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Thermodynamic Analysis of Isobutane Dehydrogenation Reaction

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Abstract

The thermodynamics of isobutane dehydrogenation reaction was investigated thoroughly using most reliable literature data. Conversion and reaction mixture distribution at equilibrium were computed for various process conditions. Reaction enthalpy, $\Delta_R H_T^o$, ranges between 122±1.1 and 123±1.2 kJ.mol^{-1} over the temperature 773.15 to 923.15 K where the equilibrium constant K_T value varies between 0.12±0.03 and 2.6±0.7. The reaction becomes thermodynamically favorable at temperatures higher than 873.15 K.

Keywords: *Isobutane; 2-methylpropane; dehydrogenation; thermodynamic analysis.*

1. Introduction

Dehydrogenation reactions are largely employed in the chemical industry. The route to obtain principally olefins, for example, isobutene, is generally carried out using isobutane dehydrogenation on Cr- or Pt-based catalysts. $iC_4H_{10}(g) = iC_4H_8(g) + H_2(g)$ Open literature lacks however technically convenient information about thermodynamic equilibrium description of this reaction.

The Catofin® and the Snamprogetti-Yarsintezi®-FBD4 are the only two commercially proven dehydrogenation processes using Cr-based catalysts. Both processes do not use diluent to the feed gas. Catofin® process operates at sub-atmospheric pressure in the temperature range 860 to 920 K. While the FBD4 process operates at slightly higher than atmospheric pressure in the temperature range 800 to 860 K [1-3]. The Oleflex® process is the sole commercial process based on platinum catalyst, it operates at slightly higher than atmospheric pressure using feed gas enriched with hydrogen under moderate temperatures [2,4].

Literature described a variety of methods for prediction of thermodynamic properties of isobutane, isobutene and hydrogen. Therefore, wide discrepancy exists among experimental and estimated values of equilibrium constants and conversions [5-12].

In this work it is attempted to estimate thermodynamic parameters, including molar enthalpy, molar Gibbs free energy, equilibrium constant, conversion and product distribution of isobutane dehydrogenation reaction. Emphasis will be given to industrially relevant conditions.

2. Computational Work

2.1 Criteria for Input Data Selection

The main difficulty in analyzing thermodynamic equilibrium of reactions is to evaluate the Gibbs free energy, $\Delta_R G_T^o$. As ±1 kJ.mol^{-1} uncertainty in Gibbs free energy amplifies to ±12 % uncertainty in equilibrium constant at 1000 K due to exponential dependency between both parameters [13a, 14].

Differences in estimated or measured quantities of standard enthalpy of formation ΔH_f^o, standard free enthalpy of formation (Gibbs free energy of formation) ΔG_f^o, standard entropy of formation S_i^o, and molar gas phase heat capacity C_p^o (contributors to $\Delta_R G_T^o$) are frequently at the core of disputes among groups of researchers.

Accuracy of thermodynamic quantities usually differs following to the technique of measurement, or following to the method of estimation. For example, ΔH_f^o usually measured by bomb or flame calorimetric techniques. Both techniques are trustworthy [14], however each yields own accuracy. On the other hand, estimation methods exhibit dissimilar accuracies [6-9,12,15]. The thermodynamic quantity should be therefore defined with sufficient completeness with respect to the required accuracy so that all practical purposes associated with this quantity is unique. The usefulness of thermodynamic data, and thus much of the information that it provides, is therefore largely determined by the quality of the statements of uncertainty. To meet the needs of some industrial and commercial applications expanded uncertainty U_e is moreover favored [16]. Hence, both uncertainty information will be provided throughout this work.

The first part of this work will be devoted to evaluate available experimental thermodynamic data involved in calculation. Estimated thermodynamic quantities will be used, whenever experimental values are missing.

Best available experimental quantity (x) will be selected based on relative standard uncertainty $u_r(x)$, which is defined as the absolute difference Δx between measured and a reference quantity $x_{calc.}$ divided by the reference quantity: $u_r(x) = \frac{|\Delta x|}{x_{calc.}}$, whereby $x_{calc.}$ is a "conventional true value" of the described thermodynamic quantity estimated favorably by Benson's method [12,13a,17] or through its improvement by Domalski and Hearing [7]. Exceptions will be indicated if any. This criteria is expected to act as uniform uncertainty information of thermodynamic quantities in literature. Calculation is then proceeded as follow.

2.2 Calculation Method

The following gives the summary of calculations:

$$\Delta_R H^o_{298.15} = \sum \upsilon_i \Delta H^o_{f,i} \tag{1}$$

$$\Delta_R S^o_{298.15} = \sum \upsilon_i S^o_{f,i} \tag{2}$$

$$\Delta_R G^o_{298.15} = \sum \upsilon_i \Delta G^o_{f,i} \tag{3}$$

$$ln\, K_T = \frac{-\Delta_R G^o_T}{RT} = \frac{-\Delta_R H^o_T}{RT} + \frac{\Delta_R S^o_T}{R} \tag{4}$$

Both $\Delta_R H^o_T$ and $\Delta_R S^o_T$ are temperature dependent according to Eqs. (5) and (6).

$$\Delta_R H^o_T = \Delta_R H^o_{298.15} + \int_{298.15}^{T} \Delta_R {C_p}^o_T \mathrm{dT} \tag{5}$$

$$\Delta_R S^o_T = \Delta_R S^o_{298.15} + \int_{298.15}^{T} \frac{\Delta_R {C_p}^o_T}{T} \mathrm{dT} \tag{6}$$

The heat capacity of reaction mixture can be defined as follows:

$$\Delta_R {C_p}^o_T = \sum \upsilon_i C^o_{p_T,i} \tag{7}$$

The values of individual molar heat capacities $C^o_{p_T,i}$ follow diverse temperature functions. Thus, the results of Eq. (5) or (6) differ accordingly.

Temperature dependency of the heat capacities of gases is commonly represented by polynomials of the form [13b,18,19]:

$$C^o_{p_T,i} = a_{o,i}\, T + a_{1,i/2} T^2 + a_{2,i/3} T^3 + a_{3,i/4} T^4 + \ldots. \tag{8}$$

Poling et. al [13b], Reid et. al [18] and Kyle [20] give a set of thermodynamically consistent polynomials of the order four or five for estimation the ideal gas heat capacity. These polynomials functions will be critically evaluated in next section. Shomate function specified in [21], and other functions given in [22] and [19] were excluded due to less properly fitting to existing experimental data.

Thus, using Eqs. (7) and (8), it is now possible to compensate for temperature-induced changes in both the enthalpy and entropy terms respectively in Eqs. (5) and (6), allowing the calculation of thermodynamic equilibrium constants. This is accomplished by substitution and rearrangement that yields the followings:

$$\Delta_R {C_p}^o_T = \Delta a_o T + \frac{\Delta a_1}{2} T^2 + \frac{\Delta a_2}{3} T^3 + \frac{\Delta a_3}{4} T^4 \tag{9}$$

whereby: $\Delta a_n = \Delta_R a_n = \sum \upsilon_i a_{n,i}$ (9a)
n: 0, 1, 2 or 3 *and i: reaction species*

$$ln\, K_T = [\frac{-\Delta_R H^o_{298.15}}{T} + \Delta_R S^o_{298.15} + \Delta a_o \left(ln \frac{T}{298.15} + (\frac{298.15}{T} - 1) \right) + \Delta a_1 \left((T - 298.15) - \frac{1}{2T}(T^2 - 298.15^2) \right) + \Delta a_2 \left(\frac{1}{2}(T^2 - 298.15^2) - \frac{1}{3T}(T^3 - 298.15^3) \right) + \Delta a_3 \left(\frac{1}{3}(T^3 - 298.15^3) - \frac{1}{4T}(T^4 - 298.15^4) \right)] \frac{1}{R} \tag{10}$$

It is also possible to compute free reaction enthalpy at temperature *T* from Eq. (4) or from Eq. (11):

$$\Delta_R G^o_T = \Delta_R H^o_T - T\, \Delta_R S^o_T \tag{11}$$

The relationship between *K* and equilibrium conversion $X_{(iC4H10,e)}$ can be determined using the following path:

$$K = \frac{y_{iC4H8} \cdot y_{H2}}{y_{iC4H10}} (\frac{P^o}{P})^{-\upsilon} \tag{12}$$

where υ is the reaction stoichiometric coefficients

$$\upsilon = \sum \upsilon_i \tag{13}$$

Mole fraction can be expressed by using reaction number ε:

$$y_i = \frac{\dot{n}_{io} + \upsilon_i \varepsilon}{\dot{n}_o + \upsilon \varepsilon} \tag{14}$$

$$\dot{n}_o = \sum_i^{feed} \dot{n}_{io} \tag{15}$$

= sum of mole streams of all feed components (iC_4H_{10}, and H_2, inert gas if any)

$$\varepsilon = \dot{n}_{iC4H10,o} . X \tag{16}$$

Thus, using Eqs. (12)-(16), it is possible to express the relationship between the *K* and *X*:

$$K = \frac{X\,(h+X)}{(1+h+i+X)(1-X)}\, P \tag{17}$$

where *i* and *h* are:

$$i = \frac{\dot{n}_{inert}}{\dot{n}_{iC4H10,o}} \;,\; h = \frac{\dot{n}_{H2}}{\dot{n}_{iC4H10,o}} \tag{18}$$

i and *h* are the number of moles of inert gases and hydrogen per mole of isobutane in the feed, respectively.

In some industrial operations, like in Oleflex process, part of the hydrogen produced is recycled to inhibit the formation of coke on the catalyst. However this is not the case with the other two commercial processes. Thus, for inert/hydrogen free isobutane feed the equilibrium conversion can be readily calculated by

$$K = \frac{X^2}{1-X^2}\, P \tag{19}$$

2.3 Heat Capacity Regression Coefficients

Regression of several mathematical polynomials for gas phase heat capacity was compared with experimental data from literature. Regression coefficients of these polynomials for related reaction species are given in Tables 1 - 3. Evaluation criteria is described in section 2.1.

Table 1. Gas Phase Heat Capacity Regression Coefficients for ***Isobutane****, over the T-range 298-1000K.*

Coefficients	Poling et. al [13b]	Reid et. al [18]
$a_{0,i}$	27.860214	-1.39
$a_{1,i}$	0.148679262	3.85E-01
$a_{2,i}$	0.000455358	-1.85E-04
$a_{3,i}$	-6.73E-07	2.90E-08
$a_{4,i}$	2.69E-10	

Table 2. Gas Phase Heat Capacity Regression Coefficients for ***Isobutene****, over the T-range 298-1000K.*

coefficients	Poling et. al [13b]	Reid et. al [18]
$a_{0,i}$	26.862534	1.61E+01
$a_{1,i}$	1.74E-01	2.80E-01
$a_{2,i}$	0.000192303	-1.09E-04
$a_{3,i}$	-3.2832E-07	9.10E-09
$a_{4,i}$	1.30197E-10	

*Table 3. Gas Phase Heat Capacity Regression Coefficients for **Hydrogen**, over the T-range 298-1000K.*

coefficients	Poling et. al [13b]	Reid et. al [18]	Kyle [20]
$a_{0,i}$	23.969262	27.14	29.11
$a_{1,i}$	0.030603834	9.274E-03	-1.92E-03
$a_{2,i}$	-6.4184E-05	-1.381E-05	4.00E-06
$a_{3,i}$	5.75329E-08	7.645E-09	-8.70E-10
$a_{4,i}$	-1.7709E-11		

Tables 4 - 6 compare heat capacities estimated using these polynomials with experimental data. Due to absence of experimental data for isobutene, estimated values from Kilpatrick and Pitzer [15] have been used.

*Table 4. Experimental and Estimated Gas Phase Heat Capacities C_p of **Isobutane** between 298.15 and 1000K.*

T /K	Exp.C_p [23]	Est.C_p [18]	$u_r(C_p)$x100	Est. C_p [13b]	$u_r(C_p)$x100
298	96.56	97.67	1.15	96.95	0.41
300	97.06	98.19	1.16	97.45	0.40
500	149.10	148.43	0.45	148.71	0.26
700	**188.28**	**187.38**	**0.48**	188.78	0.26
800	**203.64**	**203.05**	**0.29**	203.81	0.08
900	**216.94**	**216.42**	**0.24**	216.37	0.26
1000	**228.45**	**227.66**	**0.35**	227.92	0.23

*Table 5. Experimental and Estimated Gas Phase Heat Capacities C_p **Isobutene** between 298.15 and 1000K.*

T /K	Est.C_p [15]	Est.C_p [18]	$u_r(C_p)$x100	Est. C_p [13b]	$u_r(C_p)$x100
298.15	89.12	90.16	1.17	88.18	1.05
300	89.5	90.60	1.23	88.61	0.99
400	111.17	111.34	0.15	109.62	1.39
500	130.71	130.11	0.46	129.12	1.22
600	147.70	146.98	0.49	146.55	0.78
700	**162.38**	**161.99**	**0.24**	161.66	0.45
800	**175.14**	**175.20**	**0.04**	174.50	0.36
900	**186.31**	**186.67**	**0.19**	185.46	0.46
1000	**196.02**	**196.45**	**0.22**	195.21	0.41

*Table 6. Experimental and Estimated Gas Phase Heat Capacities C_p of **Hydrogen** between 298.15 and 1000K.*

T /K	Exp.C_p [24]	Est.C_p [18]	$u_r(C_p)$ x100	Est.C_p [13b]	$u_r(C_p)$ x100	Est.C_p [20]	$u_r(C_p)$ x100
298	28.84	28.88	0.13	28.77	0.24	28.87	0.10
300	28.84	28.89	0.15	28.78	0.20	28.87	0.10
400	29.18	29.13	0.19	29.17	0.05	28.93	0.87
500	29.26	29.28	0.07	29.31	0.18	29.04	0.73
600	29.32	29.38	0.20	29.36	0.11	29.21	0.38
700	**29.44**	**29.49**	**0.15**	29.42	0.06	29.43	0.03
800	**29.63**	**29.64**	**0.03**	29.58	0.16	29.69	0.23
900	**29.88**	**29.87**	**0.02**	29.85	0.12	29.99	0.38
1000	**30.21**	**30.25**	**0.14**	30.21	0.02	30.33	0.40

It is obvious that polynomials described in Reid et al. [18] fit with smallest relative uncertainty to experimental data in the range 700 to 1000K. The heat capacity polynomial of isobutane according to Poling at al. [13b] exhibited excellent accuracy. However, it is a fifth order polynomial. Hence for consistency reason the polynomial after Reid et al. [18] is adopted for following estimations.

Figure 1, displays the excellent fit of adopted polynomials to experimental and data of gas phase heat capacities of reaction species.

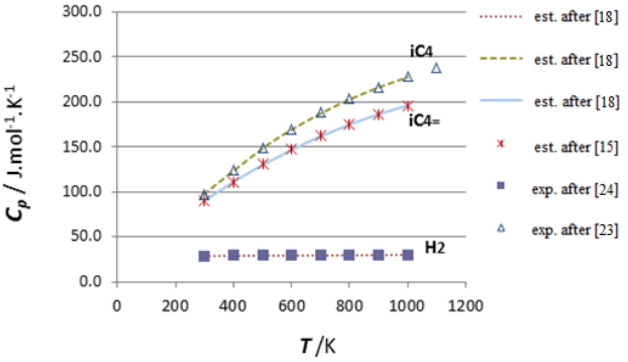

Figure 1. Estimated and experimentally measured gas phase heat capacity of isobutane (iC_4), isobutene ($iC_4^{=}$), and hydrogen (H_2) as a function of temperature.

2.4 $\Delta H^o_{f,i}$ and $\Delta G^o_{f,i}$ from Literature

Many studies reported various values for $\Delta H^o_{f,i}$, $\Delta G^o_{f,i}$, and $\Delta S^o_{f,i}$ for isobutane and isobutene. Main sources and values are summarized in Table 7 and 8. Selection of most reliable data follows lowest relative uncertainty; mainly for $\Delta H^o_{f,i}$ and $\Delta S^o_{f,i}$ as explained in section 2.1.

*Table 7. Reported Standard Enthalpy of Formation, Standard Gibbs Energy of Formation and Standard Entropy of Formation for **Isobutane** In Literature at 298.15 K and 1 bar.*

	Prosen et al.[25]	Benson et al. [12]	Dom/Hea [7]	97TRC^{a} [19]	Scott [26]	Uncertainty $^{b)}$
Δ $\boldsymbol{H^o_f}$**(298.15),** kJ.mol^{-1}						
Experimental	-135.65^{f}	**-134.387**	-134.18^{e}	-134.99	-134.387	0.42
Estimated		-134.35	-134.73			
Relative Uncertainty $^{c)}$	0.97	0.03	0.12	0.48	0.03	
Δ $\boldsymbol{G^o_f}$**(298.15),** kJ.mol^{-1}						
Experimental		**-21.23^{d}**	-21.07	-21.47^{d}	-20.93^{d}	0.16
Estimated		-21.22^{d}	-20.78			
Relative Uncertainty $^{c)}$		0.05	0.71	1.16	1.39	
Δ $\boldsymbol{S^o_f}$**(298.15),** J.mol^{-1}.K^{-1}						
Experimental		**-379.53^{d}**	-379.37	-380.85^{d}	-380.54^{d}	0.43
Estimated		-379.45^{d}	-382.07			
Relative Uncertainty $^{c)}$		0.02	0.02	0.37	0.29	

a) Poling et al. [13b]. Same figures reported in reference [19]

b) Standard uncertainty estimated after Eq.(27) under assumption rectangular probability

c) x100, estimated based on Benson's el al. [12]

d) corrected reference value from 1atm to 1 bar

e) quoted experimental value after [27], expanded uncertainty ∓0.63 kJ.mol^{-1}, The reference used flame calorimeter

f) ∓0.54 kJ.mol^{-1}, given by source, The reference used Bomb calorimeter

Table 8. Reported Standard Enthalpy of Formation, Standard Gibbs Energy of Formation and Standard Entropy of Formation for ***Isobutene****. Standard Conditions: at 298.15K and 1 bar.*

	Prosen et al.[25]	Benson et al.[12]	Zwolinski et al. [28]	Dom/Hea [7]	97TRC [a] [19]	Alb/Geh [8]	Uncertainty b)
ΔH_f^o(298.15), kJ.mol^{-1}							
Experimental	-17.95[f]	-16.89	-16.9	**-16.9**[e]	-17.1		0.31
Estimated		(-15.90)[g]		-18.58		-16.9	
Relative Uncertainty c)	0.06	0.06	0.0	0.0	1.17		
ΔG_f^o(298.15), kJ.mol^{-1}							
Experimental		57.82[d]	58.05[d]	**57.76**	58.15[d]		0.11
Estimated		58.56[d]		55.57		58.17	
Relative Uncertainty c)		0.60	0.21	0.70	0.03		
ΔS_f^o(298.15), J.mol^{-1}.K^{-1}							
Experimental		-250.58[d]		**-250.41**[d]	-252.39[d]	251.38[d,h]	0.57
Estimated		-249.74[d]		-248.60 [d]		-250.19[d]	
Relative Uncertainty c)		0.15		0.09	0.88	0.48	

a) , b) and d) see Table 7 foot note
c) x100, estimated based on reference [8]
e) quoted experimental value, reference not given
f) ∓1.09 kJ.mol^{-1}, given by the source
g) Benson [17]
h) Scott [26]

Table 9. Standard Molar Enthalpy and Standard Molar Gibbs Free Energy of Isobutane Dehydrogenation Reaction Based on Formation Energies Given by Several Authors, in kJ.mol^{-1}.

	Prosen et al.[25]	Benson et al.[12]	97TRC [a] [19]	Dom/Hea [7]	This work	max. Δ[b]	Expanded Uncertainty
$\Delta_R H^o$(298.15)	117.70[c]	117.50	117.89	117.28	**117.49**	0.61	1.04
$\Delta_R G^o$(298.15)		79.05	79.62	78.83	**78.99**	0.79	0.38

a) Poling et al. [13b]
b) maximum difference between highest and lowest values
c) ∓1.63 kJ.mol^{-1}

Due to diversity of measurement/estimation techniques, it appears convenient to consider that all thermodynamic figures given in these tables have equal probability to be correct. Uncertainty is then estimated following to the method described in [16] for rectangular distribution of type B. Standard uncertainty is therefore calculated from the following equation:

$$u(x) = a/\sqrt{3} \tag{20}$$

where x is the variable; for $\Delta H_{f,i}^o$or $\Delta G_{f,i}^o$, a is the half of the interval between measurand's upper- and lower bounds.

The values for each compound listed in bold were selected for all subsequent calculations. Maximum difference in reported $\Delta H_{f,i}^o$ values according to Tables 7 and 8 is 1.47 kJ.mol^{-1}. Whereas maximum difference in reported values $\Delta G_{f,i}^o$ is 0.54 kJ.mol^{-1}. These differences are generally accounted as usual fluctuation in reported thermodynamic data.

3. Results and Discussion

3.1 Sensitivity Analysis

Equilibrium constant, K_T, is very sensitive to the thermodynamic quantity, $\Delta_R G_T^o$. In following it is demonstrated how much available information can affect the value of K_T and other thermodynamic parameters for isobutane dehydrogenation reaction.

Table 9 compares calculated standard molar reaction enthalpy and standard molar Gibbs free energy, while Table 10 compares the equilibrium constants. Maximum difference in $\Delta_R H_{298.15}^o$and in $\Delta_R G_{298.15}^o$values is 0.61 and 0.79 kJ.mol^{-1}, respectively. Standard molar enthalpy of isobutane dehydrogenation reaction is 118±1.0 kJ.mol^{-1}, while standard molar Gibbs free energy equals to 79.0 ± 0.4 kJ.mol^{-1}.

It is to recognize that mathematical analysis of uncertainties in thermodynamic parameters usually follows reasonable assumptions. Expanded uncertainty of standard molar enthalpy, 1.0 kJ.mol^{-1}, for example, is calculated based on equal probability assumption for all literary available enthalpies of formations since they have different origin and methods as described above.

The calculation of uncertainty in equilibrium constant is rather more complicated. Thus reasonable assumption must be made to simplify the calculation. One could make here two different, however both seem reasonable, assumptions:

a. Each of temperature and heat capacity coefficients have negligible error:

In this case expanded uncertainty of equilibrium constant, $U_e(K_T)$, could be calculated according to Eqs. (4), (10), and (21) - (24):

$$U_e = k\, u_c(x_i) \tag{21}$$

whereby k =2 is the coverage factor for 95% confidence level, $u_c(x_i)$ is the combined uncertainty (propagated uncertainty), calculated according to Eq. (22):

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) \tag{22}$$

where f is the function according to Eq. (1) or (3), while $u(x_i)$ values are calculated based on Eq. (20) and related values from Tables 7 and 8.

$$u_c^2(\ln K_T) = \frac{u_c^2(\Delta_R H_{298.15}^o)}{(RT)^2} + \frac{u_c^2(\Delta_R S_{298.15}^o)}{R^2} \tag{23}$$

$$u_c(K_T) = K_T \,.\, u_c(\ln K_T) \qquad (24)$$

whereby (according to Eq. 22 and Tables 7- 9):
$u_c(\Delta_R H^o_{298.15}) = 0.52$ kJ.mol^{-1}
$u_c(\Delta_R S^o_{298.15}) = 0.7$ J.mol^{-1}.K^{-1}
b. Temperature only has negligible error:

In this case uncertainty is propagated according to Eqs. (4) through (10) as follows: From Eq.(5) and Eq.(22):

$$u_c^2(\Delta_R H^o_T) = u_c^2(\Delta_R H^o_{298.15}) + (T - 298.15)^2 . u_c^2(\Delta_R C_p) \qquad (25)$$

whereby: $u_c(\Delta_R C_p)$ is the combined uncertainty in heat capacity of reaction mixture at temperature T according to Eqs. (7), (22) and (28). Uncertainty in heat capacity for each reaction species $u(C_{pi})$ is estimated using differences ΔCp_i between experimental- and C_{pi}-data after Reid et al. [18]. The variance of differences for concerned T range between 700 and 1000K ($N = 4$ points, typed in bold in the tables 4-6) are calculated using Eqs. (26) and (27), following to the method described in [16] for "type A evaluation" under assumption that individual observations of C_{pi} differ in values due to random effects.

The further uncertainty calculation is accomplished using Eqs. (27 through 31):

$$s(C_{p_i}) = \sqrt{\frac{1}{N-1}\sum_1^{N=4} \Delta Cp_i} \qquad (26)$$

$$u_c^2(\mathrm{Cp}_i) = s^2(C_{p_i})/N \qquad (27)$$

Intermediate results: $u_c^2(\mathrm{Cp}_{iC4}) = 0.172$, $u_c^2(\mathrm{Cp}_{iC4^=}) = 0.04$, $u_c^2(\mathrm{Cp}_{H2}) = 0.0001$ (J.mol^{-1}.K^{-1})^2
From Eq.(7) and Eq.(22):

$$u_c^2(\Delta_\mathrm{R} C_p) = \sum u_c^2(C_{p_i}) \qquad (28)$$

Eq.(25) can be resolved after T, using following input data:
$u_c(\Delta_R H^o_{298.15}) = 0.52$ kJ.mol^{-1}
$u_c(\Delta_\mathrm{R} C_p) = 0.46$ J.mol^{-1}.K^{-1}
From Eq.(6) and Eq.(22):

$$u_c^2(\Delta_\mathrm{R} S^o_T) = u_c^2(\Delta_\mathrm{R} S^o_{298.15}) + \left(\ln \frac{T}{298.15}\right)^2 . u_c^2(\Delta_\mathrm{R} C_p) \qquad (29)$$

Eq.(29) can be resolved after T, using following input data:
$u_c(\Delta_R S^o_{298.15}) = 0.7$ J.mol^{-1}.K^{-1}
$u_c(\Delta_\mathrm{R} C_p) = 0.46$ J.mol^{-1}.K^{-1}
From Eq.(11) and Eq.(22):

$$u_c^2(\Delta_\mathrm{R} G^o_T) = u_c^2(\Delta_\mathrm{R} H^o_T) + T^2 . u_c^2(\Delta_\mathrm{R} S^o_T) \qquad (30)$$

Eq. (30) to be resolved after T and outcomes of Eqs.(29) and (25)
From equations (4), (22) and (24):

$$u_c(K_T) = K_T . \frac{u_c(\Delta_\mathrm{R} G^o_T)}{RT} \qquad (31)$$

Expanded uncertainty $U_e(K_T)$ is then calculated according to Eq. (21).

Table 10 reports equilibrium constant with expanded uncertainties ranging between 21.5 and 23.5% of K value following to the first assumption, versus 26 to 26.5% following to the second assumption. It is apparent that both assumptions give reasonably matching uncertainty. Besides, one can see that slight difference in standard molar reaction enthalpy (0.61 kJ.mol^{-1}, Table 9) or in standard molar Gibbs free energy (0.79 kJ.mol^{-1}, Table 9) leads up to 16% difference in equilibrium constant at high temperatures. Thus it is important to select accurate input data from literature for calculation. Figure 2 shows equilibrium constants calculated according to various data sources, under usage of same C_p-Temperature regression function. All values are within the given uncertainty limits, using first assumption.

Table 10. Equilibrium Constant K_T of Isobutane Dehydrogenation Reaction at Various Temperatures, Based on Several Data Sources.

T /K	[7]	[13b]	[12]	This work	U_e(K$_\mathrm{T}$)^a	U_e(K$_\mathrm{T}$)^b
773.15	0.12	0.10	0.11	**0.12**	**0.03**	**0.03**
783.15	0.15	0.13	0.14	**0.15**	**0.04**	**0.03**
793.15	0.19	0.16	0.18	**0.19**	**0.05**	**0.04**
803.15	0.24	0.20	0.23	**0.24**	**0.06**	**0.05**
813.15	0.30	0.25	0.29	**0.30**	**0.08**	**0.07**
823.15	0.37	0.32	0.36	**0.37**	**0.10**	**0.08**
833.15	0.46	0.39	0.45	**0.46**	**0.12**	**0.10**
843.15	0.57	0.49	0.55	**0.56**	**0.15**	**0.13**
853.15	0.70	0.60	0.68	**0.69**	**0.18**	**0.15**
863.15	0.86	0.73	0.83	**0.85**	**0.22**	**0.19**
873.15	1.04	0.89	1.01	**1.03**	**0.27**	**0.23**
883.15	1.26	1.08	1.22	**1.25**	**0.33**	**0.27**
893.15	1.52	1.30	1.47	**1.50**	**0.39**	**0.33**
903.15	1.82	1.56	1.76	**1.80**	**0.47**	**0.39**
913.15	2.17	1.87	2.11	**2.16**	**0.56**	**0.47**
923.15	2.59	2.22	2.51	**2.57**	**0.67**	**0.56**

a) Expanded uncertainty, assuming that both of temperature and heat capacity coefficients have negligible error.
b) Expanded uncertainty, assuming that the temperature only has negligible error.

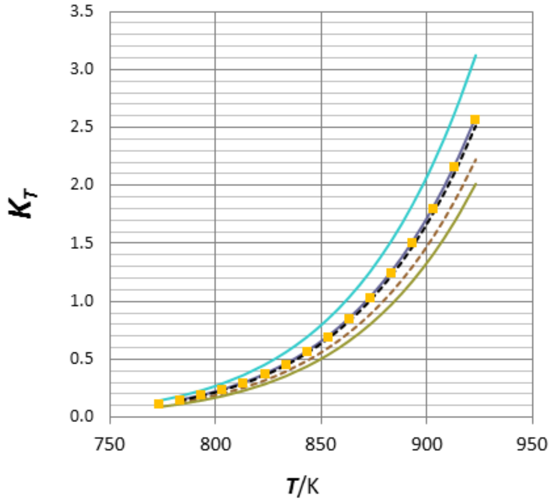

Figure 2: Equilibrium constant variation with temperature for isobutane dehydrogenation reaction using several input data

3.2 Equilibrium of Isobutane Dehydrogenation Reaction

The set of data selected above has the advantage of including "best available" thermodynamic quantities: $\Delta H^o_{f,i}$, and $\Delta G^o_{f,i}$, and $C^o_{p_i}$ and best fitting C_p-T regression function in literature. The reaction enthalpy, the Gibbs free energy change and equilibrium constant of isobutane dehydrogenation reaction have been calculated for industrially relevant temperatures. Results are shown in Tables 10 and 11.

The reaction is strongly endothermic. Reaction enthalpy, $\Delta_\mathrm{R} H^o_T$, ranges between 122±1.1 and 123±1.2 kJ.mol^{-1}. Free Gibbs energy, $\Delta_\mathrm{R} G^o_T$, shows that isobutane dehydrogenation becomes thermodynamically favorable at temperatures higher than 873.15 K. The values of equilibrium constant K_T varies with temperature between 0.12±0.03 and 2.6±0.7.

Table 11. Calculated Reaction Enthalpy and Free Gibbs Energy at Various Temperatures for Isobutane Dehydrogenation, in kJmol^{-1}.

T °C	T K	$\Delta_R H_T^o$	$U_e(\Delta_R H_T^o)^a$	$\Delta_R G_T^o$	$U_e(\Delta_R G_T^o)^a$
500	773.15	122.38	1.13	13.84	1.70
510	783.15	122.40	1.13	12.43	1.72
520	793.15	122.42	1.14	11.03	1.74
530	803.15	122.44	1.14	9.63	1.76
540	813.15	122.45	1.14	8.22	1.78
550	823.15	122.47	1.15	6.82	1.80
560	833.15	122.48	1.15	5.41	1.82
570	843.15	122.49	1.15	4.01	1.84
580	853.15	122.50	1.16	2.60	1.86
590	863.15	122.51	1.16	1.19	1.88
600	873.15	122.51	1.17	-0.21	1.90
610	883.15	122.52	1.17	-1.62	1.92
620	893.15	122.52	1.18	-3.02	1.94
630	903.15	122.52	1.18	-4.43	1.96
640	913.15	122.52	1.18	-5.83	1.98
650	923.15	122.52	1.19	-7.24	2.00

a) Expanded uncertainty calculated under assumption that only temperature measurements has negligible error.

From industrial point of view, to achieve reasonable equilibrium conversion, the reaction is usually operated at high temperature and low pressure in Catofin process. FBD4 and Oleflex processes, however, operate at pressure slightly above atmospheric. Therefore, equilibrium conversion has been calculated for wide range of temperatures and pressures. Calculations followed Eq. (17). Results are presented in Tables 12 through 16 and Figure 3.

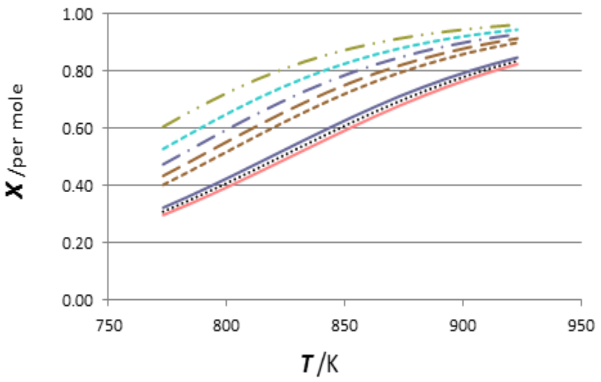

Figure 3: Isobutane conversion as a function of temperature in isobutane dehydrogenation reaction carried out under several presures.

Table 12. Equilibrium Conversion per Mole Isobutane at Various Temperatures and Pressures, Feed Gas without Diluent. Expanded Uncertainties are Given in Table 13.

T/°C	T /K	0.12 MPa	0.11 MPa	0.1 MPa	0.07 MPa	0.06 MPa	0.05 MPa	0.04 MPa	0.03 MPa	0.02 MPa
500	773.15	0.2971	0.3091	0.3227	0.3773	0.4028	0.4343	0.4745	0.5284	0.6062
510	783.15	0.3314	0.3445	0.3592	0.4179	0.4449	0.4780	0.5198	0.5749	0.6523
520	793.15	0.3678	0.3818	0.3975	0.4598	0.4881	0.5224	0.5651	0.6204	0.6958
530	803.15	0.4058	0.4207	0.4374	0.5026	0.5318	0.5668	0.6096	0.6640	0.7361
540	813.15	0.4451	0.4607	0.4782	0.5454	0.5750	0.6101	0.6524	0.7050	0.7727
550	823.15	0.4852	0.5014	0.5194	0.5877	0.6173	0.6518	0.6929	0.7429	0.8055
560	833.15	0.5255	0.5421	0.5604	0.6289	0.6579	0.6914	0.7306	0.7773	0.8343
570	843.15	0.5657	0.5824	0.6007	0.6682	0.6963	0.7283	0.7651	0.8081	0.8593
580	853.15	0.6051	0.6217	0.6398	0.7054	0.7321	0.7622	0.7963	0.8354	0.8809
590	863.15	0.6432	0.6595	0.6771	0.7399	0.7650	0.7929	0.8241	0.8593	0.8994
600	873.15	0.6795	0.6953	0.7122	0.7715	0.7948	0.8204	0.8486	0.8800	0.9151
610	883.15	0.7138	0.7288	0.7449	0.8002	0.8216	0.8448	0.8701	0.8978	0.9283
620	893.15	0.7456	0.7598	0.7748	0.8259	0.8453	0.8662	0.8887	0.9130	0.9394
630	903.15	0.7749	0.7881	0.8020	0.8487	0.8662	0.8848	0.9047	0.9259	0.9488
640	913.15	0.8015	0.8137	0.8265	0.8689	0.8845	0.9010	0.9184	0.9369	0.9566
650	923.15	0.8256	0.8367	0.8484	0.8865	0.9003	0.9149	0.9302	0.9463	0.9632

Table 13. Expanded Uncertainty $U_e(X)$ in Equilibrium Conversion of Table 12, per Mole Isobutane at T and P ^{A}.

T/°C	T /K	0.12 MPa	0.11 MPa	0.1 MPa	0.07 MPa	0.06 MPa	0.05 MPa	0.04 MPa	0.03 MPa	0.02 MPa
500	773.15	0.0348	0.0363	0.0379	0.0445	0.0476	0.0516	0.0568	0.0641	0.0754
510	783.15	0.0387	0.0403	0.0420	0.0492	0.0526	0.0569	0.0625	0.0703	0.0823
520	793.15	0.0428	0.0445	0.0464	0.0542	0.0579	0.0625	0.0684	0.0767	0.0892
530	803.15	0.0472	0.0490	0.0511	0.0595	0.0634	0.0683	0.0746	0.0832	0.0960
540	813.15	0.0517	0.0537	0.0559	0.0649	0.0691	0.0742	0.0809	0.0898	0.1026
550	823.15	0.0565	0.0586	0.0610	0.0705	0.0749	0.0803	0.0872	0.0962	0.1089
560	833.15	0.0615	0.0637	0.0663	0.0763	0.0809	0.0864	0.0934	0.1024	0.1147
570	843.15	0.0666	0.0690	0.0717	0.0821	0.0868	0.0925	0.0995	0.1083	0.1199
580	853.15	0.0719	0.0744	0.0772	0.0880	0.0927	0.0984	0.1053	0.1137	0.1245
590	863.15	0.0773	0.0799	0.0827	0.0937	0.0985	0.1040	0.1107	0.1187	0.1285
600	873.15	0.0827	0.0854	0.0883	0.0993	0.1039	0.1093	0.1156	0.1230	0.1319
610	883.15	0.0881	0.0908	0.0937	0.1045	0.1091	0.1142	0.1201	0.1269	0.1348
620	893.15	0.0934	0.0961	0.0990	0.1095	0.1138	0.1186	0.1240	0.1302	0.1372
630	903.15	0.0985	0.1011	0.1040	0.1140	0.1181	0.1225	0.1274	0.1330	0.1392
640	913.15	0.1034	0.1059	0.1086	0.1182	0.1219	0.1260	0.1304	0.1353	0.1407
650	923.15	0.1080	0.1104	0.1130	0.1218	0.1253	0.1289	0.1329	0.1373	0.1420

a) Calculated based on equations (21) and (22), whereby f is the function according to equation (19)

The resulted equation is the following: $\left(\frac{u_c(X)}{X}\right)^2 = \left(\frac{1}{2}\right)^2 \left(\frac{u_c(K_T)}{K_T}\right)^2 + \left(\frac{1}{2}\right)^2 \left(\frac{u_c(K_T)}{P+K_T}\right)^2$ (32)

Table 14. Equilibrium Conversion per Mole Isobutane at Technically Relevant Temperatures and Pressures When 1 Volume Hydrogen is Mixed to 100 Volumes Isobutane Feed.

	0.12 MPa		0.11 MPa		0.1 MPa	
T /K	X	U_e [a)]	X	U_e [a)]	X	U_e [a)]
773.15	0.2937	0.0391	0.3057	0.0407	0.3193	0.0425
783.15	0.3281	0.0437	0.3412	0.0454	0.3560	0.0474
793.15	0.3646	0.0486	0.3787	0.0505	0.3946	0.0526
803.15	0.4029	0.0538	0.4179	0.0558	0.4346	0.0581
813.15	0.4423	0.0593	0.4580	0.0614	0.4756	0.0638
823.15	0.4826	0.0651	0.4989	0.0673	0.5170	0.0698
833.15	0.5232	0.0712	0.5399	0.0735	0.5582	0.0760
843.15	0.5635	0.0775	0.5804	0.0799	0.5988	0.0824
853.15	0.6031	0.0841	0.6198	0.0864	0.6380	0.0890
863.15	0.6414	0.0908	0.6578	0.0931	0.6755	0.0956
873.15	0.6779	0.0976	0.6938	0.0999	0.7108	0.1023
883.15	0.7123	0.1044	0.7275	0.1066	0.7436	0.1090
893.15	0.7443	0.1112	0.7586	0.1133	0.7737	0.1155
903.15	0.7738	0.1177	0.7871	0.1198	0.8011	0.1219
913.15	0.8005	0.1241	0.8128	0.1260	0.8257	0.1280
923.15	0.8247	0.1301	0.8359	0.1319	0.8476	0.1337

a) Calculated based on equations (21) and (32), whereby h assumed negligible

Table 15. Equilibrium Conversion per Mole Isobutane at Technically Relevant Temperatures and Pressures When 5 Volume Hydrogen is Mixed to 100 Volumes Isobutane Feed.

	0.12 MPa		0.11 MPa		0.1 MPa	
T /K	X	U_e [a)]	X	U_e [a)]	X	U_e [a)]
773.15	0.2805	0.0373	0.2927	0.0390	0.3066	0.0409
783.15	0.3156	0.0420	0.3289	0.0438	0.3439	0.0459
793.15	0.3527	0.0470	0.3670	0.0490	0.3831	0.0512
803.15	0.3916	0.0523	0.4068	0.0545	0.4239	0.0569
813.15	0.4317	0.0579	0.4478	0.0602	0.4656	0.0628
823.15	0.4728	0.0638	0.4894	0.0663	0.5078	0.0691
833.15	0.5141	0.0700	0.5311	0.0726	0.5498	0.0756
843.15	0.5552	0.0764	0.5723	0.0792	0.5911	0.0824
853.15	0.5955	0.0830	0.6126	0.0860	0.6311	0.0893
863.15	0.6345	0.0898	0.6512	0.0929	0.6693	0.0963
873.15	0.6717	0.0967	0.6879	0.0999	0.7052	0.1034
883.15	0.7068	0.1036	0.7222	0.1068	0.7387	0.1103
893.15	0.7394	0.1104	0.7540	0.1136	0.7694	0.1171
903.15	0.7694	0.1171	0.7830	0.1202	0.7972	0.1237
913.15	0.7967	0.1235	0.8092	0.1266	0.8223	0.1299
923.15	0.8213	0.1296	0.8328	0.1325	0.8447	0.1357

a) see Table 14 foot note

Table 16. Equilibrium Conversion per Mole Isobutane at Technically Relevant Temperatures and Pressures When 10 Volume Hydrogen is Mixed to 100 Volumes Isobutane Feed.

	0.12 MPa		0.11 MPa		0.1 MPa	
T /K	X	U_e [a)]	X	U_e [a)]	X	U_e [a)]
773.15	0.2656	0.0353	0.2780	0.0370	0.2921	0.0389
783.15	0.3012	0.0401	0.3147	0.0419	0.3300	0.0440
793.15	0.3390	0.0452	0.3535	0.0472	0.3699	0.0494
803.15	0.3786	0.0506	0.3941	0.0527	0.4115	0.0552
813.15	0.4194	0.0563	0.4358	0.0586	0.4540	0.0613
823.15	0.4613	0.0623	0.4782	0.0648	0.4970	0.0676
833.15	0.5035	0.0685	0.5208	0.0712	0.5399	0.0743
843.15	0.5454	0.0751	0.5629	0.0779	0.5821	0.0811
853.15	0.5866	0.0818	0.6040	0.0848	0.6229	0.0881
863.15	0.6264	0.0887	0.6435	0.0918	0.6619	0.0952
873.15	0.6644	0.0957	0.6809	0.0989	0.6986	0.1024
883.15	0.7003	0.1026	0.7160	0.1059	0.7328	0.1095
893.15	0.7336	0.1096	0.7484	0.1128	0.7642	0.1163
903.15	0.7642	0.1163	0.7781	0.1195	0.7927	0.1230
913.15	0.7921	0.1228	0.8049	0.1259	0.8183	0.1292
923.15	0.8173	0.1289	0.8290	0.1319	0.8412	0.1351

a) see Table 14 foot note

It is clear that to theoretically achieve conversions higher than 90%, the reaction in Catofin process has to be carried at temperatures above 873.15K (600 ºC) and pressures as low as 0.02 MPa. This level of per pass conversion is not achievable with other commercial processes FBD4 and Oleflex. Maximum achievable per pass conversion under 0.12 MPa is 82.6±10.8% if to operate under drastic conditions such as at 923.15 K. When operating at 873.15 K (600 ºC) achievable conversion without hydrogen diluent is 68 ± 8.3%.

Composition of isobutane dehydrogenation reaction mixture at thermodynamic equilibrium was calculated using Eqs. (13) – (16). Results are tabulated in Tables 17 - 24.

4. Conclusions

In this study thermodynamic parameters, including molar enthalpy, molar Gibbs free energy, equilibrium constant, conversions and product distribution were calculated for isobutane dehydrogenation reaction at industrially relevant conditions for various processes. The outcome of the study is believed to form a potent source of information for plants operators, researchers and process developers.

Table 17. Molar Fractions of Reaction Species in Equilibrium at Different Temperatures and Pressures, Isobutane Feed without Diluent. Expanded Uncertainties are Given in Table 18.

	0.12 MPa			0.11 MPa			0.1 MPa			0.07 MPa			0.06 MPa	
T /K	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}
773.15	0.5419	0.2291	0.2291	0.5278	0.2361	0.2361	0.5121	0.2439	0.2439	0.4521	0.2739	0.2739	0.4257	0.2871
783.15	0.5021	0.2489	0.2489	0.4876	0.2562	0.2562	0.4715	0.2643	0.2643	0.4106	0.2947	0.2947	0.3841	0.3079
793.15	0.4622	0.2689	0.2689	0.4474	0.2763	0.2763	0.4311	0.2845	0.2845	0.3700	0.3150	0.3150	0.3440	0.3280
803.15	0.4227	0.2887	0.2887	0.4077	0.2961	0.2961	0.3914	0.3043	0.3043	0.3310	0.3345	0.3345	0.3057	0.3472
813.15	0.3840	0.3080	0.3080	0.3692	0.3154	0.3154	0.3530	0.3235	0.3235	0.2942	0.3529	0.3529	0.2698	0.3651
823.15	0.3467	0.3267	0.3267	0.3321	0.3340	0.3340	0.3163	0.3418	0.3418	0.2597	0.3702	0.3702	0.2366	0.3817
833.15	0.3110	0.3445	0.3445	0.2969	0.3516	0.3516	0.2817	0.3592	0.3592	0.2279	0.3861	0.3861	0.2063	0.3968
843.15	0.2774	0.3613	0.3613	0.2639	0.3681	0.3681	0.2494	0.3753	0.3753	0.1989	0.4006	0.4006	0.1790	0.4105
853.15	0.2460	0.3770	0.3770	0.2333	0.3834	0.3834	0.2196	0.3902	0.3902	0.1728	0.4136	0.4136	0.1547	0.4227
863.15	0.2172	0.3914	0.3914	0.2052	0.3974	0.3974	0.1925	0.4037	0.4037	0.1495	0.4252	0.4252	0.1331	0.4334
873.15	0.1908	0.4046	0.4046	0.1797	0.4101	0.4101	0.1681	0.4160	0.4160	0.1290	0.4355	0.4355	0.1143	0.4428
883.15	0.1670	0.4165	0.4165	0.1569	0.4216	0.4216	0.1462	0.4269	0.4269	0.1110	0.4445	0.4445	0.0979	0.4510
893.15	0.1457	0.4271	0.4271	0.1365	0.4318	0.4318	0.1269	0.4366	0.4366	0.0953	0.4523	0.4523	0.0838	0.4581
903.15	0.1268	0.4366	0.4366	0.1185	0.4408	0.4408	0.1098	0.4451	0.4451	0.0818	0.4591	0.4591	0.0717	0.4642
913.15	0.1102	0.4449	0.4449	0.1027	0.4487	0.4487	0.0950	0.4525	0.4525	0.0702	0.4649	0.4649	0.0613	0.4694
923.15	0.0956	0.4522	0.4522	0.0889	0.4556	0.4556	0.0820	0.4590	0.4590	0.0602	0.4699	0.4699	0.0524	0.4738

Table 17 - Continued-

T /K	0.06 MPa	0.05 MPa			0.04 MPa			0.03 MPa			0.02 MPa		
	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}
773.15	0.2871	0.3945	0.3028	0.3028	0.3564	0.3218	0.3218	0.3086	0.3457	0.3457	0.2452	0.3774	0.3774
783.15	0.3079	0.3532	0.3234	0.3234	0.3160	0.3420	0.3420	0.2699	0.3650	0.3650	0.2105	0.3948	0.3948
793.15	0.3280	0.3137	0.3432	0.3432	0.2778	0.3611	0.3611	0.2343	0.3829	0.3829	0.1794	0.4103	0.4103
803.15	0.3472	0.2765	0.3617	0.3617	0.2425	0.3787	0.3787	0.2019	0.3990	0.3990	0.1520	0.4240	0.4240
813.15	0.3651	0.2422	0.3789	0.3789	0.2104	0.3948	0.3948	0.1730	0.4135	0.4135	0.1282	0.4359	0.4359
823.15	0.3817	0.2108	0.3946	0.3946	0.1814	0.4093	0.4093	0.1475	0.4262	0.4262	0.1078	0.4461	0.4461
833.15	0.3968	0.1825	0.4088	0.4088	0.1557	0.4222	0.4222	0.1253	0.4373	0.4373	0.0904	0.4548	0.4548
843.15	0.4105	0.1572	0.4214	0.4214	0.1331	0.4335	0.4335	0.1061	0.4469	0.4469	0.0757	0.4622	0.4622
853.15	0.4227	0.1350	0.4325	0.4325	0.1134	0.4433	0.4433	0.0897	0.4552	0.4552	0.0633	0.4684	0.4684
863.15	0.4334	0.1155	0.4422	0.4422	0.0964	0.4518	0.4518	0.0757	0.4622	0.4622	0.0530	0.4735	0.4735
873.15	0.4428	0.0987	0.4507	0.4507	0.0819	0.4591	0.4591	0.0639	0.4681	0.4681	0.0444	0.4778	0.4778
883.15	0.4510	0.0841	0.4579	0.4579	0.0695	0.4653	0.4653	0.0539	0.4731	0.4731	0.0372	0.4814	0.4814
893.15	0.4581	0.0717	0.4641	0.4641	0.0590	0.4705	0.4705	0.0455	0.4773	0.4773	0.0312	0.4844	0.4844
903.15	0.4642	0.0611	0.4694	0.4694	0.0500	0.4750	0.4750	0.0385	0.4808	0.4808	0.0263	0.4869	0.4869
913.15	0.4694	0.0521	0.4740	0.4740	0.0425	0.4787	0.4787	0.0326	0.4837	0.4837	0.0222	0.4889	0.4889
923.15	0.4738	0.0444	0.4778	0.4778	0.0362	0.4819	0.4819	0.0276	0.4862	0.4862	0.0187	0.4906	0.4906

Table 18. Expanded Uncertainties [a] in Molar Fractions Reported in Table 17.

T /K	0.12 MPa			0.11 MPa			0.1 MPa			0.07 MPa			0.06 MPa	
	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}
773.15	0.0152	0.0275	0.0275	0.0313	0.0285	0.0285	0.0322	0.0295	0.0295	0.0355	0.0335	0.0335	0.0369	0.0353
783.15	0.0154	0.0299	0.0299	0.0333	0.0309	0.0309	0.0342	0.0320	0.0320	0.0375	0.0362	0.0362	0.0390	0.0381
793.15	0.0155	0.0324	0.0324	0.0353	0.0334	0.0334	0.0362	0.0345	0.0345	0.0396	0.0389	0.0389	0.0411	0.0409
803.15	0.0155	0.0349	0.0349	0.0372	0.0360	0.0360	0.0382	0.0371	0.0371	0.0417	0.0417	0.0417	0.0433	0.0438
813.15	0.0154	0.0375	0.0375	0.0392	0.0386	0.0386	0.0401	0.0398	0.0398	0.0438	0.0445	0.0445	0.0454	0.0467
823.15	0.0153	0.0400	0.0400	0.0411	0.0412	0.0412	0.0421	0.0424	0.0424	0.0459	0.0474	0.0474	0.0476	0.0496
833.15	0.0152	0.0426	0.0426	0.0431	0.0438	0.0438	0.0441	0.0451	0.0451	0.0480	0.0502	0.0502	0.0498	0.0525
843.15	0.0151	0.0453	0.0453	0.0451	0.0465	0.0465	0.0461	0.0478	0.0478	0.0502	0.0530	0.0530	0.0520	0.0553
853.15	0.0151	0.0479	0.0479	0.0471	0.0491	0.0491	0.0482	0.0505	0.0505	0.0523	0.0558	0.0558	0.0542	0.0581
863.15	0.0153	0.0505	0.0505	0.0491	0.0518	0.0518	0.0502	0.0532	0.0532	0.0545	0.0585	0.0585	0.0563	0.0608
873.15	0.0158	0.0531	0.0531	0.0512	0.0544	0.0544	0.0523	0.0558	0.0558	0.0565	0.0611	0.0611	0.0583	0.0633
883.15	0.0165	0.0557	0.0557	0.0532	0.0570	0.0570	0.0543	0.0584	0.0584	0.0584	0.0636	0.0636	0.0602	0.0657
893.15	0.0176	0.0582	0.0582	0.0551	0.0595	0.0595	0.0562	0.0608	0.0608	0.0602	0.0658	0.0658	0.0619	0.0678
903.15	0.0192	0.0606	0.0606	0.0570	0.0618	0.0618	0.0580	0.0631	0.0631	0.0619	0.0679	0.0679	0.0634	0.0697
913.15	0.0213	0.0628	0.0628	0.0587	0.0640	0.0640	0.0597	0.0653	0.0653	0.0634	0.0697	0.0697	0.0648	0.0714
923.15	0.0240	0.0649	0.0649	0.0603	0.0660	0.0660	0.0613	0.0672	0.0672	0.0647	0.0714	0.0714	0.0660	0.0729

a) Calculated based on equations (21) and (22), whereby *f* is the function between y_i and X resulting from substitution K in equations (12) and (17). Thus resulted equations are the followings:

For isobutane: $$\left(\frac{u_c(y)}{y}\right)^2 = \left(\frac{u_c(X)}{1-X}\right)^2 + \left(\frac{u_c(X)}{(h+1+X)}\right)^2 \qquad (33)$$

For isobutene: $$\left(\frac{u_c(y)}{y}\right)^2 = \left(\frac{u_c(X)}{X}\right)^2 + \left(\frac{u_c(X)}{(h+1+X)}\right)^2 \qquad (34)$$

For hydrogen: $$\left(\frac{u_c(y)}{y}\right)^2 = \left(\frac{u_c(X)}{(h+1+X)}\right)^2 + \left(\frac{u_c(X)}{(h+1+X)}\right)^2 \qquad (35)$$

Table 18 -Continued-

T /K	0.06 MPa	0.05 MPa			0.04 MPa			0.03 MPa			0.02 MPa		
	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}
773.15	0.0353	0.0387	0.0376	0.0376	0.0409	0.0405	0.0405	0.0439	0.0443	0.0443	0.0483	0.0502	0.0502
783.15	0.0381	0.0408	0.0405	0.0405	0.0431	0.0435	0.0435	0.0462	0.0475	0.0475	0.0509	0.0535	0.0535
793.15	0.0409	0.0430	0.0434	0.0434	0.0454	0.0465	0.0465	0.0486	0.0507	0.0507	0.0534	0.0568	0.0568
803.15	0.0438	0.0452	0.0463	0.0463	0.0477	0.0496	0.0496	0.0510	0.0539	0.0539	0.0559	0.0601	0.0601
813.15	0.0467	0.0474	0.0493	0.0493	0.0500	0.0526	0.0526	0.0534	0.0570	0.0570	0.0584	0.0632	0.0632
823.15	0.0496	0.0497	0.0523	0.0523	0.0523	0.0556	0.0556	0.0558	0.0600	0.0600	0.0607	0.0660	0.0660
833.15	0.0525	0.0520	0.0552	0.0552	0.0546	0.0586	0.0586	0.0581	0.0629	0.0629	0.0628	0.0687	0.0687
843.15	0.0553	0.0542	0.0581	0.0581	0.0569	0.0614	0.0614	0.0602	0.0656	0.0656	0.0647	0.0710	0.0710
853.15	0.0581	0.0563	0.0608	0.0608	0.0590	0.0641	0.0641	0.0622	0.0681	0.0681	0.0663	0.0731	0.0731
863.15	0.0608	0.0584	0.0634	0.0634	0.0609	0.0666	0.0666	0.0640	0.0703	0.0703	0.0677	0.0749	0.0749
873.15	0.0633	0.0603	0.0659	0.0659	0.0627	0.0688	0.0688	0.0656	0.0723	0.0723	0.0690	0.0764	0.0764
883.15	0.0657	0.0621	0.0681	0.0681	0.0644	0.0708	0.0708	0.0669	0.0739	0.0739	0.0700	0.0776	0.0776
893.15	0.0678	0.0637	0.0701	0.0701	0.0658	0.0726	0.0726	0.0681	0.0754	0.0754	0.0708	0.0786	0.0786
903.15	0.0697	0.0651	0.0718	0.0718	0.0670	0.0741	0.0741	0.0691	0.0766	0.0766	0.0714	0.0794	0.0794
913.15	0.0714	0.0663	0.0733	0.0733	0.0680	0.0754	0.0754	0.0699	0.0776	0.0776	0.0719	0.0801	0.0801
923.15	0.0729	0.0674	0.0746	0.0746	0.0689	0.0764	0.0764	0.0706	0.0784	0.0784	0.0723	0.0806	0.0806

Table 19. Molar Fractions of Reaction Species in Equilibrium of Isobutane Dehydrogenation to Isobutene Reaction at Technically Relevant Temperatures and Pressures when 1 Volume Hydrogen Is Mixed To 100 Volumes Isobutane Feed, Uncertainties are Given in Table 20.

T /K	0.12 MPa			0.11 MPa			0.1 MPa		
	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}
773.15	0.2329	0.2253	0.5418	0.2399	0.2323	0.5277	0.2477	0.2402	0.5121
783.15	0.2527	0.2452	0.5021	0.2599	0.2525	0.4875	0.2679	0.2606	0.4715
793.15	0.2725	0.2653	0.4622	0.2799	0.2727	0.4474	0.2880	0.2809	0.4311
803.15	0.2922	0.2851	0.4226	0.2997	0.2926	0.4077	0.3078	0.3009	0.3914
813.15	0.3114	0.3046	0.3840	0.3188	0.3120	0.3692	0.3269	0.3201	0.3530
823.15	0.3300	0.3233	0.3466	0.3373	0.3306	0.3321	0.3451	0.3386	0.3163
833.15	0.3478	0.3412	0.3110	0.3548	0.3483	0.2969	0.3623	0.3560	0.2817
843.15	0.3645	0.3581	0.2774	0.3712	0.3649	0.2639	0.3784	0.3722	0.2494
853.15	0.3801	0.3739	0.2460	0.3864	0.3803	0.2332	0.3932	0.3871	0.2196
863.15	0.3945	0.3884	0.2172	0.4004	0.3944	0.2052	0.4067	0.4008	0.1925
873.15	0.4076	0.4016	0.1908	0.4131	0.4072	0.1797	0.4189	0.4131	0.1681
883.15	0.4194	0.4136	0.1670	0.4244	0.4187	0.1569	0.4297	0.4240	0.1462
893.15	0.4300	0.4243	0.1457	0.4346	0.4289	0.1365	0.4394	0.4338	0.1269
903.15	0.4394	0.4338	0.1268	0.4435	0.4380	0.1185	0.4478	0.4423	0.1098
913.15	0.4477	0.4422	0.1102	0.4514	0.4459	0.1027	0.4552	0.4498	0.0950
923.15	0.4549	0.4495	0.0956	0.4583	0.4528	0.0889	0.4617	0.4563	0.0820

Table 20. Expanded Uncertainties ^{a} in Molar Fractions Reported in Table 19.

T /K	0.12 MPa			0.11 MPa			0.1 MPa		
	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}
773.15	0.0341	0.0307	0.0308	0.0350	0.0317	0.0318	0.0359	0.0329	0.0329
783.15	0.0365	0.0336	0.0337	0.0374	0.0347	0.0347	0.0383	0.0358	0.0359
793.15	0.0389	0.0366	0.0366	0.0398	0.0377	0.0377	0.0408	0.0389	0.0389
803.15	0.0413	0.0396	0.0397	0.0422	0.0407	0.0408	0.0432	0.0420	0.0420
813.15	0.0438	0.0427	0.0428	0.0446	0.0438	0.0439	0.0455	0.0451	0.0452
823.15	0.0462	0.0459	0.0460	0.0470	0.0470	0.0471	0.0479	0.0483	0.0483
833.15	0.0486	0.0491	0.0492	0.0495	0.0502	0.0503	0.0503	0.0514	0.0515
843.15	0.0511	0.0523	0.0525	0.0519	0.0535	0.0536	0.0528	0.0547	0.0548
853.15	0.0537	0.0557	0.0558	0.0544	0.0567	0.0568	0.0553	0.0579	0.0580
863.15	0.0563	0.0590	0.0591	0.0570	0.0600	0.0601	0.0578	0.0611	0.0612
873.15	0.0589	0.0623	0.0624	0.0596	0.0633	0.0634	0.0603	0.0643	0.0645
883.15	0.0615	0.0656	0.0657	0.0621	0.0665	0.0667	0.0628	0.0675	0.0676
893.15	0.0640	0.0688	0.0690	0.0646	0.0697	0.0698	0.0653	0.0706	0.0708
903.15	0.0665	0.0719	0.0721	0.0671	0.0728	0.0729	0.0677	0.0736	0.0737
913.15	0.0689	0.0749	0.0751	0.0695	0.0757	0.0758	0.0700	0.0764	0.0766
923.15	0.0712	0.0777	0.0779	0.0717	0.0784	0.0786	0.0722	0.0791	0.0793

a) Calculated based on equations (21) and (33 through 35)

Table 21. Molar Fractions of Reaction Species in Equilibrium of Isobutane Dehydrogenation to Isobutene Reaction at Technically Relevant Temperatures and Pressures When 5 Volume Hydrogen is Mixed to 100 Volumes Isobutane Feed, Uncertainties are Given in Table 22.

T /K	0.12 MPa			0.11 MPa			0.1 MPa		
	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}
773.15	0.2484	0.2108	0.5408	0.2552	0.2180	0.5268	0.2628	0.2260	0.5112
783.15	0.2677	0.2311	0.5012	0.2748	0.2385	0.4867	0.2826	0.2467	0.4707
793.15	0.2871	0.2514	0.4615	0.2943	0.2590	0.4467	0.3022	0.2673	0.4304
803.15	0.3063	0.2716	0.4220	0.3136	0.2793	0.4071	0.3215	0.2876	0.3909
813.15	0.3251	0.2914	0.3835	0.3323	0.2990	0.3687	0.3402	0.3072	0.3526
823.15	0.3433	0.3105	0.3462	0.3504	0.3179	0.3317	0.3581	0.3260	0.3160
833.15	0.3607	0.3287	0.3107	0.3675	0.3359	0.2966	0.3749	0.3437	0.2814
843.15	0.3770	0.3459	0.2771	0.3836	0.3528	0.2636	0.3906	0.3602	0.2492
853.15	0.3923	0.3619	0.2458	0.3985	0.3684	0.2330	0.4051	0.3754	0.2194
863.15	0.4064	0.3767	0.2170	0.4122	0.3828	0.2050	0.4184	0.3893	0.1924
873.15	0.4192	0.3902	0.1907	0.4246	0.3958	0.1796	0.4303	0.4018	0.1679
883.15	0.4308	0.4023	0.1669	0.4357	0.4075	0.1567	0.4409	0.4130	0.1461
893.15	0.4412	0.4132	0.1456	0.4457	0.4179	0.1364	0.4504	0.4229	0.1268
903.15	0.4504	0.4229	0.1267	0.4544	0.4272	0.1184	0.4586	0.4316	0.1098
913.15	0.4585	0.4314	0.1101	0.4621	0.4352	0.1026	0.4659	0.4392	0.0949
923.15	0.4656	0.4389	0.0955	0.4689	0.4423	0.0888	0.4722	0.4458	0.0820

Table 22. Expanded Uncertainties [a] in Molar Fractions Reported in Table 21.

T /K	0.12 MPa			0.11 MPa			0.1 MPa		
	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}
773.15	0.0319	0.0287	0.0289	0.0328	0.0297	0.0300	0.0338	0.0309	0.0311
783.15	0.0344	0.0316	0.0318	0.0353	0.0327	0.0329	0.0364	0.0339	0.0342
793.15	0.0369	0.0345	0.0349	0.0378	0.0357	0.0360	0.0389	0.0370	0.0373
803.15	0.0394	0.0376	0.0379	0.0404	0.0388	0.0392	0.0414	0.0402	0.0405
813.15	0.0419	0.0407	0.0411	0.0429	0.0420	0.0424	0.0440	0.0434	0.0438
823.15	0.0443	0.0439	0.0443	0.0454	0.0452	0.0456	0.0465	0.0467	0.0471
833.15	0.0469	0.0471	0.0476	0.0479	0.0485	0.0489	0.0491	0.0500	0.0505
843.15	0.0494	0.0504	0.0509	0.0505	0.0518	0.0523	0.0517	0.0533	0.0539
853.15	0.0520	0.0537	0.0542	0.0531	0.0551	0.0557	0.0544	0.0567	0.0573
863.15	0.0546	0.0570	0.0576	0.0557	0.0585	0.0591	0.0570	0.0601	0.0607
873.15	0.0572	0.0603	0.0609	0.0584	0.0618	0.0624	0.0597	0.0635	0.0641
883.15	0.0598	0.0636	0.0642	0.0610	0.0651	0.0657	0.0623	0.0667	0.0674
893.15	0.0624	0.0668	0.0674	0.0636	0.0683	0.0690	0.0649	0.0699	0.0706
903.15	0.0649	0.0699	0.0706	0.0661	0.0713	0.0721	0.0673	0.0729	0.0737
913.15	0.0673	0.0728	0.0736	0.0684	0.0742	0.0750	0.0697	0.0758	0.0765
923.15	0.0696	0.0756	0.0764	0.0707	0.0772	0.0777	0.0718	0.0787	0.0792

a) Calculated based on equations (21) and (33 through 35)

Table 23. Molar Fractions of Reaction Species in Equilibrium of Isobutane Dehydrogenation to Isobutene Reaction at Technically Relevant Temperatures and Pressures When 10 Volume Hydrogen is Mixed to 100 Volumes Isobutane Feed, Uncertainties are Given in Table 24.

T /K	0.12 MPa			0.11 MPa			0.1 MPa		
	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}
773.15	0.2677	0.1945	0.5378	0.2743	0.2018	0.5239	0.2816	0.2098	0.5085
783.15	0.2863	0.2150	0.4987	0.2932	0.2225	0.4844	0.3007	0.2308	0.4685
793.15	0.3051	0.2356	0.4594	0.3120	0.2432	0.4448	0.3197	0.2517	0.4286
803.15	0.3237	0.2560	0.4203	0.3307	0.2638	0.4055	0.3384	0.2722	0.3894
813.15	0.3419	0.2761	0.3821	0.3489	0.2838	0.3674	0.3565	0.2921	0.3514
823.15	0.3595	0.2955	0.3450	0.3664	0.3030	0.3306	0.3738	0.3112	0.3150
833.15	0.3763	0.3140	0.3097	0.3830	0.3213	0.2957	0.3902	0.3292	0.2806
843.15	0.3922	0.3315	0.2763	0.3986	0.3385	0.2629	0.4055	0.3460	0.2485
853.15	0.4071	0.3478	0.2451	0.4131	0.3545	0.2324	0.4196	0.3615	0.2189
863.15	0.4208	0.3628	0.2164	0.4264	0.3691	0.2045	0.4324	0.3757	0.1919
873.15	0.4332	0.3766	0.1902	0.4385	0.3823	0.1792	0.4440	0.3884	0.1675
883.15	0.4445	0.3890	0.1665	0.4493	0.3943	0.1564	0.4544	0.3998	0.1458
893.15	0.4546	0.4001	0.1453	0.4590	0.4049	0.1361	0.4636	0.4099	0.1265
903.15	0.4636	0.4099	0.1265	0.4675	0.4143	0.1182	0.4716	0.4188	0.1095
913.15	0.4715	0.4186	0.1099	0.4750	0.4226	0.1024	0.4787	0.4266	0.0947
923.15	0.4784	0.4263	0.0953	0.4816	0.4298	0.0887	0.4849	0.4333	0.0818

Table 24. Expanded Uncertainties [a] in Molar Fractions Reported in Table 23.

T /K	0.12 MPa			0.11 MPa			0.1 MPa		
	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}	y_{C4H10}	y_{C4H8}	y_{H2}
773.15	0.0294	0.0264	0.0268	0.0303	0.0274	0.0279	0.0314	0.0286	0.0290
783.15	0.0320	0.0293	0.0298	0.0329	0.0304	0.0309	0.0340	0.0316	0.0321
793.15	0.0345	0.0322	0.0328	0.0355	0.0334	0.0340	0.0366	0.0347	0.0353
803.15	0.0371	0.0353	0.0359	0.0381	0.0365	0.0372	0.0392	0.0379	0.0386
813.15	0.0396	0.0384	0.0391	0.0407	0.0397	0.0404	0.0418	0.0411	0.0419
823.15	0.0422	0.0416	0.0424	0.0432	0.0429	0.0437	0.0444	0.0444	0.0452
833.15	0.0447	0.0448	0.0457	0.0458	0.0462	0.0471	0.0470	0.0477	0.0486
843.15	0.0473	0.0481	0.0490	0.0484	0.0495	0.0504	0.0497	0.0510	0.0520
853.15	0.0499	0.0513	0.0524	0.0511	0.0528	0.0538	0.0524	0.0544	0.0555
863.15	0.0526	0.0546	0.0557	0.0537	0.0561	0.0572	0.0550	0.0577	0.0589
873.15	0.0552	0.0579	0.0591	0.0564	0.0594	0.0606	0.0577	0.0611	0.0623
883.15	0.0578	0.0612	0.0624	0.0590	0.0627	0.0639	0.0603	0.0643	0.0656
893.15	0.0604	0.0644	0.0656	0.0616	0.0658	0.0671	0.0629	0.0674	0.0688
903.15	0.0629	0.0674	0.0688	0.0641	0.0689	0.0702	0.0654	0.0704	0.0718
913.15	0.0653	0.0703	0.0717	0.0664	0.0717	0.0732	0.0677	0.0732	0.0747
923.15	0.0675	0.0731	0.0745	0.0687	0.0744	0.0759	0.0698	0.0759	0.0773

a) Calculated based on equations (21) and (33 through 35)

Nomenclature

$a_{n,i}$	Gas phase heat capacity constants ($a_{0,i}$, $a_{1,i}$, $a_{2,i}$, $a_{3,i}$, $a_{4,i}$) of the species *i*, in J mol^{-1} K^{-1}
$\Delta_R a_n$	Reaction mixture gas phase heat capacity constants ($\Delta_R a_0$, $\Delta_R a_1$, $\Delta_R a_2$, $\Delta_R a_3$) , in J mol^{-1} K^{-1}
$C^o_{p_T,i}$	Ideal gas heat capacity of species *i* at *T*, in J mol^{-1} K^{-1}
$\Delta_R C_{p_T}^{\,o}$	Reaction mixture heat capacity at *T*
$\Delta H^o_{f,i}$	Ideal gas standard enthalpy of formation
ε	Reaction number
$\Delta G^o_{f,i}$	Ideal gas standard free enthalpy of formation

$\Delta_\mathrm{R} G_T^o$	Reaction free Gibbs energy at temperature T
$\Delta_\mathrm{R} H_T^o$	Reaction enthalpy at temperature T
K	Equilibrium constant
K_T	Equilibrium constant at temperature T
$\dot{n}_i$	Mole stream of species i out of reactor
$\dot{n}_{i,o}$	Mole stream of species i in the feed
υ_i	Stoichiometric number of moles of species i
υ	Reaction stoichiometric number
P	Reaction pressure, bar
P^o	Standard pressure, bar
R	Ideal gas constant, (8.314 J mol^{-1} K^{-1})
$S_{f,i}^o$	Ideal gas standard entropy of formation
$\Delta_\mathrm{R} S_T^o$	Reaction entropy at temperature T
T	Temperature, in Kelvin
$u_e(x)$	Expanded uncertainty in the variable x
$u_r(x)$	Relative uncertainty in the variable x
X	Conversion, per mole isobutane
y_i	Mole fraction of species i

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