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SIMULATION MODULE OF CATALYTIC EQUILIBRATION IN CRYOGENIC DISTILLATION COLUMN OF HYDROGEN ISOTOPES

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Abstract
In a cascade of hydrogen isotopes cryogenic distillation the equilibrators are necessary because *HT* (unwished component) and D_2 cannot be separate; they yield the percentage of *HT* decrease by an isotopic exchange reaction. These new elements impose to amend the simulated model of the simple cryogenic distillation column of hydrogen isotopes.

Keywords: hydrogen, isotope, cryogenic, distillation, simulation, mixer.

1. Introduction

In a cascade of hydrogen isotopes cryogenic distillation, the principal device is the catalytic equilibrator. The objective of location of that is to promote the isotopic exchange reaction, $HT + D_2 \leftrightarrows HD + DT$ which to yield the percentage of HT decrease.

The equilibrators are necessary because *HT* and D_2 cannot be separate (by porous membrane diffusers alone for example) on account of equality of their molecular weights. Each cascade has a sidestream which is recycled to the feed stream after being passed through the equilibrator.

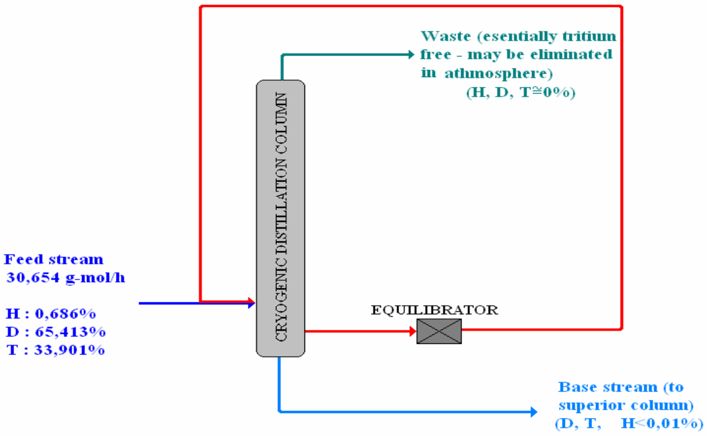

Fig. 1. System configuration of cascade with equilibrator

Certainly, these new elements of distillation impose to amend the simulated model of the simple column. The present study provides a mathematical model of the physics phenomena of catalytic equilibration and - depending on that - a simulated module (as part of a computer code developed for exact simulation of hydrogen isotopes cryogenic distillation process).

2. Method and samples

The mathematic model for equilibration process begins with three component material balances and three phenomenological equations of isotopic exchange. Therefore the composition of stream after equilibrator is the solution of the following system:

$$x_H = x'_{H_2} + \frac{1}{2}\left(x'_{HD} + x'_{HT}\right); \quad x_D = x'_{D_2} + \frac{1}{2}\left(x'_{HD} + x'_{DT}\right); \quad x_T = x'_{T_2} + \frac{1}{2}\left(x'_{HT} + x'_{DT}\right);$$
$$\frac{x'_{HD} \cdot x'_{HT}}{x'_{H_2} \cdot x'_{DT}} = K_4; \quad \frac{x'_{HD} \cdot x'_{DT}}{x'_{D_2} \cdot x'_{HT}} = K_5; \quad \frac{x'_{HT} \cdot x'_{DT}}{x'_{T_2} \cdot x'_{HD}} = K_6; \qquad (1)$$

Where x_H, x_D, x_T - atomic ratios of *H, D, T,* before equilibrator;

K_4, K_5, K_6 - constants of equilibration at 25 °C for the isotopic reactions (constants of reaction):

$$\begin{aligned} &H_2 + DT \rightleftarrows HD + HT && \mapsto K_4; \\ &D_2 + HT \rightleftarrows HD + DT && \mapsto K_5; \\ &T_2 + HD \rightleftarrows HT + DT && \mapsto K_6. \end{aligned} \qquad (2)$$

It is assumed that the equilibrium composition established by the following isotopic exchange reactions at 25 °C is obtained at the exit of the equilibrator:

$$\begin{aligned} &H_2 + D_2 \rightleftarrows 2HD && \mapsto K_1 = 3{,}25; \\ &H_2 + T_2 \rightleftarrows 2HT && \mapsto K_2 = 2{,}57; \\ &D_2 + T_2 \rightleftarrows 2DT && \mapsto K_3 = 3{,}82. \end{aligned} \qquad (3)$$

Accounting of reaction constant definition it results:

$$K_4 = \sqrt{\frac{K_1 K_2}{K_3}} = 1{,}48; \quad K_5 = \sqrt{\frac{K_1 K_3}{K_2}} = 2{,}20; \quad K_6 = \sqrt{\frac{K_2 K_3}{K_1}} = 1{,}74. \qquad (4)$$

Atomic ratios of *H, D, T,* before equilibrator, x_H, x_D, x_T are calculated with similar relations of mixing process:

$$x_H = x_{H_2} + \frac{1}{2}\left(x_{HD} + x_{HT}\right); \quad x_D = x_{D_2} + \frac{1}{2}\left(x_{HD} + x_{DT}\right); \quad x_T = x_{T_2} + \frac{1}{2}\left(x_{HT} + x_{DT}\right); \qquad (5)$$

where $x_{H_2}, x_{HD}, x_{HT}, x_{D_2}, x_{DT}, x_{T_2}$ - molar ratios of species before equilibration.

With notes:

$$a = K_4 ; b = K_5 ; c = K_6 ;$$
$$\alpha = x_H ; \beta = x_D ; \gamma = x_T ; \tag{6}$$
$$x = x'_{HD} ; y = x'_{HT} ; z = x'_{DT} ,$$

the system (1) becomes:

$$x'_H = \alpha - \frac{1}{2}(x + y); \quad x'_D = \beta - \frac{1}{2}(x + z); \quad x'_T = \gamma - \frac{1}{2}(y + z);$$
$$x = \frac{2yz}{c(2\gamma - y - z)}; \quad y = \frac{2xz}{b(2\beta - x - z)}; \quad z = \frac{2xy}{a(2\alpha - x - y)}. \tag{7}$$

Finally it obtains:

$$y = \frac{a_2 x^2 + a_1 x + a_0}{b_1 x + b_0}; \quad x = \frac{c_2 y^2 + c_1 y + c_0}{d_1 y + d_0}; \tag{8}$$

where

$$a_0 = -4ab\alpha\beta; \quad a_1 = 2ab(\alpha + \beta); \quad a_2 = 4 - ab; \quad b_0 = -2ab\beta; \quad b_1 = b(a - 2);$$
$$c_0 = -4ac\alpha\gamma; \quad c_1 = 2ac(\alpha + \gamma); \quad c_2 = 4 - ac; \quad d_0 = -2ac\gamma; \quad d_1 = c(a - 2). \tag{9}$$

For the numeric solving of the system I have chosen the method of successive approximates; the calculation algorithm is showed in figure 2.

3. Results and Discussions

The experimental input values and the results of mixing simulation are the follows:

	COMPOZITIA INITIALA	COMPOZITIA FINALA
H2	1.4724E-0012	8.5384E-0008
HD	2.7958E-0004	5.2239E-0004
HT	2.4685E-0004	3.86410E-0006
D2	9.8366E-0001	9.83418E-0001
DT	1.5747E-0002	1.59880E-0002
T2	6.5993E-0005	6.69824E-0005

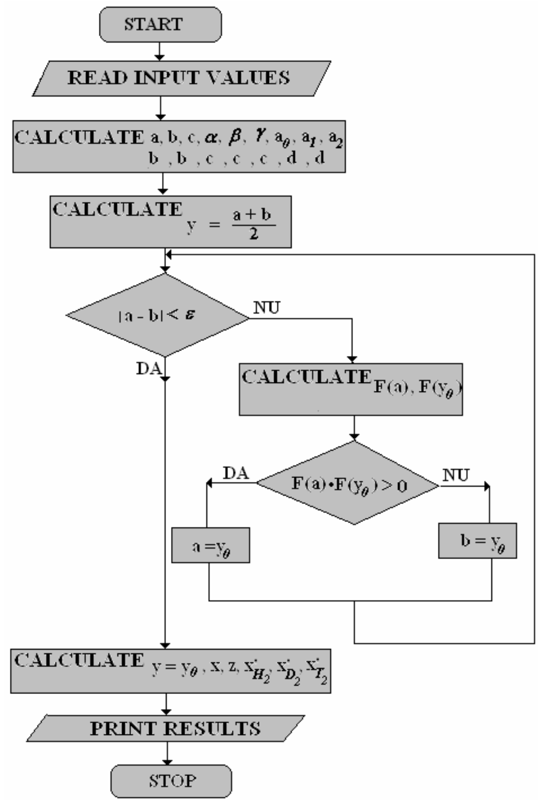

Fig. 2. Calculation algorithm

4. Conclusions

The module dedicated of equilibration process is valid and may be considered a routine (external) for the simulated code of hydrogen isotopes cryogenic distillation.

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