Stabilizing Nitrous Oxide in Strong Nitric Acid for Industrial Purposes

Ahmed Mohammed Ibrahim, Hamid Mohamed Mustafa, and Babiker Karama Abdalla

***Abstract*—The nitrous oxide is determined by the content of (NO_x) in the strong nitric acid, the increase of nitrous oxide by the way of either acid decomposition or temperature modification [1], [2] influence the safe production of military products and environmental pollutions [3]. The required specifications of the acids should meet the requirement of desired industry and safety during the transportations from site to site and storage. If the specifications (nitrous oxide) changed rapidly during transportation, decomposition takes place. It is believed that the Sudanese ambient temperature plays the main role. The strong nitric acid that has been stored for long time and transferred away will thermally and catalytically decompose and specifications will change. This study aims to develop a set of preliminary guide lines and recommendations for stabilizing the nitrous oxide (HNO_2) in strong nitric acid. The equilibrium relations between acids systems (Nitrous oxide NOx expressed by "nitrous acid HNO_2 concentration" and strong nitric acid HNO_3) were reviewed and explained. The effects of Sudan ambient temperatures on acceleration of nitrous oxide (HNO_2) in strong nitric acid, determine the optimum cooling temperature to slow the decomposition and to stabilize the nitrous oxide were investigated. This is done through incubation of three samples of strong nitric acid (97.5%) at the temperatures 20°C, 25°C and 30°C. Laboratory analysis was done to observe the nitrous oxide exit rate as function of temperatures, concentration of strong nitric acid within four days, Table I, II, III and Fig. 2, 4, 6 show the obtained experimental data. A noticeable increase of nitrous oxide at respective temperatures (20 ^{0}C, 25 ^{0}C, 30 ^{0}C) at the beginning was observed then the curve levels after three days' incubation. It is concluded that (20^{0}C) is the higher temperature at which the strong nitric acid is either stored or transported. Hence it is the optimum temperature to slow the decomposition and stabilize the nitrous oxide. Recommendations for checking Strong Nitric Acid storage tank, transportation system design and design of a conventional jacket heat exchanger to cool nitric acid from (40 ^{0}C to 20 ^{0}C) were made.**

***Index Terms*—Nitrous Oxide; NOx; Strong Nitric Acid; Nitrous Acid; Stabilizing.**

I. INTRODUCTION

The decomposition of concentrated nitric acid is accelerated by temperature and radiolysis, thermal and radio lytic reactions result in the formation of redox active species (nitrous oxide) [2]. The nitrous oxides (NO_x) is particular concerned with strong or weak nitric acid, the effect of nitrous oxides (NO_x) exacerbated as are present on nitric acid system, so we need to understand what nitrogen species are present and nature of it. The equilibrium relations between acids systems (Nitrous oxide NO_x expressed by nitrous acid HNO_2 concentration" and strong nitric acid HNO_3) were review and explain below. Nitrogen can form several different oxides with oxygen are considered as a class and called nitrogen oxides "often denoted as "NO_x". The abbreviation NO_x usually relates to nitric oxide NO, nitrogen dioxide NO_2, and nitrous oxide N_2O [4],[5]. Very little are known about nitrogen trioxide (NO_3) or its dimeric form (N_2O_6).

N_2O Nitrous oxide is theoretically the anhydride of hypo nitrous acid ($H_2N_2O_2$), but the acid is not formed by the solution of nitrous oxide in water [7]. This gas has been used to provide pain and anxiety relief for patients undergoing surgical procedures [8]. Nitrogen monoxide also called nitric oxide, (NO) is a colorless, toxic, nonflammable gas at room temperature. As soon as it comes in contact with atmospheric oxygen, it is oxidized to nitrogen dioxide; nitrogen monoxide is at dynamic equilibrium with its dimer as [6]:

$$2NO_{(g)} \rightleftharpoons N_2O_{(g)} \tag{1}$$

Above oxide is generally considered to be the first oxidation product of nitrogen at high temperatures, however, the equilibrium is shifted all the way toward nitrogen monoxide and liquid nitrogen monoxide is completely dimerized. The oxidation of nitric oxide takes place in two stages, nitrogen trioxide first being formed, which is then further oxidized to nitrogen tetroxide as:

$$2NO_{(g)} + \frac{1}{2}O_{2\,(g)} \rightleftharpoons N_2O_3 \tag{2}$$

$$N_2O_3 + \frac{1}{2}O_{2\,(g)} \rightleftharpoons N_2O_{4\,(L)} \tag{3}$$

This shows that the possibility of existence of gaseous nitrogen trioxide must be considered; under ordinary condition nitrogen trioxide is almost completely dissociated into a mixture of nitric oxide and oxygen .When nitric oxide and nitrogen tetroxide are mixed as in(7) , or when the necessary theoretical proportion of oxygen is added to nitric oxide as in (6) , a gas is obtained which behaves as if it had the composition denoted by the formula (N_2O_3) Dinitrogen trioxide, also called nitrous anhydride, is stable only below (0°C), taking the form of a deep-blue liquid. When cooled further, it solidifies as pale blue crystals, even below (0°C),

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dinitrogen trioxide dissociates to a considerable extent [6], [7].

$$N_2O_{4\,(L)} + H_2O_{(L)} \rightleftharpoons 2HNO_{2\,(L)} \quad (4)$$

$$3HNO_{2\,(L)} \rightleftharpoons HNO_{3\,(L)} + 2NO_{(g)} + H_2O_{(L)} \quad (5)$$

$$N_2O_{3\,(g)} \rightleftharpoons NO_{(g)} + NO_{2\,(g)} \quad (6)$$

$$2N_2O_{3\,(g)} \rightleftharpoons NO_{(g)} + N_2O_{4\,(g)} \quad (7)$$

Dinitrogen trioxide does exist in equilibrium with nitric oxide and nitrogen tetroxide at ordinary temperatures. When mineral acids act upon a nitrite and dinitrogen trioxide, is owing to the production and decomposition of nitrous acid as in (4), which is very unstable, is take place and concentrated solution decomposes into dinitrogen trioxide [9]. Dinitrogen trioxide may also be obtained by treating dinitrogen tetroxide with a small quantity of water.

$$N_2O_{4\,(L)} + H_2O_{(L)} \rightleftharpoons HNO_{3\,(L)} + HNO_{2\,(L)} \quad (8)$$

Dinitrogen tetroxide (N_2O_4) rapidly vaporizes to an orange-brown gas of peculiar odor, dissolves readily in water with the formation of mixture of nitric and nitrous acids as in (8). The nitrous acid subsequently decomposes in one of two ways .If the amount of water is relatively small the reaction takes place approximately according to the (4) [7],[10] .If an excess of water be present, however, the reaction is represented by the (5) . The dinitrogen tetroxide is capable of existence as pure (NO_2) only between very narrow limits of temperature.

Nitrous acid (HNO_2) occurs as an intermediate product when NO_x gases are absorbed in water. Nitrous acid can act as both a reducing and an oxidizing agent. Strong oxidizing agents, Nitrous acid in aqueous solutions is assumed to be in dynamic equilibrium with its anhydride. The acid is stable only in cold dilute aqueous solution, at low temperature, it disproportionate as in (4), (5). This disproportionation reaction influences the properties of nitrous acid solutions and is important in the production of nitric acid [11].

Nitric acid (HNO_3) was known to the ancient Egyptians because of its special ability to separate gold and silver. Many well-known chemists experimented with the acid system [6]. The development of nitric acid usage in the united states (USA) can be traced by reviewing the changes in the military specifications as depicted, originally, there are four types of nitric acid defined in "MIL-N-7254A" [8]. Nitric acid is main important material for military industries, pure anhydrous nitric acid boils at (83 – 87 °C); the reason a range of boiling points are cited in the literature is that the acid decomposes on heating [6], [12], as well as low solubility of the oxygen in the equilibrium mixture (9).

$$4HNO_{3\,(L)} \rightleftharpoons 2H_2O_{(L)} + 4NO_{2\,(g)} + O_{2\,(g)} \quad (9)$$

Pure (100 wt. %) nitric acid is in some respects a unique solvent system. The extensive and unusual self-dissociation [1], [2], [13];

$$HNO_2 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \quad (10)$$

$$NO_2^+ + NO_3^- \rightleftharpoons N_2O_5 \quad (11)$$

$$N_2O_5 \rightleftharpoons NO_2^* + NO_3^* \quad (12)$$

$$HNO_3 + NO_2^* \rightleftharpoons HNO_2 + NO_3^* \quad (13)$$

$$HNO_3 + HNO_2 \rightleftharpoons 2NO_2^* + H_2O \quad (14)$$

$$NO_3^* = NO + O_2 \quad (15)$$

$$2NO + O_2 \rightleftharpoons NO_2^* \quad (16)$$

II. MATERIALS AND METHODS

The availability of decomposition or self-dissociation of strong nitric acid catalytically can be enhanced by many factors which play an important role; those factors can be summarized as (a) Effects of thermal heating or cooling resulting from surrounding nature as well as local climate temperature. (b). Effects of lightening and direct sun light. (c). Effect of instability of nitrous oxide in nitric acid and reverse reaction system as well as strong nitric acid production technology. The purpose of this study is to investigate the effects of Sudan ambient temperatures on acceleration of nitrous oxide (HNO_2) in strong nitric acid and to determine the optimum cooling temperature to slow the decomposition and to stabilize the nitrous oxide.

To investigate the effects of Sudan local temperatures on acceleration of nitrous oxide (HNO_2) in strong nitric acid:

a). Subjecting a sample of available strong nitric acid (1000 ml on glass bottle) to surrounding temperature of (20°C, 25°C and 30°C), by incubation, these represent the strong nitric acid storage and transport conditions.

b). The laboratory analysis was done to observe the nitrous oxide exit rate as function of temperatures, time and concentration of strong nitric acid.

A. *Determination of Nitric Acid (HNO_3) Concentration*

Principle: Add sample to excess standard sodium hydroxide solution, and titrate back with sulfuric acid standard titration solution.

Procedure: Weigh the ampoule bubble to the accuracy of "0.0002g". Filled ampoule bubble up to (1.5- 2.0 ml) of the sample. Weigh the ampoule bubble containing the sample. Transfer the ampoule bubble with content to a conical flask (or wide-opening bottle) containing "100ml" of distilled water and "50ml" of standard sodium hydroxide solution. Shaking the flask (or wide-opening bottle) until acid fume is absorbed completely. Add "2 drops" of methyl orange indicator solution to the flask, and titrates the excessive sodium hydroxide standard solution with sulfuric acid standard titration solution until the solution assumes orange as termination, Calculate mass fraction of nitric acid, (X_1), according to (17).

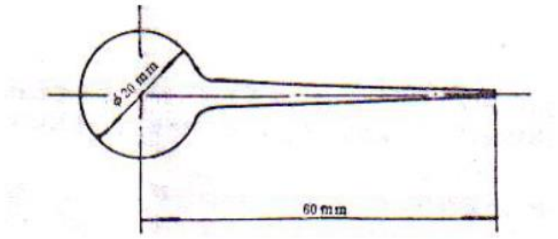

Fig. 1. Ampoule Bubble

$$X_1 = 100\left(\left(\frac{(50\,C - V\,C_1)}{1000}\right)\left(\frac{63.02}{m}\right)\right) - 1.34\,X_2 \qquad (17)$$

where, X_1 represents mass fraction of strong nitric acid, X_2 represents mass fraction of nitrous acid, C is the concentration of sodium hydroxide standard titration solution (mole L^{-1}), C_1 is the concentration of sulfuric acid standard titration solution (mole L^{-1}), V is the Sulfuric acid standard titration solution consumed in the titration (ml), *m* represents mass of the sample (g), 50 is added volume of sodium hydroxide standard solution (ml) , (63.02) is the mole mass of nitric acid, (g. $mole^{-1}$) and (1.34) represents a factor for converting nitrous acid to nitric acid.

B. Determination of Nitrous Acid (HNO2) Content

Principle: Oxidize the nitrous acid compound in the sample with excess standard potassium permanganate solution, and add excess ammonium ferrous sulfate solution, then titrate the excess of ammonium ferrous sulfate solution with potassium permanganate standard titration solution.

Procedure: Weigh 20g of the sample: Pour the sample into a "50ml" conical flask. To a (500 ml) conical flask, add (100ml) of distilled water of below 25ºC and 20ml of sulfuric acid solution respectively. Add a definite volume （V_0） of the potassium permanganate standard solution by using a burette (10ml). Rapidly add the sample to the flask and shake until acid fume fully disappears. Pipet (20ml) of ammonium ferrous sulfate solution to the flask and titrate the excessive ammonium ferrous sulfate standard solution with standard potassium permanganate solution until the solution assumes pink color (V_1). Add (20ml) of ammonium ferrous sulfate solution to the above conical flask, and continue the titration until the solution assumes pink color (V_2). Calculate mass fraction of nitrous acid, (X_2), according to (18).

$$X_1 = 100\left(\frac{[(V_1+V_0)-V_2]}{1000m}\right)23.5\,C \qquad (17)$$

where, X_2 represents mass fraction of nitrous acid, C is the actual concentration of standard potassium permanganate solution (mole. L^{-1}), V_0 is the volume of standard potassium permanganate solution added at first (ml), V_1 is the volume of standard potassium permanganate solution which is consumed in first titration (ml), V_2 is the Volume of standard potassium permanganate solution which is consumed in second titration (ml), *m* is the mass of sample (g) and (23.50) represents mole mass of nitrous acid (g.$mole^{-1}$).

III. RESULTS AND DISCUSSIONS

A. Results

Samples one, two and three after incubated at a fixed temperature "30 ^{0}C, 25 ^{0}C ,20 ^{0}C ", are subjected to four runs - within "four days" - to determine nitric acid concentration, nitrous acid concentration the density for each of the four days. The results of experiments are shown in Tables I, II, III and Fig. 2, 4, 6.

TABLE I: SAMPLE (1) ANALYSIS

Run	Storage Temperature ^{0}C	Incubation period (Day)	HNO_3 Con %	HNO_2 Con %	Density (g/cm^3)
1	30	1	97.4	1.52	1.52
2	30	2	97	2.44	1.510
3	30	3	96.8	2.67	1.505
4	30	4	96.4	2.8	1.5

TABLE II: SAMPLE (2) ANALYSIS

Run	Storage Temperature ^{0}C	Incubation period (Day)	HNO_3 Con %	HNO_2 Con %	Density (g/cm^3)
1	25	1	96.16	1.83	1.514
2	25	2	95.51	2	1.51
3	25	3	95.45	2.75	1.5
4	25	4	94.4	2.76	1.449

TABLE III: SAMPLE (3) ANALYSIS

Run	Storage Temperature ^{0}C	Incubation period (Day)	HNO_3 Con %	HNO_2 Con %	Density (g/cm^3)
1	20	1	95.7	2.68	1.514
2	20	2	95.44	2.7	1.51
3	20	3	94.8	3	1.45
4	20	4	94.21	3.01	1.44

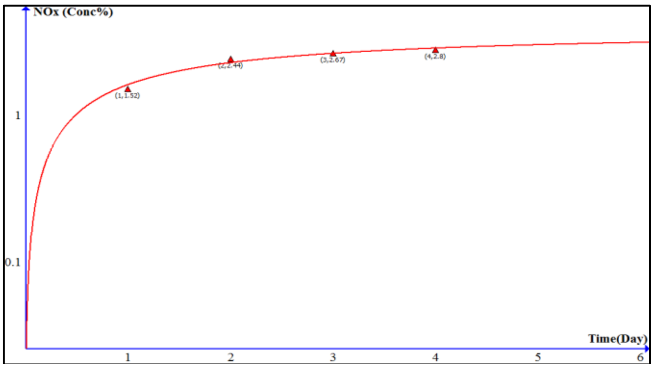

Fig. 2. Effect of Storage Temperature (30^{0}C) on Nitrous Oxide in sample (1)

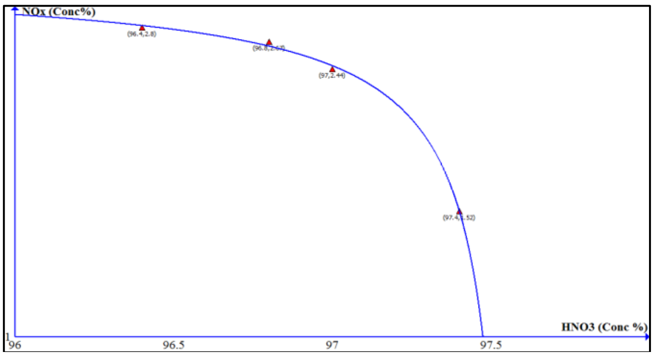

Fig. 3. The relation between Nitric Acid and Nitrous Oxide (NOx) during fixed Temperature (30^{0}C) in sample (1).

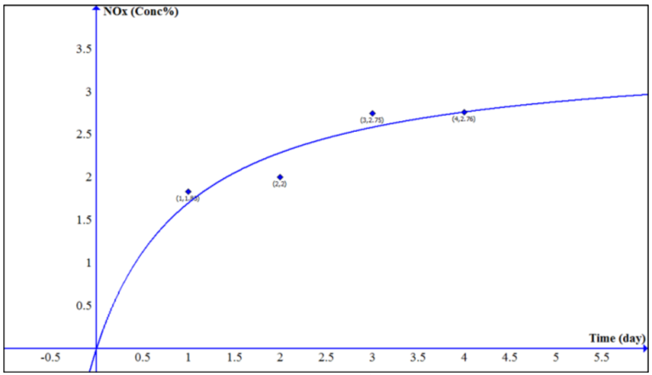

Fig. 4. Effect of Storage Temperature (25^{0}C) on Nitrous Oxide in sample (2)

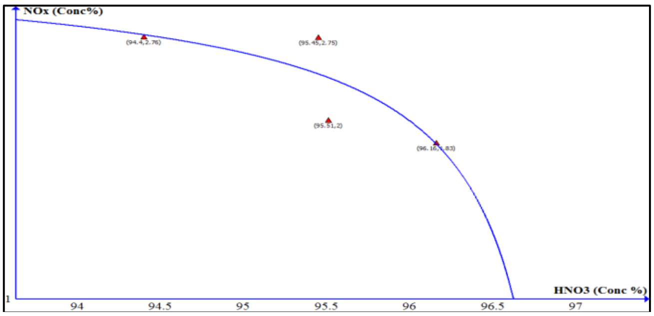

Fig. 5. The relation between Nitric Acid and Nitrous Oxide (NOx) during fixed Temperature (25^{0}C) in sample (2).

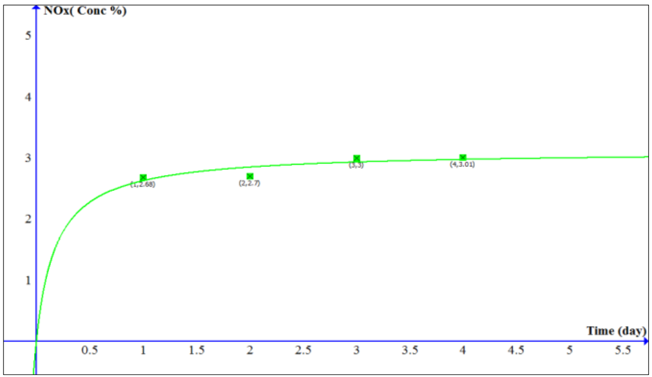

Fig.6. Effect of Storage Temperature (20^{0}C) on Nitrous Oxide in sample (3)

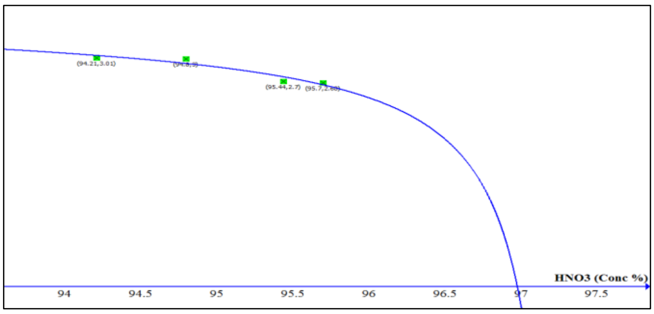

Fig. 7. The relation between Nitric Acid and Nitrous Oxide (NO$_x$) during fixed Temperature (20^{0}C) in sample (3).

Fig. 8 below shows the effect of the change of nitrous oxide (NOx) concentration with temperature at different times.

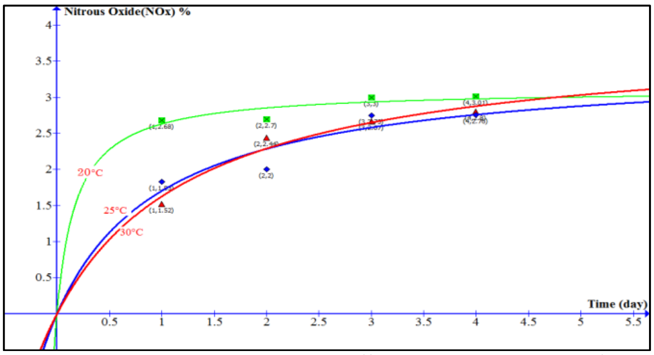

Fig. 8. Nitrous oxide concentration at different temperatures during four days.

B. *Discussions*

Fig. 2, 4, 6 clearly show a noticeable increase of nitrous oxide at respective temperatures (20 ^{0}C, 25 ^{0}C, 30 ^{0}C) at the beginning then the curve levels after three days' incubation. Elevation of incubation time (long storage life of nitric acid) is an indicator of the increase of nitrous oxide production as a result of nitric acid decomposition reaction. The concentration of strong nitric is high initially with a low nitrous content, then the concentration of strong nitric acid degreases (Fig. 3) with increase of nitrous concentration because the (HNO_3, HNO_2) in same liquid system, beside others that has been released as fume.

Fig. 6, explains the noticeable stabilization of nitrous oxide within fixed temperature (20^{0}C), during the elevating of incubation time, this gives us the indicator that, if the strong nitric acid exposure for long life storage at temperature (20^{0}C) resulting in nitrous oxide to stabilize and prevent decomposition reaction.

Fig. 8, describes the stability and non-stability of nitrous oxide for the systems studied. The curves of nitrous oxide versus storage time for temperatures (30^{0}C) and (25^{0}C) where increase after three days' incubation periods while the curve for temperature of (20^{0}C) levels; this can be explained as stabilizing of nitrous oxide, long storage life. It is believed that more lowering of the temperature than (20^{0}C) leads to more stabilization of nitrous oxide.

The area under (20^{0}C) curve is bigger than that of (30^{0}C) and (25^{0}C), this shows that a long time will be needed before nitrous oxide is produced and the decomposition takes place during either strong nitric acid storage or transportation.

IV. CONCLUSIONS AND RECOMMENDATIONS

A. *Conclusion*

According to results where samples are subjected to laboratory analysis to monitor the nitrous oxide concentration expressed by nitrous acid (HNO_2) and nitric acid concentration versus incubation time, it is concluded that noticeable increase of nitrous oxide concentration within temperature of (25 ^{0}C, 30 ^{0}C) and noticeable decreasing of nitric acid concentration after four days' incubation, (20 ^{0}C) is the higher temperature at which the strong nitric acid is either stored or transported.

Sudan ambient temperatures related with acceleration of nitrous oxide (HNO_2) in strong nitric acid, (20 ^{0}C) is the optimum temperature in which can be cool down, slow the decomposition and stabilize the nitrous oxide.

20 ^{0}C must be used as reference temperature in issues related to aspects (design, operation, etc.) of strong nitric acid.

The study agreed with all the theories and equilibrium equations that support the decomposition of concentrated nitric acid by temperature and radiolysis.

B. Recommendations

The study concluded that, Sudan ambient temperatures related with acceleration of nitrous oxide (HNO_2) in strong nitric acid, (20 ^{0}C) is the optimum temperature in which can be cool down, slow the decomposition and stabilize the nitrous oxide, so it is recommended to:

1. Check strong nitric acid storage tank and transportation system design as well as design a conventional jacket heat exchanger to cool down the temperature of nitric acid from (40 ^{0}C to 20 ^{0}C). The spacing between the jacket and tank wall is typically (10 cm).
2. Consider (20 ^{0}C) as reference temperature as well as designing, storing and transportation aspects of nitric acid system to avoid nitrous oxide (NO_x).
3. The structure of storage building, for example closed system should be equipped with air conditioning split units with well-ventilated system and gas detection tools, anti-acid coated structure.
4. Degreasing the surrounding ambient temperature, this depends on improving the environmental aspects like planting trees and proper maintenance of gardening area.
5. To use a new design for strong nitric acid transportation system, this may include a vessel cooled by refrigeration system and agitation system.
6. The strong nitric acid must transfer through transportation system at night to guarantee low ambient temperature.
7.

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