

INTEGRATED MODEL OF CHEMICAL REACTOR

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ABSTRACT

In this work, the bond graph approach is employed to develop an integrated chemical reactor model, able to be exploited for supervision and diagnosis of industrial process. The obtained model is evolutive and generic comparing with the first principle methods. Moreover, this methodology is based on systematic approach which allows to represent the dynamic behaviour of complex process under non linear state space equations. The application discussed in this work is a chemical process including CSTR (Continuous Stirred Tank Reactor), where it occurs two exothermic reversible and irreversible reactions. To illustrate the modelling procedure, a simulation results have been performed in the cases when the mixture is considered as ideal and real aqueous solution.

INTRODUCTION

In the present paper, the bond graph approach is adapted to model chemical reactors, which represents in process engineering, one of the most complex systems to model because of there non linear behaviour due to the interactions between the different energy (hydraulic, thermal and chemical) within the system. The modelling approach used here, reproduce an integrated model using a graphical unified language. Furthermore, the elaborated model is associated readily with industrial equipments models (centrifugal pumps, compressors, heat exchangers, ...etc) to get the overall process bond graph model, needed for supervision and FDI (Fault Detection and Isolation) procedures using model based methods (Iserman 1984).

Previously, the bond graph tool has been designed for hydraulic and electrical systems (Paynter 1961), and after that its application has been extended to chemical reactions (Auslander et al. 1972), thermofluid systems (Thoma 1971) (Karnopp and Azerbaijani 1981).

However, for chemical reactors, the approach is not well developed yet. Among published works, we cite (Delgado et al. 1999) (Breedveld et al. 2003).

In the pseudo bond graph models elaborated in (Delgado and al. 1999), the concentration has been chosen as effort variable in chemical domain to describe the reaction kinetic in the case of irreversible reactions. However, in our case, when the reaction is reversible, the choice of concentration is not well adapted to represent, and analyse the reaction dynamic behaviour, particularly near of the equilibrium. That is why; an adequate variable is required to be employed in such case (reversible and irreversible reactions). Thus, the chemical potential μ is chosen in this paper as effort variable, used before by (Auslander et al. 1972), (Cellier 1991), (Thoma and Ould Bouamama 1999).

In contrast to the model proposed by (Breedveld et al. 2003), where the entropy flow \dot{S} is chosen in thermal domain as flow variable, we have proposed to choose in our application the enthalpy flow \dot{H} , suitable in the case of open systems (industrial equipments, continues reactors,...etc), where the heat is transferred by convection (Karnopp and Azerbaijani 1981).

So to get the integrated reactor model needed, the choice of enthalpy flow \dot{H} is suggested instead of entropy flow \dot{S} , in order to use the overall process for supervision and diagnosis applications.

The paper is organized as follows: after brief description of the application example, the process word bond graph is presented, and the reactor bond graph model is developed in details to be written after under state space representation generated systematically. In the simulation part the bond graph model is implemented in SYMBOLS software (Mukherjee and Samantaray 2001) to get results which will be discussed and commented. Finally, the conclusions and perspectives are presented according to the results obtained before.

PROCESS DESCRIPTION

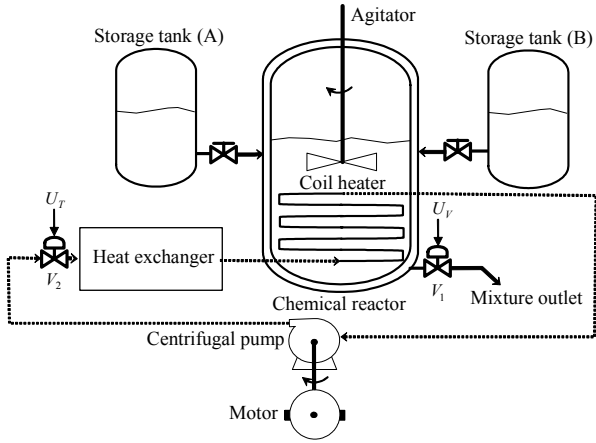
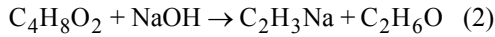
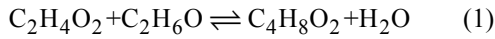
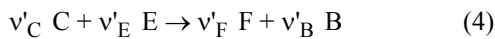
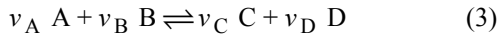


Figure 1: Chemical process diagram

The studied application shown in Fig. (1) represents chemical process including: CSTR, tanks, heater circuit coupled with heat exchanger. Within the reactor vessel occurs two exothermic reversible and irreversible reactions of esterification and saponification, which the forms are respectively expressed by:



In the esterification, the reaction of acetic acid CH_3COOH with ethanol CH_3CH_2OH will produce ethyl acetate $CH_3COOCH_2CH_3$ and water according to the Equation (1). For saponification, the ethyl acetate $CH_3COOCH_2CH_3$ produced from the esterification, reacts with sodium hydroxide (NaOH) to produce ethanol and sodium acetate (CH_3COONa) according to Equation(2). In order to simplify the notations after, the two reactions cited above are designed as reaction (1) for esterification, and reaction (2) for saponification. They are expressed under the general forms:



Where CH_3COOH , CH_3CH_2OH , $CH_3COOCH_2CH_3$, H_2O , $NaOH$, CH_3COONa , correspond respectively to A, B, C, D, E, F, and v_i , v'_j (for $i= A, B, C, D, j= C, B, E, F$) are the stoichiometric coefficients. The reactor is supplied by two tanks through two feed valves controlled manually to insure the constancy of the inlet volume flows \dot{V}_A and \dot{V}_B . It is supposed that a quantity of NaOH (sodium hydroxide) is added after. The mixture is drained out of the reactor through servo valve V_1 controlled in position U_V to maintain the volume mixture V constant. The heat is transferred to the

mixture from the heater circuit through the coil heater. The temperature T of the mixture is maintained constant due to the control position U_T of the servo valve V_2 . Within the heater circuit, circulates a coolant fluid, whose the volume flow V_j is maintained constant due to centrifugal pump entrained by electrical motor.

REACTOR BOND GRAPH MODELLING

Word bond graph

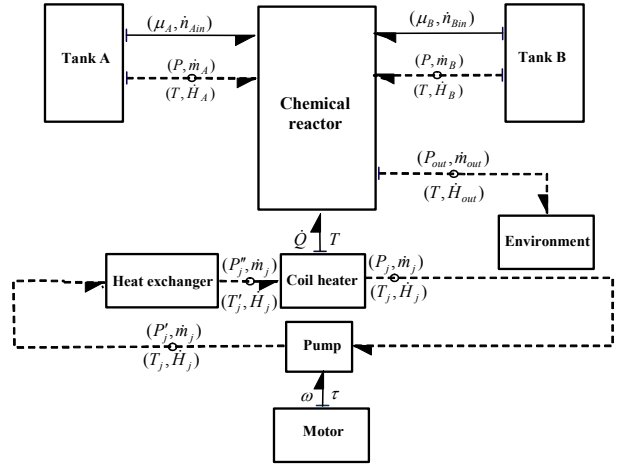


Figure 2: Word bond graph

The process word bond graph model shown in Fig. (2) represents the technological level of modelling procedure (Thoma and Ould Bouamama 1999). This architectural representation allows to model each subsystem independently; the submodels elaborated are then combined to reproduce the complete model representing the system bond graph model. Whereas, in this work we will present only the bond graph model of the reactor since the discussion will be about the phenomena occurring in this part. As it is presented in Fig.(2), the process is decomposed into subsystems represented by blocks diagram, the inputs and outputs of each subsystem is a pair of conjugated variables (effort e , flow f). In our case the pairs: (temperature T , \dot{Q} heat flow); (temperature T , \dot{H} enthalpy flow); (pressure P , mass flow \dot{m}); (chemical potential μ , molar flow \dot{n}); (torque τ , angular velocity ω) are associated respectively with thermal (conduction, convection), hydraulic, chemical and mechanical domain.

Bond graph model

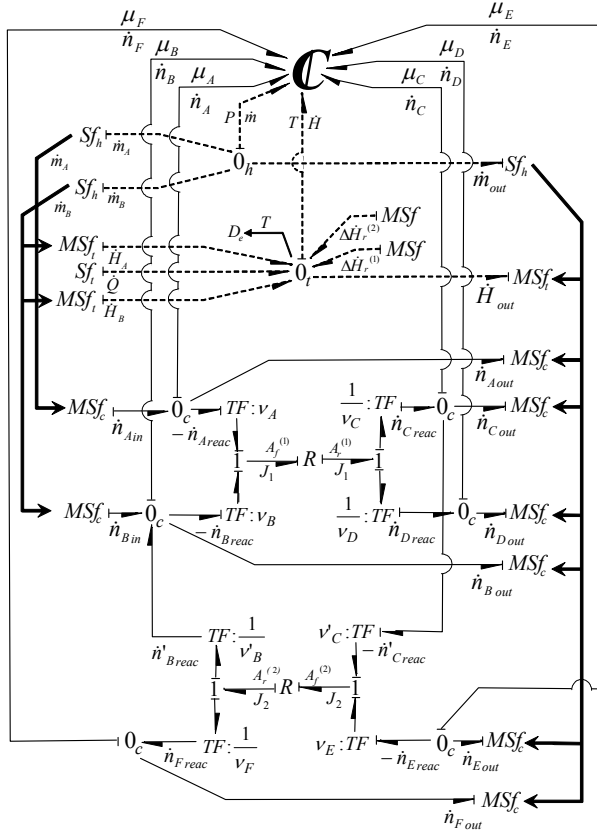


Figure 3: Bond graph model of the reactor

The bond graph model Fig. (3) represents the physical level of modeling, where the model is developed in details. The energy directions and causalities are assigned to allow the generation of the state space model representing the system dynamic after.

Multiport element C field

The stored powers, particularly chemical, hydraulic and thermal ones, are modeled by the capacitance multiport element C which appears in Fig. (3). The causality assignments of this element deals to write the effort variables $e = (\mu_i, T, P)$ in term of displacement variables $q = (n_i, H, m)$ as it will be explained in details after. In hydraulic and thermal domains, the constitutive laws representing the power storage dynamic are deduced from thermodynamic and hydrostatic laws, and they are expressed as:

$$P = \frac{g}{S} \int dm \quad (5)$$

$$T = \frac{1}{mC_p} \int dH \quad (6)$$

Where S is the vessel section, g is the gravity constant; C_p is the specific heat of the mixture. Concerning the chemical power stored in the reactor, the constitutive law describing the element dynamic is expressed

according to the general form of chemical potential:

$$\mu_i = \mu_i^\circ + RT \ln(a_i) \quad (7)$$

Where the effort μ_i is written in term of displacement n_i since the activity is expressed as $a_i = \Phi(n_i)$. Therefore, in our case where the mixture is considered as real solution the capacitance constitutive laws of each component are written as flowing:

$$\mu_i = \mu_i^\circ + RT \ln\left(\gamma_i \frac{n_i}{V}\right) \quad (8)$$

Where γ_i is the activity coefficient of the component i. Gathering all the Equations (5), (6) and (8), the global constitutive law of multiport C element is then presented by:

$$\begin{pmatrix} \mu_A \\ \mu_B \\ \mu_C \\ \mu_D \\ \mu_E \\ \mu_F \\ P \\ T \end{pmatrix} = \begin{pmatrix} \mu_A^\circ + RT \ln(\gamma_A n_A / V) \\ \mu_B^\circ + RT \ln(\gamma_B n_B / V) \\ \mu_C^\circ + RT \ln(\gamma_C n_C / V) \\ \mu_D^\circ + RT \ln(\gamma_D n_D / V) \\ \mu_E^\circ + RT \ln(\gamma_E n_E / V) \\ \mu_F^\circ + RT \ln(\gamma_F n_F / V) \\ \frac{g}{S} m \\ \frac{1}{mC_p} H \end{pmatrix} \quad (9)$$

Flow sources Sf

The hydraulic flow sources Sf_h correspond to the inlet mass flows \dot{m}_A , \dot{m}_B , and the outlet mass flow \dot{m}_{out} of the mixture expressed as:

$$Sf_h: m_{out} = U_V C_S \sqrt{(P - P_{out})} \quad (10)$$

And from Equation (5) we get:

$$Sf_h: m_{out} = U_V C_S \sqrt{\left(\frac{g}{S} m - P_{out}\right)} \quad (11)$$

Where C_S is a constant depending on the valve kind P_{out} is the pressure at the outlet. The other flow sources MSf_t , MSf_c of thermal and chemical domain respectively are modulated and written in term of mass flow sources Sf_H according to the expressions:

$$\begin{cases} MSf_t: \dot{H}_i = \dot{m}_i C_{p_i} T_i, \text{ for } i=A,B \\ MSf_t: \dot{H}_{out} = \dot{m}_{out} C_p T \\ MSf_c: \dot{n}_{i(in)} = \dot{m}_i (1/M_i), \text{ for } i=A,B \\ MSf_c: \dot{n}_{i(out)} = (\dot{m}_{out}/(\rho V)) n_i, \text{ for } i=A,B,C,D,E,F \end{cases} \quad (12)$$

Where M_i is the molar mass, ρ is the density of the mixture, T_i is temperature of A, B before entering to the reactor vessel, C_p is the specific heat.

Other thermal flow sources MSf_t are independent from mass flow sources, as heat flow source coming from coil heater and heat reactions, written as:

$$\begin{cases} MSf_t: \dot{Q} = \lambda(T-T_j) \\ MSf_t: \Delta\dot{H}_r^{(1)} = J_1\Delta H_r^{(1)} \\ MSf_t: \Delta\dot{H}_r^{(2)} = J_2\Delta H_r^{(2)} \end{cases} \quad (13)$$

Where λ is the conduction coefficient, T_j is the coolant fluid temperature, J_1, J_2 are the reactions rates and $\Delta H_r^{(1)}, \Delta H_r^{(2)}$ are the reactions heats.

The junctions

The 0 junctions correspond to flow conservation, and consequently $0_b, 0_h, 0_c$, correspond respectively to the mass, heat and components equations balance as it is shown in Fig.(3). For 1 junctions, they correspond to flow equality, so they represent in our case for chemical domain the mass action laws of the reactions expressed by:

$$\begin{cases} J_1 = \frac{-\dot{n}_{A_{\text{reac}}}}{v_A} = \frac{-\dot{n}_{B_{\text{reac}}}}{v_B} = \frac{\dot{n}_{C_{\text{reac}}}}{v_C} = \frac{\dot{n}_{D_{\text{reac}}}}{v_D} \\ J_2 = \frac{-\dot{n}'_{C_{\text{reac}}}}{v'_C} = \frac{-\dot{n}'_{E_{\text{reac}}}}{v'_E} = \frac{\dot{n}'_{B_{\text{reac}}}}{v'_B} = \frac{\dot{n}'_{F_{\text{reac}}}}{v'_F} \end{cases} \quad (14)$$

Where $n_{A_{\text{reac}}}, n_{B_{\text{reac}}}, n_{C_{\text{reac}}}, n_{D_{\text{reac}}}, n_{C_{\text{reac}}}, n'_{C_{\text{reac}}}, n'_{E_{\text{reac}}}, n'_{B_{\text{reac}}}, n'_{F_{\text{reac}}}$ are the number of moles consumed or produced in the reaction (1) and (2).

Multiport elements R field

Inside the reactor, the reactions kinetic is modelled by the R multi-ports elements Fig. (3). Below we will explain how the constitutive laws representing these elements are deduced. According to (Auslander et al. 1972), the mass action law expressing J_1 near of the equilibrium is written in term of activity a_i . For the irreversible reaction, J_2 is expressed in term of concentrations C_i .

Using the classical mass action law, the reactions rates J_1, J_2 are written then under the form:

$$\begin{cases} J_1 = \left(k_f^{(1)} \prod_{i=A,B} a_i^{\alpha_i} - k_r^{(1)} \prod_{i=C,D} a_i^{\alpha_i} \right) V \\ J_2 = \left(k_f^{(2)} \prod_{i=C,E} C_i^{\alpha_i} \right) V \end{cases} \quad (15)$$

To get the constitutive law cited in (Auslander et al. 1972), which relates the reaction rate J with affinity A ,

J_2 must be written in term of affinity, so replacing the concentration C_i in Equation (15) by its value from Equation (8), we get:

$$J_2 = \left(k_f^{(2)} \left(\frac{1}{\gamma_i} \right)^{\alpha_i} \prod_{i=C,E} a_i^{\alpha_i} \right) V \quad (16)$$

Where α_i is the partial reaction order of the component i . Replacing the activity by its value deduced from Equation (7) we obtain :

$$\begin{cases} J_1 = \left(k_f^{(1)} \prod_{i=A,B} \exp \frac{(\mu_i - \mu_i^\circ)\alpha_i}{RT} - k_r^{(1)} \prod_{i=C,D} \exp \frac{(\mu_i - \mu_i^\circ)\alpha_i}{RT} \right) V \\ J_2 = \left(k_f^{(2)} \left(\frac{1}{\gamma_i} \right)^{\alpha_i} \prod_{i=C,E} \exp \frac{(\mu_i - \mu_i^\circ)\alpha_i}{RT} \right) V \end{cases} \quad (17)$$

We have the reactions affinities $A_f^{(1)}, A_r^{(1)}, A_f^{(2)}$, are expressed by:

$$\begin{cases} A_f^{(1)} = \sum_{i=A,B} v_i \mu_i \\ A_r^{(1)} = \sum_{i=C,D} v_i \mu_i \\ A_f^{(2)} = \sum_{i=C,E} v'_i \mu_i \end{cases} \quad (18)$$

Since it is considered in our case that the order of reactions correspond to the stoichiometric coefficients $\alpha_i = v_i = v'_i$, we get the constitutive laws of the multiport R after replacing in Equation (17) the affinities values expressed in Equation (18), thus the reactions rates

J_1, J_2 are written in term of affinities and expressed by:

$$\begin{cases} J_1 = \left(k_f^{(1)} \exp \left(\sum_{i=A,B} \frac{-\mu_i \alpha_i}{RT} \right) \exp \left(\frac{A_f^{(1)}}{RT} \right) - k_r^{(1)} \exp \left(\sum_{i=C,D} \frac{-\mu_i \alpha_i}{RT} \right) \exp \left(\frac{A_r^{(1)}}{RT} \right) \right) V \\ J_2 = \left(k_f^{(2)} \left(\frac{1}{\gamma_i} \right)^{\alpha_i} \exp \left(\sum_{i=C,E} \frac{-\mu_i \alpha_i}{RT} \right) \exp \left(\frac{A_f^{(2)}}{RT} \right) \right) V \end{cases} \quad (19)$$

STATE SPACE MODEL GENERATION

The state space equation can be easily deduced from bond graph model due to the causal property. The state variables represent the displacement variable q in C elements. Thus the state space variable vector x is expressed by :

$$x = (n_A \ n_B \ n_C \ n_D \ n_E \ n_F \ m \ H)^T \quad (20)$$

The state space representation will be generated according to the general form:

$$\begin{cases} \dot{x} = f(x, u) \\ y = h(x, u) \end{cases} \quad (21)$$

Where the inputs u are the flow sources \dot{m}_A , \dot{m}_B , and valve control position U_V . The output y is the measured variables, which is the temperature in our application.

The generation procedure can be realized using the SYMBOLS software, where the bond graph model elaborated in Fig. (3) is implemented. The reactor state space representation is generated systematically, and we get the flowing equations system presented by:

$$\begin{cases} \dot{n}_A = \dot{m}_A \frac{1}{M_A} - \frac{U_V C_S \sqrt{m \frac{g}{S} - P_{out}}}{\rho V} n_A - J_1 \\ \dot{n}_B = \dot{m}_B \frac{1}{M_B} - \frac{U_V C_S \sqrt{m \frac{g}{S} - P_{out}}}{m} n_B - J_1 + J_2 \\ \dot{n}_C = - \frac{U_V C_S \sqrt{m \frac{g}{S} - P_{out}}}{m} n_C + J_1 - J_2 \\ \dot{n}_D = - \frac{U_V C_S \sqrt{m \frac{g}{S} - P_{out}}}{m} n_D + J_1 \\ \dot{n}_E = - \frac{U_V C_S \sqrt{m \frac{g}{S} - P_{out}}}{m} n_E - J_2 \\ \dot{n}_F = - \frac{U_V C_S \sqrt{m \frac{g}{S} - P_{out}}}{m} n_F + J_2 \\ \dot{m} = \dot{m}_A + \dot{m}_B - U_V C_S \sqrt{m \frac{g}{S} - P_{out}} \\ \dot{H} = \dot{m}_A C_{pA} T_A + \dot{m}_B C_{pB} T_B \\ \quad + J_1 \Delta H_r^{(1)} + J_2 \Delta H_r^{(1)} + \lambda \left(\frac{1}{m C_p} H - T_j \right) \\ y = \frac{1}{m C_p} H \end{cases} \quad (22)$$

Where J_1, J_2 are written in term of $n_A, n_B, n_C, n_D, n_E, n_F$ according to Equations (9), (8) and (17).

SIMULATION AND RESULTS

In this section we will put the emphasis on the simulation results to illustrate the adequacy of our variable choice, and the efficiency of the bond graph tool to treat readily such complicated process.

For this aim we have proceeded to implement the reactor bond graph model in SYMBOLS software. To avoid the control law synthesis, it is assumed that the volume mixture is maintained constant $V=0.25 \text{ m}^3$.

For that, the outlet volumes flow and inlet volume flow are considered constant where :

$$\dot{V}_A = \dot{V}_B = 0.003 \text{ m}^3/\text{s} = 2 \times \dot{V}_{out} = 0.006 \text{ m}^3/\text{s} .$$

Thus, the evolution of the different components is presented in Fig. (4) below.

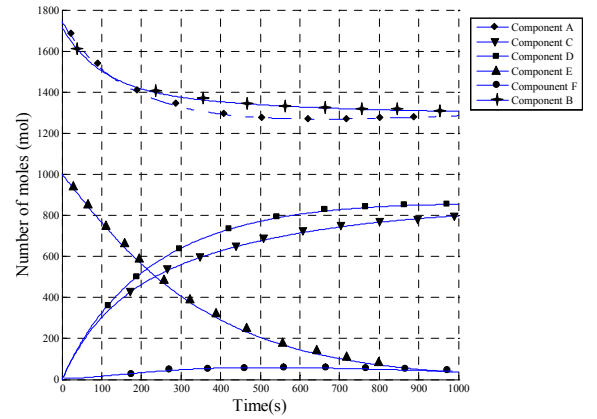


Figure 4: Components moles number

To justify the choice of the chemical potential as effort variable to represent the reaction kinetic for reversible and irreversible reactions, the influence of activity variation on the reaction evolution is studied.

We have proceeded to compare between the cases when the solution is considered ideal and real, and as it is shown in Fig. (5) there is a difference between the two behaviour, where the disappearance of the component A in the case of ideal solution is more important if we compare it with the second case (real solution).

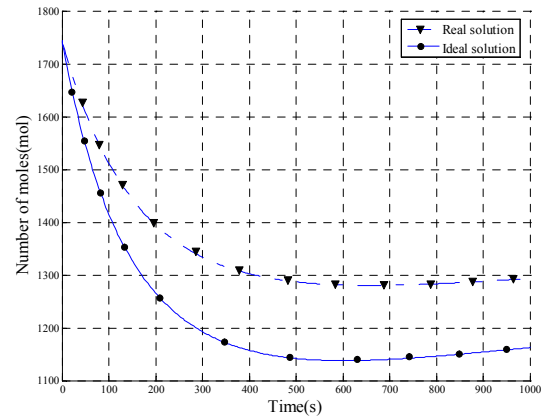


Figure 5: The component A reaction evolution

In the first case (ideal solution) the activity coefficient $\gamma_i=1$, whereas for the second case (real solution) we have $\gamma_i < 1$, that is why the activity a_i and chemical potential μ_i will be more important in the first case contrary to the second, and consequently the increase of μ_i will increase too the reaction rate J_1 according to Equation (18) and (19), which explain the disappearance phenomena of the component A in the two cases.

CONCLUSIONS

In this work the use of bond graph approach to model chemical reactors has allowed to elaborate graphical model able to be integrated in industrial installation. Moreover, it can be modified easily according to assumptions that we wish to take in consideration.

Due to the causality property we have generated systematically the state space model which can be used in the analysis or supervision applications.

Furthermore, due to the power variable choice, the impact of activity variation on the reaction behaviour has been illustrated.

Finally, this contribution adds and opens a new ways in the modelling process engineering, and will help us to resolve more complicated problems of chemical reactors modelling. However, the adequate choice of power variables is not sufficient; other considerations related to the system property must be taken into account, such compressibility, density variation....etc.

Further work deals with bond graph model for supervision design of chemical reactors will be proposed.

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