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The degradation of ammonia in absorption thermal machines

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Abstract

When water-ammonia absorption machines are used as heat pumps, the main problems can be found in the components operating at a high pressure (generator-condenser); the increase in temperature with respect to the exertion as refrigerator generates particular conditions that might unbalance the decomposition of ammonia into nitrogen. A decrease in the rate of the refrigerating fluid NH₃ in the condenser and evaporator occurs, hence of the performance coefficient of the heat pump with an increased risk of the potential generation of explosive mixtures due to the presence of the hydrogen. The aim of this study is to examine the reaction of ammonia during the dissociation process from a thermodynamic and thermokinetic point of view, focusing on the temperatures and pressures of a heat transformer. With the generator at a temperature of 170 °C it is necessary to reach a degree of dissociation at 1% a time period of the order of 1.013 seconds which is 100 times higher than the one of maximum permanence of the fluid in the components of the machines functioning at high temperatures. This is not a problem that might prevent the realization of high temperature absorption heat pumps.

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1. Introduction

Energy issues' assessment has always been one of the most important engineering research sectors and it has been performed with respect to different fields [1-13]. In particular, this study stems from the fact that absorption heat pumps allow a redistribution on new thermal levels of different amounts of heat with low working values and they can be considered interesting machines from an energetic point of view.

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Then, for what concerns the working conditions as refrigerant machine, it is well known that the available fluids are the couple H₂O-LiBr and NH₃-H₂O [14-16].

Nomenclature

| | |
|---------------------------------|--|
| 0 | pure substance; |
| 1 | component 1 (ammonia); |
| 2 | component 2 (water); |
| C | concentration [mol m ⁻³]; |
| C ₀ | concentration at the instant t = 0 [mol m ⁻³]; |
| E _a | activation energy = 209.3 [kJ mol ⁻¹]; |
| g | generator; |
| K | Boltzmann constant = 1.38 · 10 ⁻²⁶ [kJ K ⁻¹]; |
| K _a , K _p | equilibrium constants; |
| K _v | reaction rate constant [m ³ mol ⁻¹ s ⁻¹]; |
| L | Avogadro's number = 6.02252 · 10 ²³ [mol ⁻¹]; |
| P | total pressure [kg cm ⁻²]; |
| R | gases universal constant = 8.314 · 10 ⁻³ [kJ mol ⁻¹ K ⁻¹]; |
| t | time [s]; |
| T | temperature [°C; K]; |
| v | dissociation velocity [mol m ⁻³ s ⁻¹]; |
| X | concentration [mol m ⁻³]; |
| α | dissociation degree; |
| ΔG _f | free energy of formation [kJ kg ⁻¹]; |
| ΔG _r | variation in free energy of reaction [kJ kg ⁻¹]. |

The variation in the heat levels characterizing the different sections with respect to the employment as refrigerant makes further problems arise and, even if other studies focused on similar topics [17-19], new solutions have not been found yet. Many studies have been carried out to examine the limits related to the traditional mixtures, in particular for what concerns the temperature of their exertion without causing problematic situations with a decrease in a crucial parameter as the reliability of the system [20-24]. The couple NH₃-H₂O presents problems in terms of high pressure (generator-condenser): the increase in temperature, for what concerns the exertion as refrigerator, provokes a higher fluid pressure thus causing the necessity of a proper mechanical dimensioning of the components, hence higher costs. Due to a higher temperature, an abundant amount of vaporous absorbent is moved to the generator with rectification difficulties. Moreover, the particular conditions in terms of temperature and pressure might unbalance the equilibrium of the decomposition reaction of the ammonia into nitrogen and hydrogen to high values of the dissociation degree [25]. Hence it occurs a decrease in the rate of the refrigerant fluid NH₃ in the condenser and evaporator, and of the coefficient of performance of the heat pump. There is also a higher probability that explosive substances (due to the presence of hydrogen) might generate.

2. Dissociation chemical reaction

The dissociation reaction of the ammonia into nitrogen and hydrogen is:



If there is an equilibrium, that is pressure and temperature are constant, the variation in the free energy of reaction is provided by:

$$\Delta G_r = RT \ln K_a \quad (2)$$

where K_a is the constant of the equilibrium which depends on the activities. Assuming that the three gases behave as the ideal gas, the (2) can be written according to the partial pressures:

$$\Delta G_r = -RT \ln K_p \quad (3)$$

ΔG_r is related to the free energy of formation ΔG_f by the relation (4):

$$\Delta G_r = -2\Delta G_f \quad (4)$$

While taking into consideration the (4) and knowing some measured values of the ΔG_f [26], it is possible to determine, through the method of the least squares, a formula of linear interpolation providing ΔG_r values with respect to a changing temperature:

$$\Delta G_r = 9080 - 50T \quad (5)$$

where ΔG_r is expressed in cal/mol and T in °C. Through (3) and (5) it is then possible to determine:

$$K_p = e^{\frac{50T - 9080}{1.98(T + 273)}} \quad (6)$$

In (6) K_p can be expressed according to the partial pressures of the components:

$$K_p = \frac{P(N_2) \cdot [P(N_2)]^3}{[P(NH_3)]^2} \quad (7)$$

keeping in mind that in the hypothesis of an ideal gas, partial pressures are proportional to molar fractions:

$$K_p = P^2 \frac{X(N_2) \cdot [X(N_2)]^3}{[X(NH_3)]^2} \quad (8)$$

where P is the total pressure in which the chemical equilibrium occurs.

1.1. Dissociation degree

If 2 α moles of NH_3 are examined, at equilibrium the result will be α moles of N_2 and 3 α moles of H_2 with $2(1-\alpha)$ undissociated moles of NH_3 . The total number of moles is:

$$N_t = 2(1 + \alpha) \quad (9)$$

where α is the dissociation degree and it is defined as the ratio between the number of moles of NH_3 dissociated and the one initially present. The molar fractions of the components at equilibrium can be expressed in reference to the dissociation degree, hence:

$$X(NH_3) = \frac{(1-\alpha)}{(1+\alpha)} \quad (10)$$

$$X(N_2) = \frac{\alpha}{2(1+\alpha)} \quad (11)$$

$$X(H_2) = \frac{3\alpha}{2(1+\alpha)} \quad (12)$$

By substituting in the relation (8), the (10), (11), (12), the result is:

$$K_p = \frac{27}{16} P^2 \frac{\alpha^4}{1-2\alpha^2+\alpha^4} \quad (13)$$

Through (6) and (13), α can be expressed in function of temperature and pressure of equilibrium. Fig. 1a (with pressures ranging between 1 and 80 Ata and temperatures between 0 °C and 220 °C) and Fig. 1b (with temperatures ranging between 100 and 200 °C and pressures reaching 50 Ata) show the results.

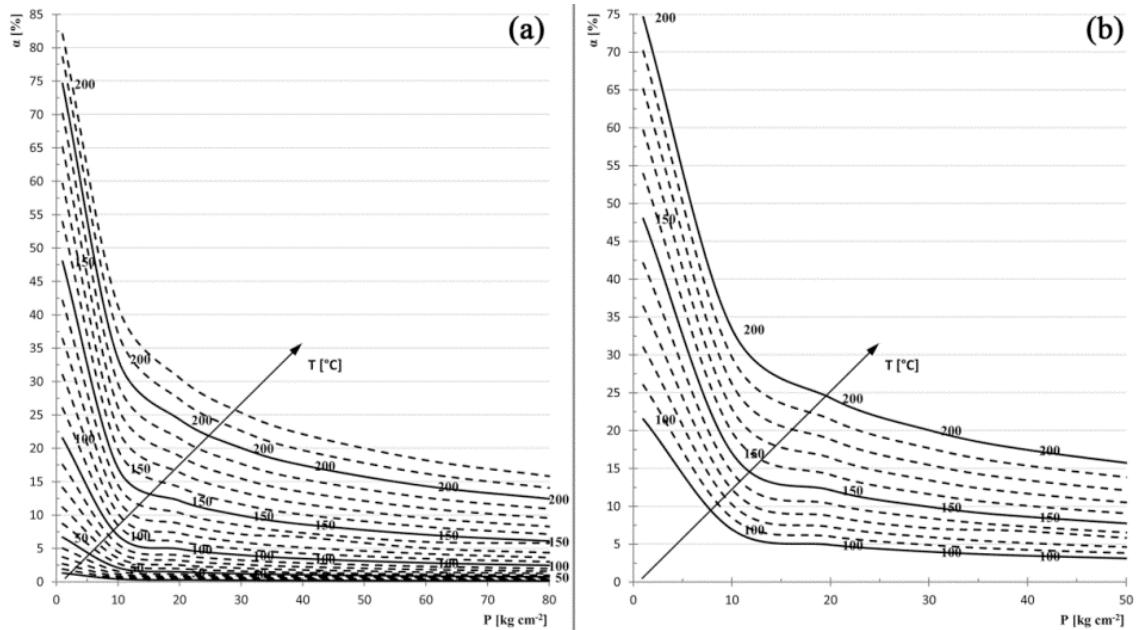


Fig. 1 – Trend of the dissociation degree α , at equilibrium, with variations in pressure.

It can be noticed a remarkable decrease of α with the pressure and an increase of α with the temperature. In the conditions where a heat pump presents a higher probability that it might function, that is where pressure can vary from 20 Ata and 50 Ata and temperatures between 120 °C and 180 °C, α is characterized by high values ranging between 5% and 15%. These values do not coincide with a proper and safe functioning of the machine, due to what was previously stated in the introduction. Hence if the reaction kinetic (1) is so high that it reaches an equilibrium, the couple NH₃-H₂O cannot be taken into consideration for the exertion in the heat pump. It is clear that a study concerning the velocity of decomposition can be useful to evaluate the discrepancy between the current dissociation degree and the one of equilibrium. If this variation is significant the afore mentioned negative consideration might be revised.

1.2. Velocity of decomposition

In order to evaluate the velocity of decomposition, it can be assumed that the reaction described through (1) is bimolecular, that is it involves a collision between 2 molecules of ammonia. In this hypothesis, the velocity of decomposition is proportional to the square of the decomposition of ammonia:

$$v = \frac{d[NH_3]}{dt} = -2K_V[NH_3]^2 \quad (14)$$

The constant of velocity K_V can be evaluated by applying the collision theory which leads to the relation:

$$K_V = \sigma L \left[\frac{8K_T}{\pi\mu} \right]^{0.5} e^{-\frac{E_a}{RT}} \quad (15)$$

where:

- a) $\sigma = (R_A + R_B)^2$, with R_A and R_B representing the radii of the colliding molecules. The case under consideration presents 2 molecules of ammonia, hence $R_A = R_B = R$ and $\sigma = 4R^2$. Since R can be considered to be of 0.85 U.A. [26], hence $\sigma = 9.07 \cdot 10^{-20}$ meters.
- b) $\mu = \frac{M_A M_B}{M_A + M_B}$ (kg) = reduced mass.
- c) T (K) = absolute temperature.

According to those numerical values listed here, the trend of K_V can be determined according to the temperature. Tab. 1 reports the results.

Tab. 1 – Constant of the reaction velocity K_V in reference to the temperature.

| T [°C] | K_V [m ³ mol ⁻¹ s ⁻¹] | T [°C] | K_V [m ³ mol ⁻¹ s ⁻¹] | T [°C] | K_V [m ³ mol ⁻¹ s ⁻¹] |
|-----------|--|-----------|--|-----------|--|
| 0 | 0 | 70 | 2.20E-26 | 140 | 6.04E-21 |
| 10 | 0 | 80 | 1.78E-25 | 150 | 2.58E-20 |
| 20 | 7.48E-32 | 90 | 1.28E-24 | 160 | 1.03E-19 |
| 30 | 1.29E-30 | 100 | 8.36E-24 | 170 | 3.87E-19 |
| 40 | 1.86E-29 | 110 | 4.90E-23 | 180 | 1.37E-18 |
| 50 | 2.27E-28 | 120 | 2.65E-22 | 190 | 4.60E-18 |
| 60 | 2.39E-27 | 130 | 1.31E-21 | 200 | 1.46E-17 |

3. Estimating the actual dissociation degree

Once the constant K_V is known, the trend of the concentration over the time can be predicted by integrating the kinetic equation [27]:

$$\int_{C_0}^C \frac{d[NH_3]}{[NH_3]^2} = -2K_V \int_0^t dt \quad (16)$$

hence:

$$C = \frac{1}{\frac{1}{C_0} + 2K_V t} \quad (17)$$

where C_0 is the concentration of ammonia in the vaporous phase with time being $t = 0$. The (17) can be related to the dissociation degree $\alpha = \sigma(t)$. As a matter of fact, if a quantity X of ammonia is subject to dissociation in the time t , it is possible to obtain:

$$\alpha = \frac{X}{C_0} = \frac{C_0 - C}{C_0} \quad (18)$$

Through (17) and (18), it is possible to write:

$$\alpha = 1 - \frac{1}{1 + 2C_0 K_V t} \quad (19)$$

The (19) is the function connecting the dissociation degree to the time of reaction; however the concentration C_0 has not been determined yet. If the equation of the state of the ideal gases is valid, it can be expressed as:

$$C_0 = \frac{n}{V} = \frac{P_1}{RT} \quad (20)$$

where P_1 is the partial pressure of the ammonia. With pure ammonia, P_1 would be the saturation pressure at temperature T . Since in the generator of an absorption heat pump there is a relevant quantity of vaporous water, a more accurate evaluation of P_1 is necessary and Raoult's law can be used:

$$P_1 = P_{1,0} X_1 + P_{2,0} X_2 \quad (21)$$

where:

$$P_1 = P_{1,0} X_1 \quad (22)$$

As an example, the following operative conditions can be considered: $T = T_g = 170^\circ\text{C}$; $P = P_g = 36 \text{ kg cm}^{-2}$; $X_2 = 35\%$ di NH_3 . The concentrations of water and ammonia in a vaporous state are respectively 13.6% and 86.4% [28]. The saturation pressure of pure water at 170°C is $7.8616 \text{ kg cm}^{-2}$ [29]. By substituting these values in (21) and (22), the value concerning the partial pressure of the ammonia in the gas mixture is determined: $P_1 = 34.94 \text{ kg cm}^{-2}$. Hence, while taking into consideration the (20), the value of $C_0 = 960 \text{ moles m}^{-3}$ can be determined. Now, through the (14) and (19), the velocity of dissociation of the ammonia and the dissociation degree based on the time factor can be assessed. Thanks to the (14), it is possible to obtain $v = 7.13 \cdot 10^{-3} \text{ moles m}^{-3} \text{ s}^{-1}$. Differently, through (19), it is possible to determine:

$$\alpha = 1 - \frac{1}{1 + 0.743 \cdot 10^{-15} t} \quad (23)$$

The Eq. (23) gives the possibility to assume that the time t (1%), necessary to get a dissociation degree of 1%, is of the order of 10^{13} s . Carrying out the same assessments for higher temperatures, the result is that within temperatures of $300 \div 400^\circ\text{C}$, t (1%) still belongs to the order of 10^{10} s .

4. Conclusion

In the generator, absorption heat pumps operate with temperatures T_g which are higher than those characterizing refrigerant machines. With an increasing temperature characterizing the user, higher T_g values will always be required and this should not cause problems to the fluid or the machine. For what concerns the $\text{NH}_3\text{-H}_2\text{O}$, one of the problems that might prevent the possibility to reach higher T_g values is the dissociation of the ammonia released in the generator. Hence the result would be a moving phenomenon of the nitrogen and hydrogen to the condenser and a storing of these incondensable gases in the evaporator, with a progressive decrease in the coefficient of performance of the machine. This study found a high value of the dissociation degree characterizing the ammonia in average conditions of exertion of a heat pump which is incompatible with a proper functioning of the machine. However, the velocity of dissociation is very low; hence the dissociation degree reached is lower than the one of the equilibrium and is unlikely that problems due to the dissociation phenomenon might arise. Then, with the generator being characterized by a temperature of 170 °C, hence a temperature of the user of 80 ÷ 90 °C (typical of the residential heating), a time t (1%) of the order of 10^{13} s was necessary in order to reach a dissociation degree of 1%. This parameter is about 1.010 times higher than the maximum value concerning the presence of the fluid in the components of those machine characterized by high temperatures. The same assessments were carried out for higher temperatures, discovering that up to 300 ÷ 400 °C, t (1%) belongs to the order of 10^{10} s. Therefore, the problems determined by the dissociation might not prevent the realization of more advanced absorption heat pumps machines working with higher temperatures in the generator than those of the present.

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