

Exercise 12: Methanation

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A detailed solution is provided at the **13th of December**.

Please see: <http://www.psi.ch/ene/ret1>

Problem: Direct Methanation of Carbon Dioxide from Biogas

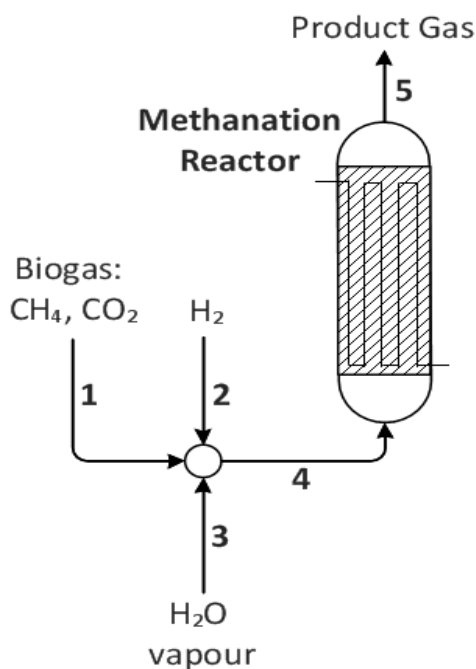
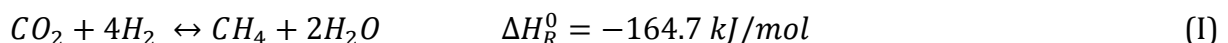


Figure 1: Flowsheet of a direct methanation

deactivation of the catalyst due to carbon deposition. The mixture (4) enters the methanation reactor, where carbon dioxide and hydrogen convert to methane and water:



The reactor is cooled by an internal heat exchanger. The outlet stream of the reactor (5) contains mainly methane and water.

Biogas is produced via fermentation of biomass, e.g. green waste, sewage sludge or manure. After the fermentation a gas was built, which contains methane and carbon dioxide. Further upgrade is needed to reach gas grid quality with a minimum of 96% of methane. Conventionally carbon dioxide is separated via scrubbing and then released into atmosphere. In a new approach carbon dioxide is not seen as waste, but as raw material for further methane production. Here the raw biogas is entering a methanation unit, in which carbon dioxide and added hydrogen is converted to further methane. The already existing methane in the biogas is passing the methanation as quasi-inert. This procedure allows an increase of the bio-methane production up to 80% with the same amount of biomass at the input.

The direct methanation is illustrated in Figure 1. Here biogas (1) is mixed with hydrogen (2) and possibly with steam (3). The steam inhibits the

Tasks:

- i. Methanation without steam:** Calculate the molar flows of all components in stream 5 $\dot{n}_{5,i}$ [mol/s] and the heat stream $\dot{Q}_{out,M}$ [kW], which must be dissipated in order to maintain a temperature of $T_{meth} = 320^\circ\text{C}$. A steady state process is assumed. Stream 4 has a temperature of $T_4 = 270^\circ\text{C}$. The conversion of CO_2 in the methanation unit reaches $C_{\text{CO}_2} = 95\%$.

Further values:

- Biogas stream: $\dot{n}_1 = 4 \frac{\text{mol}}{\text{s}}$, $x_{1,\text{CH}_4} = 0.55$, $x_{1,\text{CO}_2} = 0.45$
- In this case: No steam is added, $\dot{n}_3 = 0 \frac{\text{mol}}{\text{s}}$,
- The ratio of H_2 to CO_2 in stream 4 is stoichiometric
- $p = 5$ bar for all streams and the reactor
- Specific heat capacities: $c_{p,4mix} = 31.7 \frac{\text{J}}{\text{mol K}}$, $c_{p,5mix} = 34.4 \frac{\text{J}}{\text{mol K}}$

- ii. Equilibrium constant K_{eq}**

Calculate the equilibrium constant K_{eq} with thermodynamic data and check if the reaction reaches its equilibrium state. Use the NIST database in the appendix for standard enthalpy and entropy calculations at T_{meth} .

- iii. Equilibrium constant and methanation with steam**

The catalyst starts to deactivate due to carbon deposition. A countermeasure is the injection of steam into the reactor. How does the steam affect the maximum conversion rate of carbon dioxide? Show it in a qualitative way with the equation $K = \prod_i p_i^{v_i}$ for component i.

- iv. Equilibrium constant and operational conditions in the reactor**

How can the effect of steam addition be compensated by changing operational conditions in the reactor? Show it in a qualitative way with the equation $K = \prod_i p_i^{v_i}$ for components i at constant temperature T_{meth} .

Appendix:

NIST – Database

Correlations:

$$H^{\circ} - H^{\circ}_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$$
$$S^{\circ} = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$$

H° = standard enthalpy (kJ/mol)
 S° = standard entropy (J/mol*K)
t = temperature (K) / 1000.

$$T0 = 298.15K$$

Hydrogen

$$\Delta_f H^{\circ}_{\text{gas}}(T0) = 0.0 \text{ kJ/mol}$$

| Temperature (K) | 298. - 1000. | 1000. - 2500. | 2500. - 6000. |
|-----------------|---|---|---|
| A | 33.066178 | 18.563083 | 43.413560 |
| B | -11.363417 | 12.257357 | -4.293079 |
| C | 11.432816 | -2.859786 | 1.272428 |
| D | -2.772874 | 0.268238 | -0.096876 |
| E | -0.158558 | 1.977990 | -20.533862 |
| F | -9.980797 | -1.147438 | -38.515158 |
| G | 172.707974 | 156.288133 | 162.081354 |
| H | 0.0 | 0.0 | 0.0 |
| Reference | Chase, 1998 | Chase, 1998 | Chase, 1998 |
| Comment | Data last reviewed in March, 1977; New parameter fit October 2001 | Data last reviewed in March, 1977; New parameter fit October 2001 | Data last reviewed in March, 1977; New parameter fit October 2001 |

Carbon dioxide

$$\Delta_f H^\circ_{\text{gas}}(T_0) = -393.52 \text{ kJ/mol}$$

| Temperature (K) | 298. - 1200. | 1200. - 6000. |
|-----------------|---------------------------------------|---------------------------------------|
| A | 24.99735 | 58.16639 |
| B | 55.18696 | 2.720074 |
| C | -33.69137 | -0.492289 |
| D | 7.948387 | 0.038844 |
| E | -0.136638 | -6.447293 |
| F | -403.6075 | -425.9186 |
| G | 228.2431 | 263.6125 |
| H | -393.5224 | -393.5224 |
| Reference | Chase, 1998 | Chase, 1998 |
| Comment | Data last reviewed in September, 1965 | Data last reviewed in September, 1965 |

Methane

$$\Delta_f H^\circ_{\text{gas}}(T_0) = -74.87 \text{ kJ/mol}$$

| Temperature (K) | 298. - 1300. | 1300. - 6000. |
|-----------------|-----------------------------------|-----------------------------------|
| A | -0.703029 | 85.81217 |
| B | 108.4773 | 11.26467 |
| C | -42.52157 | -2.114146 |
| D | 5.862788 | 0.138190 |
| E | 0.678565 | -26.42221 |
| F | -76.84376 | -153.5327 |
| G | 158.7163 | 224.4143 |
| H | -74.87310 | -74.87310 |
| Reference | Chase, 1998 | Chase, 1998 |
| Comment | Data last reviewed in March, 1961 | Data last reviewed in March, 1961 |

Water (gaseous)

$$\Delta_f H^\circ_{\text{gas}}(T_0) = -241.83 \text{ kJ/mol}$$

| Temperature (K) | 500. - 1700. | 1700. - 6000. |
|-----------------|-----------------------------------|-----------------------------------|
| A | 30.09200 | 41.96426 |
| B | 6.832514 | 8.622053 |
| C | 6.793435 | -1.499780 |
| D | -2.534480 | 0.098119 |
| E | 0.082139 | -11.15764 |
| F | -250.8810 | -272.1797 |
| G | 223.3967 | 219.7809 |
| H | -241.8264 | -241.8264 |
| Reference | Chase, 1998 | Chase, 1998 |
| Comment | Data last reviewed in March, 1979 | Data last reviewed in March, 1979 |

Slides:



Equilibrium Constant via Thermodynamic Data

$$K_{eq} = e^{-\Delta G_R^0(T)/RT}$$

$$\Delta G_R^0(T) = \Delta H_R^0(T) - T \cdot \Delta S_R^0(T)$$

→ Gibbs Enthalpy = Enthalpy – Entropy
↳ useful part of enthalpy

$$\Delta H_R^0(T) = \sum_i \nu_i \cdot \Delta H_{f,i}^0(T)$$

$\Delta H_{f,i}^0(T)$ = standard enthalpy of formation of compound *i*
Wiki says: is the change of enthalpy during the formation of 1 mole of the compound from its constituent elements, with all substances in their standard states at 1 atmosphere (1 atm or 101.3 kPa).

$$\Delta S_R^0(T) = \sum_i \nu_i \cdot \Delta S_i^0(T)$$

$\Delta S_i^0(T)$ = standard entropy of compound *i*
Is the entropy content of 1 mole of compound at 1 atm.

How do we determine $\Delta H_{f,i}^0(T)$ and $\Delta S_i^0(T)$?

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Either via Integration:

$$\Delta H_{f,i}^0(T) = \Delta H_{f,i}^0(T^0) + \int_{T^0}^T c_{p,i}(T) dT$$

$$\Delta S_i^0(T) = \Delta S_i^0(T^0) + \int_{T^0}^T \frac{c_{p,i}(T)}{T} dT$$

Or via given correlations of databases, like 'NIST' database
(<http://webbook.nist.gov/chemistry/>)

$$H^\circ - H^\circ_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$$

$$S^\circ = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$$

H° = standard enthalpy (kJ/mol)

S° = standard entropy (J/mol*K)

t = temperature (K) / 1000

And given constants A ... H in tables for each component

For example:

Hydrogen

$\Delta_f H^\circ_{\text{gas}}(T^0) = 0.0$ kJ/mol

| Temperature (K) | 298. - 1000. | 1000. - 2500. | 2500. - 6000. |
|-----------------|---|---|---|
| A | 33.066178 | 18.563083 | 43.413560 |
| B | -11.363417 | 12.257357 | -4.293079 |
| C | 11.432816 | -2.859786 | 1.272428 |
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<http://webbook.nist.gov/cgi/cbook.cgi?ID=C1333740&Units=SI&Mask=1#Thermo-Gas>