO<sub>2</sub> solubility, the normal procedure is to use the N<sub>2</sub>O analogy since the CO<sub>2</sub> solubility cannot be directly measured. Solubility was measured volumetrically in absorption flask using a shaking waterbath. The increase of DEA concentration in solution gives higher Henry's constant or lower gas solubility. It also makes the empirical correlation between Henry's constant and temperature in various concentrations of MDEA and DEA. The results of N<sub>2</sub>O analogy experiment were used to calculate the vapor liquid equilibria of CO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub>-MDEA+DEA-H<sub>2</sub>O system by using the electrolyte NRTL model. The model gives a good representation of the experimental VLE data for CO<sub>2</sub> partial pressures with Root Mean Square Deviation (RMSD) of 5.93%.

**Keywords:** CO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub>-MDEA+DEA-H<sub>2</sub>O system, solubility, vapor-liquid equilibria, N<sub>2</sub>O analogy, electrolyte NRTL model

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is acid gas, and it is very harmful acid. Various industries such as petrochemical, fuel oil, and natural gas industries, require the separation process of CO<sub>2</sub> gas. One of the various methods widely used is the chemical absorption process using a basic alkanolamine solution as a solvent. The method is widely used for the removal of acid gases from natural gases. Conventionally, aqueous solutions of monoethanolamine (MEA) (Clarke, 1964; Liu et al., 1999), diethanolamine (DEA) (Li & Lee, 1996), and methyldiethanolamine (MDEA) (Haimour & Sandall, 1984) are examples of well-known and industrially important amine solutions.

In addition, knowledge of the amine solvent mixtures need to be developed continuously. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) has a low regeneration heat but the reaction rate is lower compared with the amine. Several studies have shown that blending with amines can accelerate the process of absorption (Savage et al., 1984; Cullinane & Rochelle, 2004; Thee et al., 2012).

To design a gas absorption unit, physical property such as solubility of acid gases in amine solvent is needed. Physical solubility measurements are generally carried out to determine the concentration of the absorbed gas in solution at equilibrium. If the absorbed gas react with the solvent, the equilibrium can not be physically measured. In other words, the physical solubility of CO<sub>2</sub> gas in alkanolamine can not be measured directly. Therefore, N<sub>2</sub>O analogy is often used to estimate the solubility of CO<sub>2</sub> gas in the amine solvent (Haimour & Sandall, 1984; Weiland & Browning, 1994).

A similar gas that is unreactive in the test solution was used to measure the solubility. Proportional constants are then used to calculate the solubility of CO<sub>2</sub>. Nitrogen oxide gas (N<sub>2</sub>O) was successfully used to predict the physical solubility of CO<sub>2</sub> because it has similarity in size, shape, and electron configuration of Lennard-Jones potential to CO<sub>2</sub> (Clarke, 1964).

The  $N_2O$  analogy is expressed in eq.1 (Haimour and Sandall, 1984):

$$\frac{H_{CO_2}}{H_{N_2O}} = \frac{H^{\circ}_{CO_2}}{H^{\circ}_{N_2O}} \quad (1)$$

where  $H^{\circ}_{CO_2}$  and  $H^{\circ}_{N_2O}$  are the Henry's law constants of  $CO_2$  and  $N_2O$  in pure water, while  $H_{CO_2}$  and  $H_{N_2O}$  are the Henry's law constants of  $CO_2$  and  $N_2O$  in amine solution.

There are several models that can be used to estimate the solubility of  $CO_2$  in the absorption process. The electrolyte NRTL model have been used to predict the solubility of  $CO_2$  in the removal of  $CO_2$  from flue gases using a mixture of potassium carbonate-piperazine-ethanolamine (Hilliard, 2005). The electrolyte UNIQUAC model was used to predict the solubility of acid gases in Monoethanolamine (MEA) and Methyldiethanolamine (MDEA) (Kaewsichan et al., 2001).

In the present study, the solubility data of  $CO_2$  in potassium carbonate solution with MDEA-DEA mixtures as a promotor using  $N_2O$  analogy were presented over the range of temperatures from 30 to 50 °C. Furthermore, the  $CO_2$  partial pressures obtained from experimental results were correlated using the E-NRTL model.

## 2. Method

The purpose of this research is to determine the solubility data of  $CO_2$  gas in aqueous solution of potassium carbonate with DEA-MDEA mixtures as a promotor at various temperatures of 30-50°C with 30%  $K_2CO_3$ , 1-3% MDEA and 1-3% DEA using the apparatus shown schematically in **Figure 1**. The apparatus is kept at constant temperature inside a temperature-controlled water bath. The densities of aqueous solutions were determined by using a 10-mL pycnometer. The measurement of the solubility data was conducted in an equilibrium cell with  $N_2O$  analogy method. The modified apparatus is based on that of used by Haimour and Sandall (1984). Some authors have also developed this method to estimate the solubility data of  $CO_2$  in various amine solutions (Versteeg & van Swaaij, 1988; Al-Ghawas et al., 1989; Versteeg et al., 1992; Wang et al., 1992; Weiland & Browning, 1994; Li & Lai, 1995; Li & Lee, 1996).

The principle of this method is to bring a certain volume of liquid into contact with a gas in a closed system at constant temperature and pressure. Equilibrium is reached by stirring the solution until there is no change in the volume of the gas. The volume of the gas absorbed is measured.

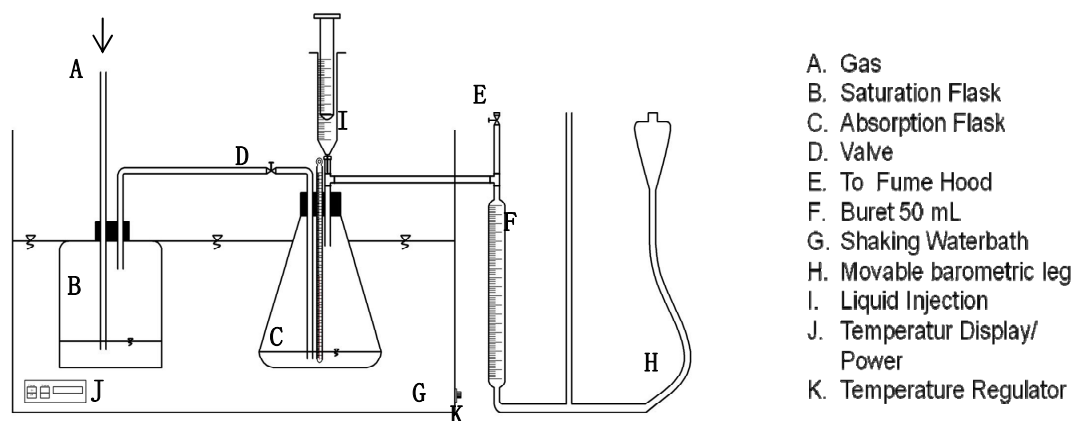


Figure 1. Solubility apparatus

The solubility measurements were carried out as follows: A gas saturated with vapors in a saturation flask was passed through the system to purge the absorption flask at constant temperature. Then the inlet and outlet valves were closed. The height of the liquid water in the three branches was leveled to indicate that the pressure in the flask was atmospheric, and its position was recorded. 20 mL sample of aqueous solution of  $K_2CO_3$ -MDEA+DEA was injected into the absorption flask. After mechanical shaking for 20 to 30 min, the surface of the water was maintained at the same level every few minutes, ensuring that the gas phase was at atmospheric pressure. The volume change of the system can be determined by the levels of the water in the burette. Equilibrium is reached when the volume of the gas remains constant. The volume of gas absorbed can be determined by the measured volume change and the volume of liquid sample.

After obtaining the data from the experiment, the partial pressure of  $CO_2$  was calculated using the E-NRTL model

for  $\text{CO}_2\text{-K}_2\text{CO}_3\text{-MDEA-DEA-H}_2\text{O}$  system. This model consists of two contributions. First, the local interaction showed from the interaction between all species. The second contribution is long-range ion-ion interaction appeared due to the interaction between ionic species (Austgen et al., 1989; Chen, 1993; Pitzer, 1980).

### 3. Results and Discussion

The validation of the apparatus used in this study was conducted by using water as a solvent. The validation refers to the results of previous experiments (Versteeg & van Swaaij, 1988; Al-Ghawas et al., 1989; Li & Lai, 1995) and was carried out at a temperature range of 30-50 °C.

Figure 2 shows the validation results of the apparatus representing the solubility data  $\text{N}_2\text{O}$  in water illustrated as Henry's constants of  $\text{N}_2\text{O}$  vs temperatures. From the figure it is also shown the solubility data from the literatures. It can be seen that the results found in this work are in good agreement with data of Versteeg & van Swaaij (1988) and Li & Lai (1995), but there is a significant deviation from data of Al-Ghawas et al. (1989).

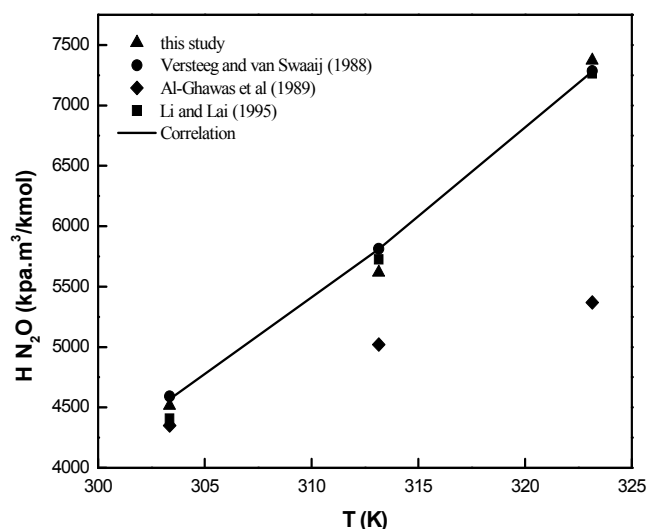


Figure 2. Solubility data of  $\text{N}_2\text{O}$  in water as a function of temperature

Physical solubility of  $\text{CO}_2$  in alkanolamine can not be directly measured. Therefore,  $\text{N}_2\text{O}$  analogy often used to estimate the solubility of  $\text{CO}_2$  in the amine solvent. In this study the solvent mixtures used are 30%  $\text{K}_2\text{CO}_3$ , 1-3% MDEA and 1-3% DEA with variation of temperatures in range of 30-50 °C. The solubility of  $\text{N}_2\text{O}$  and  $\text{CO}_2$  in  $\text{K}_2\text{CO}_3\text{+MDEA+DEA+water}$  system at this concentration is shown in **Figures 3 and 4**. It can be seen in **Figure 3** that the rise of temperature caused the increase of Henry's constant of  $\text{N}_2\text{O}$ .

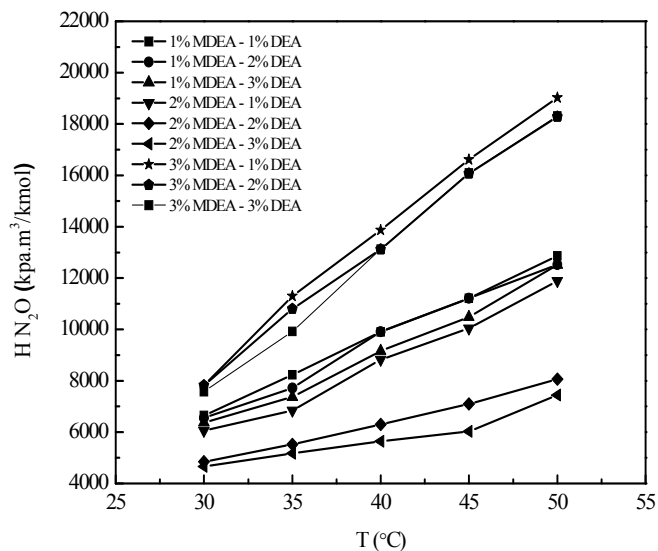


Figure 3. Solubility of  $\text{N}_2\text{O}$  in  $\text{K}_2\text{CO}_3\text{+MDEA+DEA+water}$  system for various compositions of MDEA-DEA at temperatures 30-50 °C

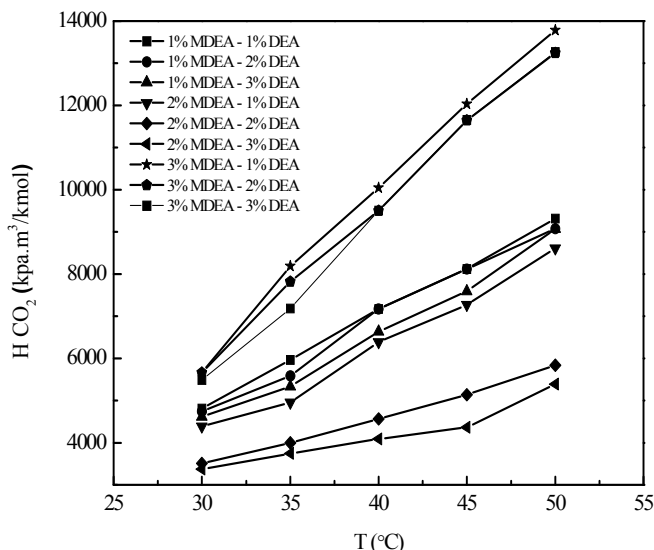


Figure 4. Solubility of CO<sub>2</sub> in K<sub>2</sub>CO<sub>3</sub>+MDEA+DEA+water system for various compositions of MDEA-DEA at temperatures 30-50 °C

Meanwhile, the solubility data of CO<sub>2</sub> (N<sub>2</sub>O analogy) at 30% K<sub>2</sub>CO<sub>3</sub>, 1-3% MDEA, and 1-3% DEA are shown in Figure 4. Physical solubility data of CO<sub>2</sub> were obtained from the equation correlated N<sub>2</sub>O analogy into the empirical equation (eq. 2) for various concentrations of MDEA and DEA.

$$H = K_1 \exp \frac{-K_2}{T(K)} \tag{2}$$

$$K_1 = 1,067 \times 10^{10} [MDEA]^{0.5089} [DEA]^{0.3875} \tag{3}$$

$$K_2 = 5754.896 [MDEA]^{0.149} [DEA]^{-0.00835} \tag{4}$$

The E-NRTL model was used to correlate the experimental data. The activity coefficients of CO<sub>2</sub> were calculated using the binary interaction parameters obtained by fitting the experimental data with the minimization of the deviation between calculated and experimental CO<sub>2</sub> partial pressures. The relationships between the calculated and experimental results of CO<sub>2</sub> partial pressure and CO<sub>2</sub> loading for CO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub>-MDEA+DEA-H<sub>2</sub>O system are presented in Figures 5-9.

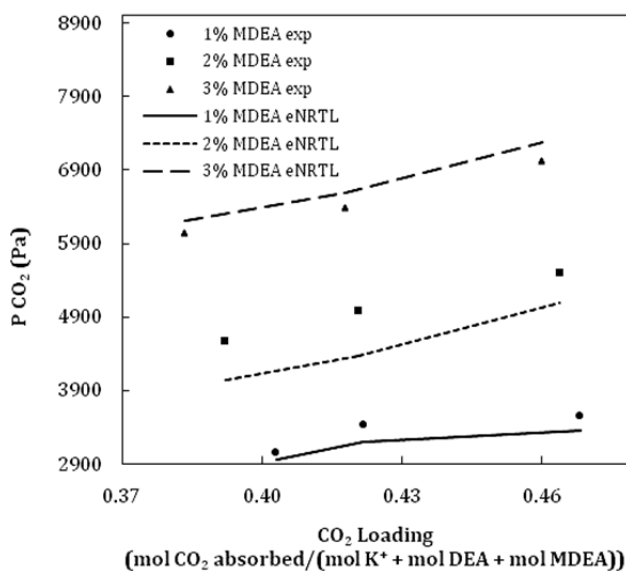


Figure 5. The relationship between the calculated and experimental CO<sub>2</sub> partial pressure and CO<sub>2</sub> loading with 30% K<sub>2</sub>CO<sub>3</sub>, 1-3% DEA and 1-3% MDEA at temperature 30 °C

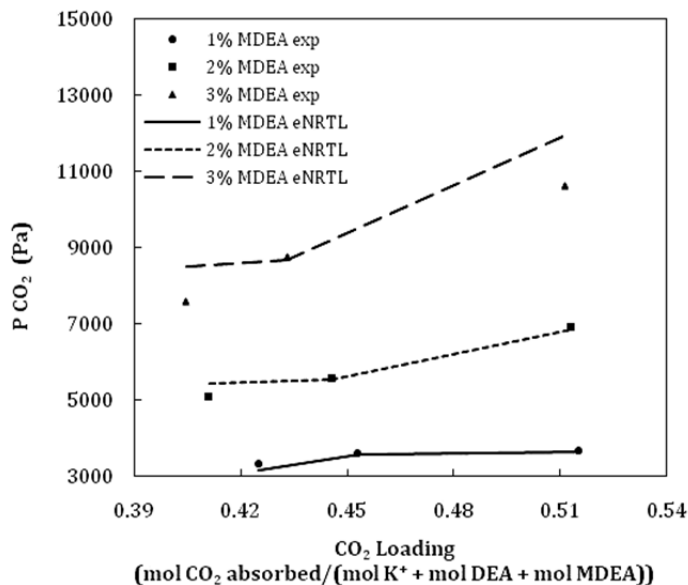


Figure 6. The relationship between the calculated and experimental  $\text{CO}_2$  partial pressure and  $\text{CO}_2$  loading with 30%  $\text{K}_2\text{CO}_3$ , 1-3% DEA and 1-3% MDEA at temperature 35 °C

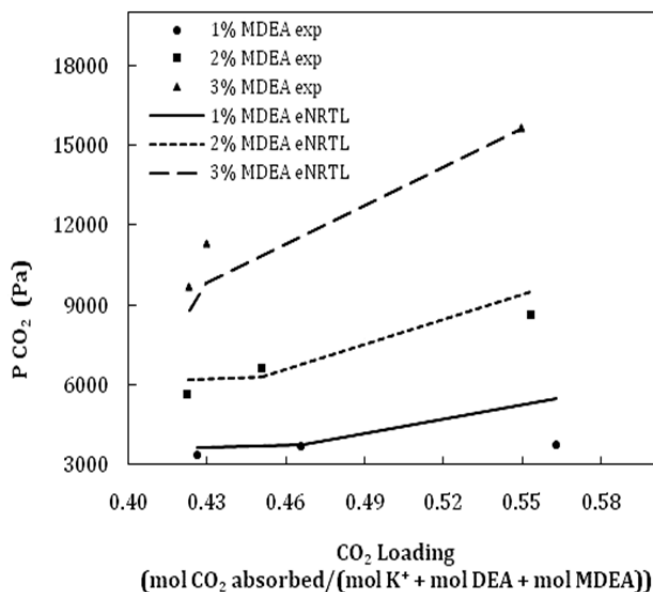


Figure 7. The relationship between the calculated and experimental  $\text{CO}_2$  partial pressure and  $\text{CO}_2$  loading with 30%  $\text{K}_2\text{CO}_3$ , 1-3% DEA and 1-3% MDEA at temperature 40 °C

In these figures, it can be seen that at constant temperature, the partial pressure of  $\text{CO}_2$  increases with the increase of  $\text{CO}_2$  loading. The addition of MDEA concentration of 1-3%, decreases  $\text{CO}_2$  loading. This indicates that the amount of  $\text{CO}_2$  dissolved in the solution is increased, and the partial pressure of  $\text{CO}_2$  will also be greater. From Figure 5-9, it can also be seen that the experimental results give a similar profile to those of the correlation. The addition of concentration of 1% MDEA and 3% DEA results in the smallest partial pressure of  $\text{CO}_2$ . The model gives a good representation of the experimental VLE data for  $\text{CO}_2$  partial pressures with Root Mean Squared Deviation (RMSD) of 5.93%.

From the description above, it can be concluded that Henry's Law constants have been obtained for the absorption of  $\text{CO}_2$  into a solution of 30%  $\text{K}_2\text{CO}_3$  with DEA-MDEA mixtures, through  $\text{N}_2\text{O}$  analogy. Effect of temperature rise in a solution of 30%  $\text{K}_2\text{CO}_3$ , 1-3% MDEA and 1-3% DEA over the temperature range 30-50 °C

can increase CO<sub>2</sub> loading and partial pressure of CO<sub>2</sub>. The model gives a good representation of the experimental VLE data for CO<sub>2</sub> partial pressures with Root Mean Squared Deviation (RMSD) of 5.93%.

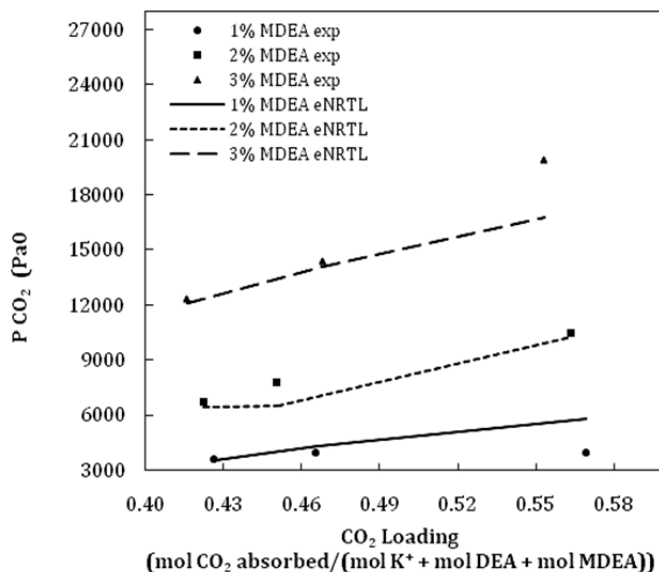


Figure 8. The relationship between the calculated and experimental CO<sub>2</sub> partial pressure and CO<sub>2</sub> loading with 30% K<sub>2</sub>CO<sub>3</sub>, 1-3% DEA and 1-3% MDEA at temperature 45 °C

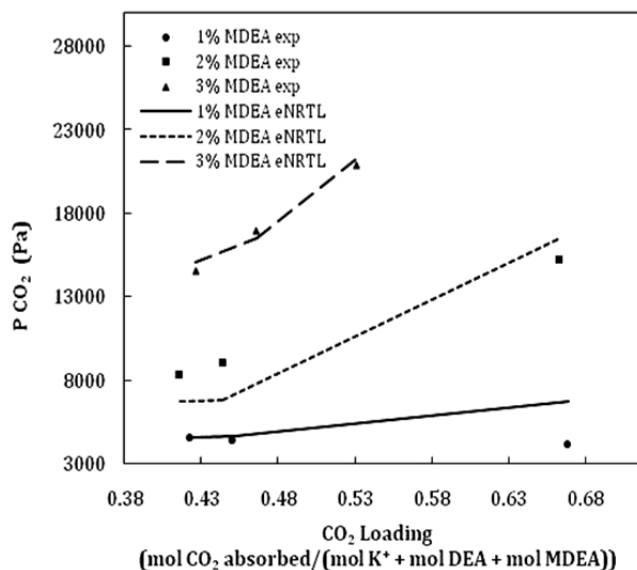


Figure 9. The relationship between the calculated and experimental CO<sub>2</sub> partial pressure and CO<sub>2</sub> loading with 30% K<sub>2</sub>CO<sub>3</sub>, 1-3% DEA and 1-3% MDEA at temperature 50 °C

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