CAPE1330

Energy Balances

Heat of Formation

General procedures

1. **Perform** all the required mass balance calculations.

2. **Use** the appropriate form of the energy balances:

   closed system: $\quad Q + W = m\Delta\widehat{U} + m\Delta\widehat{E}_k + m\Delta\widehat{E}_p$

   open system: $\quad \dot{Q} + \dot{W}_s = \dot{n}\Delta\widehat{H} + \dot{n}\Delta\widehat{E}_k + \dot{n}\Delta\widehat{E}_p$

3. **Choose** a reference state (phase, temperature and pressure) for each species involved in the process.

4. **Calculate** all the required values of m, $\dot{n}$, $\widehat{U}_i$, or $\widehat{H}_i$.

5. **Solve** the mass and energy balances for unknown variables.

Objectives

1. Determine a heat of reaction from heats of formation or heats of combustion using Hess's law.

2. Write and solve an energy balance on a chemical reactor using either the heat of reaction method or the heat of formation method.

3. Solve reactive system energy balance problems for

   a the heat transfer required for specified inlet and outlet conditions,
   b the outlet temperature corresponding to a specified heat input,
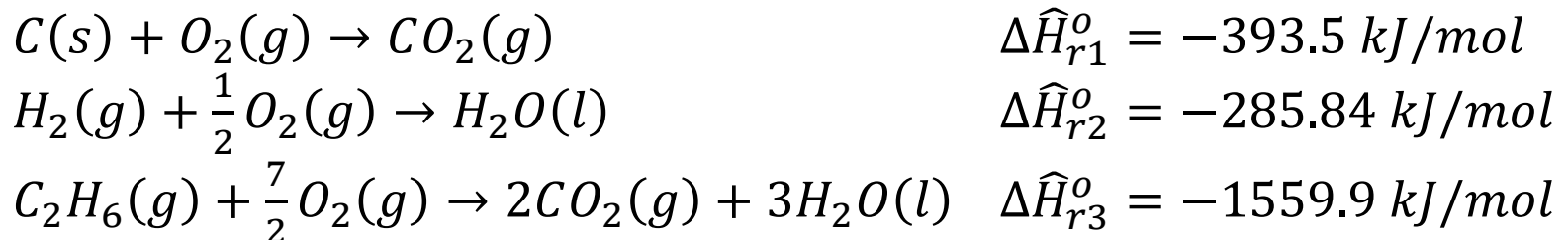   c the product composition corresponding to a specified heat input and a specified outlet temperature.

Hess's law:

Hess's law: if the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2, 3, …, then the heat of reaction 1 can be obtained by performing the same operations on the heats of reactions 2, 3, ….

Hess's law is also known as the law of constant heat summation which was later recognised as a consequence of the first law of thermodynamics, but his statement was not explicitly concerned with the relation between energy exchanges by heat and work.

Example 1:

The standard heats of following reactions have been determined experimentally:

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad\qquad \Delta \widehat{H}_{r1}^o = -393.5 \ kJ/mol$$

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad\qquad \Delta \widehat{H}_{r2}^o = -285.84 \ kJ/mol$$

$$C_2H_6(g) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta \widehat{H}_{r3}^o = -1559.9 \ kJ/mol$$

Use Hess's law to determine the standard heat of formation of ethane

$$2C(s) + 3H_2(g) \rightarrow C_2H_6(g) \qquad\qquad \Delta \widehat{H}_f^o = ? \ kJ/mol$$
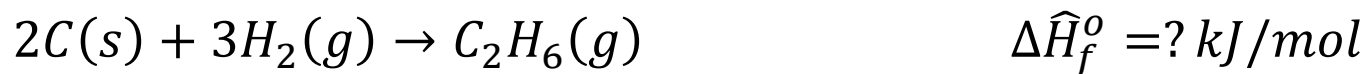
Heat of formation:

A **formation reaction** of a compound is the reaction in which the compound is formed from its elemental constituents as they normally occur in the nature (e.g. O_2 rather than O).
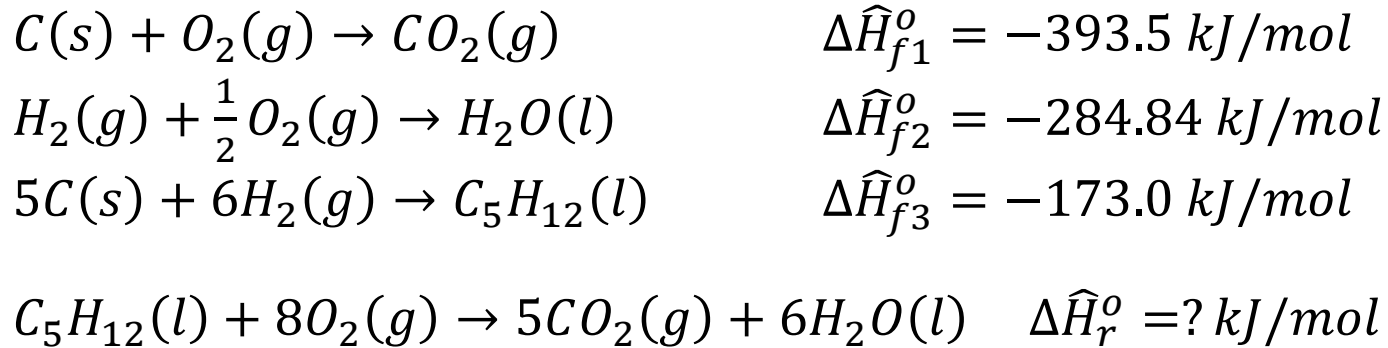
The enthalpy change associated with the formation of 1 mole of the compound at a reference temperature and pressure (usually $25°\text{C}$ and $1\ atm$) is the **standard heat of formation** of the compound, $\Delta \widehat{H}_f^o$. Standard heats of formation for many compounds are listed in *Perry's Chemical Engineer's Handbook*.

If v_i is the stoichiometric coefficient of the ith species participating in a reaction and $\Delta \widehat{H}_{fi}^o$ is the standard heat of formation of this species, then

$$\Delta \widehat{H}_r^o = \sum_{products} v_i \Delta \widehat{H}_{fi}^o - \sum_{reactants} v_i \Delta \widehat{H}_{fi}^o$$

Example 2:

Determine the standard heat of reaction from heats of formation for the combustion of liquid *n*-pentane, $C_5H_{12}(l)$, assuming $H_2O(l)$ is the combustion product.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta\widehat{H}^o_{f1} = -393.5 \; kJ/mol$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta\widehat{H}^o_{f2} = -284.84 \; kJ/mol$$

$$5C(s) + 6H_2(g) \rightarrow C_5H_{12}(l) \qquad \Delta\widehat{H}^o_{f3} = -173.0 \; kJ/mol$$

$$C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l) \qquad \Delta\widehat{H}^o_r = ? \; kJ/mol$$

Test yourself:

1. The standard heat of the reaction

$$2CO(g) \rightarrow 2C(s) + O_2(g) \qquad \Delta \widehat{H}_r^o = 221.04 \; kJ/mol$$

Use this result to calculate the standard heat of formation of $CO(g)$.
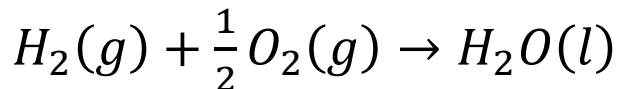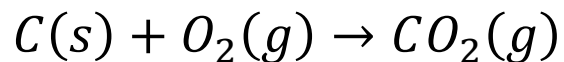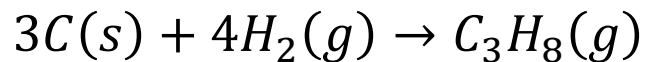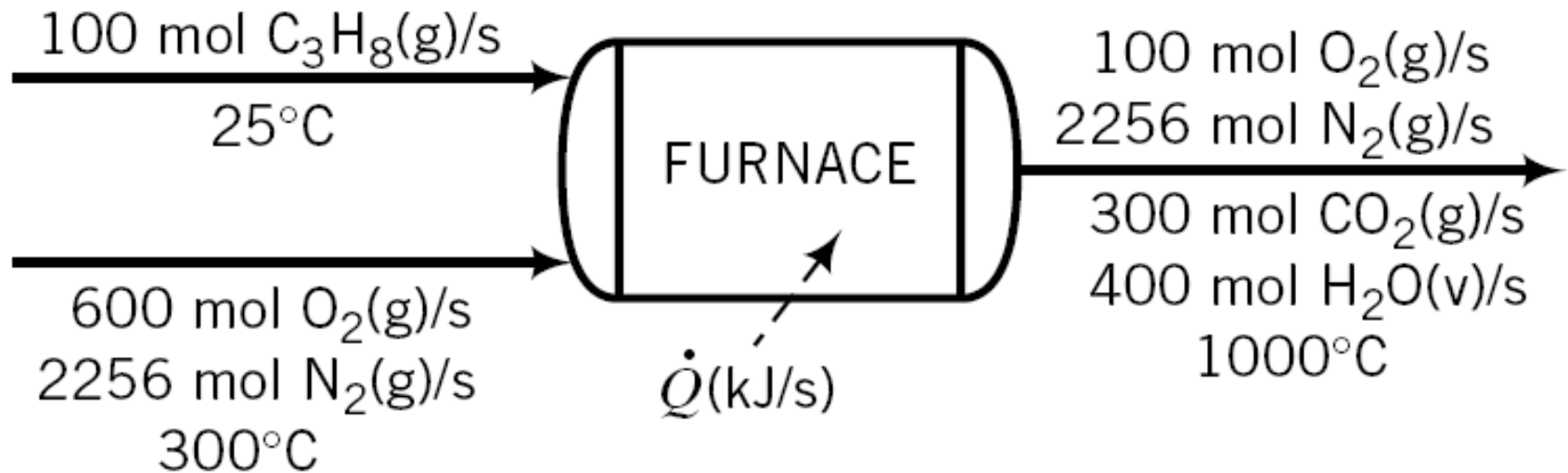
2. $\Delta \widehat{H}_f^o$ is $-119.8 \; kJ/mol$ for $C_3H_8(l)$ and $-103.8 \; kJ/mol$ for $C_3H_8(g)$. What is the physical significance of the difference between these values?

3. Consider the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$
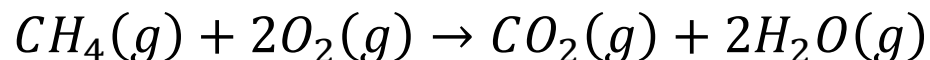
Write the formula for $\Delta \widehat{H}_r^o$ in terms of the standard heats of formation of the reactants and products.
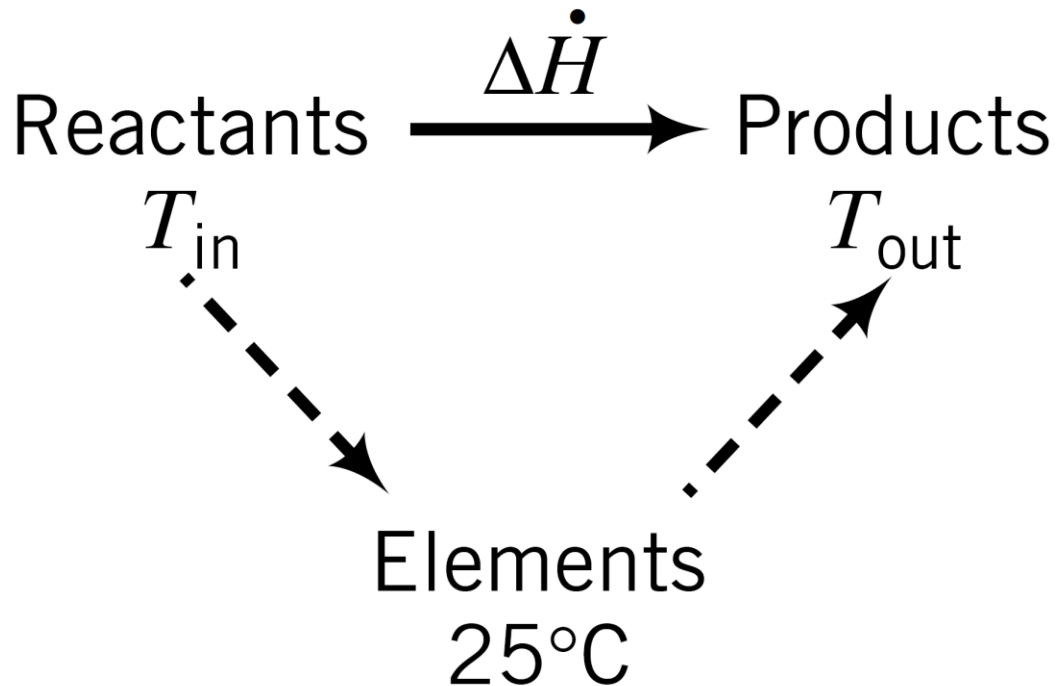
Propane combustion:

$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g) \qquad \Delta\widehat{H}^o_{f,C_3H_8(g)} = -103.8 \, kJ/mol$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta\widehat{H}^o_{f,CO_2(g)} = -393.5 \, kJ/mol$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta\widehat{H}^o_{f,H_2O(l)} = -285.84 \, kJ/mol$$

Calculate $\dot{Q}$

Propane combustion:

(b) Process path for heat of formation method

Propane combustion:

This method is generally preferable for single and multiple reactions for which $\Delta \hat{H}_r^o$ is not readily available.

1. Complete the materials balance calculations on the reactor to the greatest extent possible.

2. Choose reference states for enthalpy calculations. The choices should be the elemental species that constitute the reactants and products in the states in which the elements are found at $25°\text{C}$ and $1 \; atm$ and nonreacting species at any suitable temperature.

3. Prepare the inlet-outlet enthalpy table, inserting known molar amounts or flow rates for all inlet and outlet stream components.

Propane combustion:

$References: C(s), H_2(g), O_2(g), N_2(g)$ at 25°C and 1 atm

Substance	$\dot{n}_{in}$ mol/s	$\hat{H}_{in}$ kJ/mol	$\dot{n}_{out}$ mol/s	$\hat{H}_{out}$ kJ/mol
$C_3H_8(g)$	100	$\hat{H}_1$	—	—
$O_2(g)$	600	$\hat{H}_2$	100	$\hat{H}_4$
$N_2(g)$	2256	$\hat{H}_3$	2256	$\hat{H}_5$
$CO_2(g)$	—	—	300	$\hat{H}_6$
$H_2O(l)$	—	—	400	$\hat{H}_7$

4. Calculate each unknown specific enthalpy, $\hat{H}_i$ for a reactant or product, starting with the elemental species at 25°C and 1 atm and form 1 mol of the process species at the references. Then bring the species from 25°C and 1 atm to its process state, using the appropriate heat capacities and latent heats.

Propane combustion:

$$c_p = a + bT + cT^2 + dT^3 \; kJ/mol°C$$

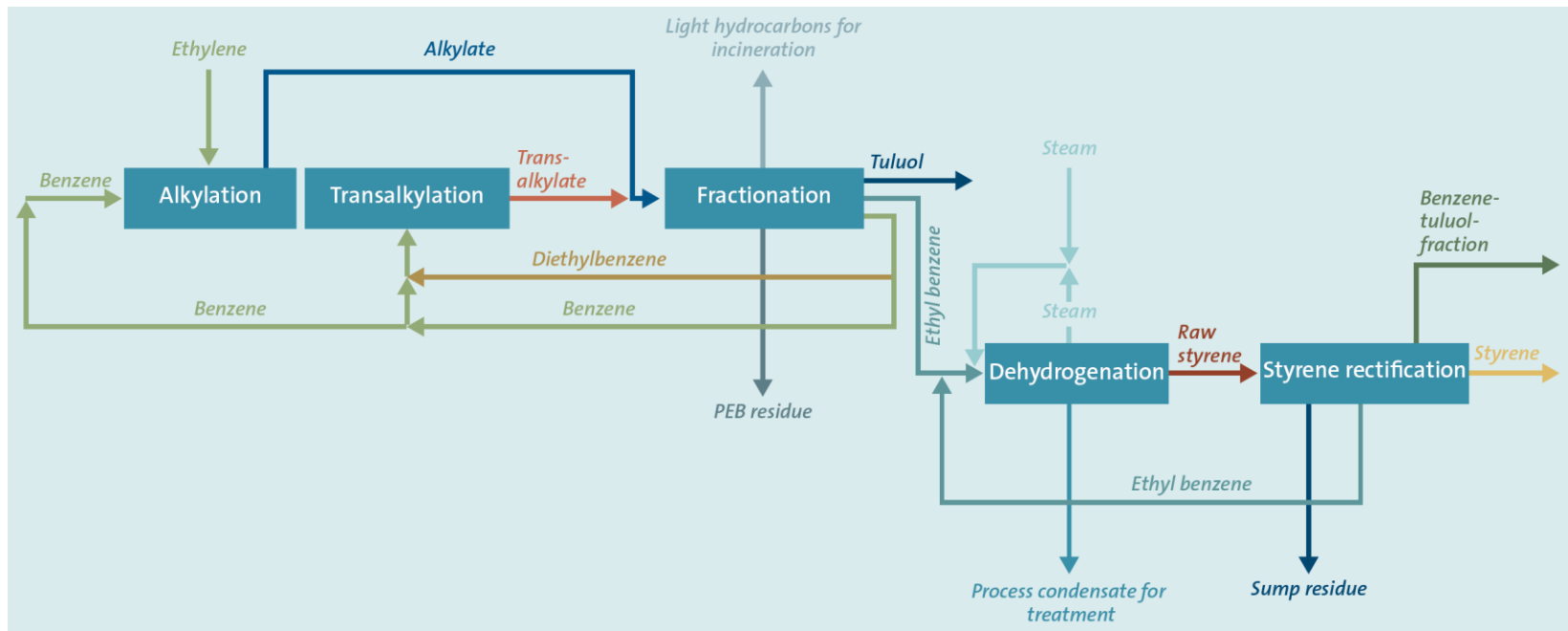| Substance	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$
$C_3H_8(g)$	68.032	22.59	-13.11	31.71
$O_2(g)$	29.10	1.158	-0.6076	1.311
$N_2(g)$	29.00	0.2199	0.5723	-2.871
$CO_2(g)$	36.11	4.233	-2.887	7.464
$H_2O(g)$	33.46	0.6880	0.7604	-3.593
$H_2O(l)$	75.4	—	—	—

$$\widehat{H}_1 = \Delta\widehat{H}^o_{f,C_3H_8(g)} + \int_{25}^{25} c_{p,C_3H_8(g)}dT = -103.8 + 0 = 103.8 \; kJ/mol$$

Styrene production:

Styrene production:

Production of styrene by means of catalytic dehydrogenation of ethylbenzene with water vapor and under vacuum in 2 adiabatic radial reactors with external intermediate superheating. Location: Salawat, Russia. Capacity: $230{,}000$ t/y ethylbenzene, $200{,}000$ t/y styrene. Commissioned: July 2003.
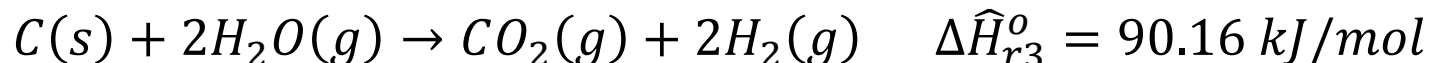
Styrene production:

Styrene, C_8H_8, is an important chemical compound in plastics industry. Direct dehydrogenation of ethylbenzene, C_8H_{10}, to styrene accounts for majority of its commercial productions. The main reaction is carried out adiabatically at $600°C$ in the vapour phase with superheated steam over an iron-oxide based catalyst:

$$C_8H_{10}(g) \rightarrow C_8H_8(g) + H_2(g) \qquad \Delta\widehat{H}^o_{r1} = 117.48 \; kJ/mol$$

The competing thermal reaction degrades ethylbenzene to carbon and hydrogen:

$$C_8H_{10}(g) \rightarrow 8C(s) + 5H_2(g) \qquad \Delta\widehat{H}^o_{r2} = -29.92 \; kJ/mol$$

The self-cleaning reaction of carbon with steam prevents catalyst poison:

$$C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g) \qquad \Delta\widehat{H}^o_{r3} = 90.16 \; kJ/mol$$

Styrene production:

The results from mass balance calculations in terms of $5\ mol$ ethylbenzene feed are given in the flowchart below.

$5\ mol\ C_8H_{10}, 600°C$

$n_{in}\ mol\ H_2O, 700°C$

Adiabatic Reactor

$2.7\ mol\ C_8H_{10}$
$2.2\ mol\ C_8H_8$
$0.8\ mol\ CO_2$

$4.3\ mol\ H_2$
$n_{out}\ mol\ H_2O$
$600°C$
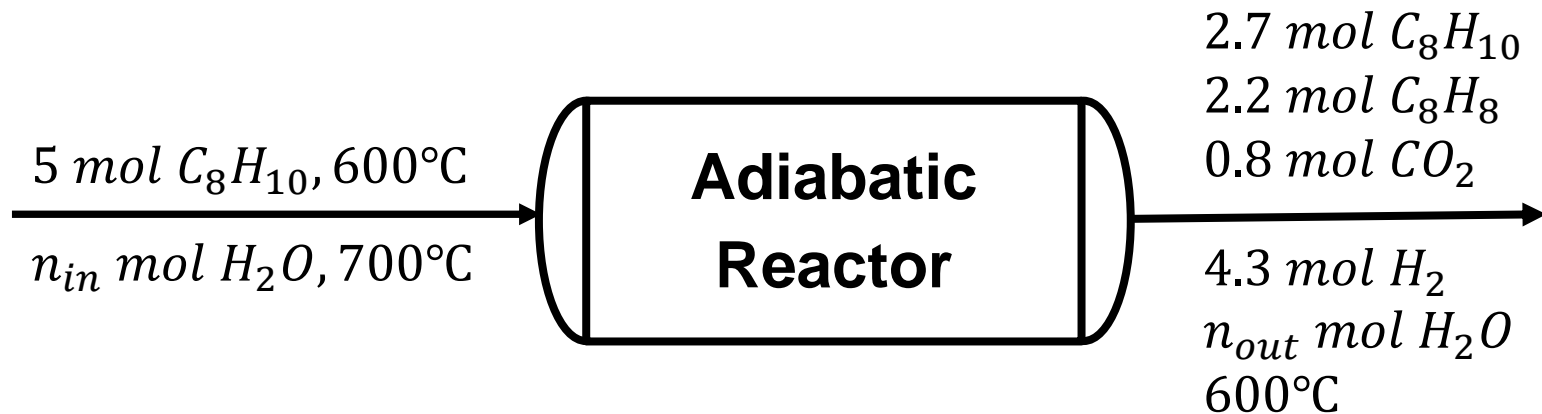
Calculate the required superheated steam to ethylbenzene feed ratio, SOR (steam over reactant), in kg (steam)/kg (ethylbenzene).

Styrene production:

$$c_p = a + bT + cT^2 + dT^3 \ kJ/mol°C \qquad Form \ 1$$

$$c_p = a + bT + cT^{-2} \ kJ/mol°C \qquad Form \ 2$$

Substance	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Form
$C_8H_{10}(l)$	185.6	—	—	—	1 (T in K)
$C_8H_{10}(g)$	−43.1	70.72	−48.11	130.1	1 (T in K)
$C_8H_8(l)$	182.6	—	—	—	1 (T in K)
$C_8H_8(g)$	−28.25	61.59	−40.23	99.35	1 (T in K)
$C(s)$	11.18	1.095	-4.891×10^{10}	—	2 (T in K)
$H_2(g)$	28.84	0.00765	0.3288	−0.8698	1 (T in °C)
$CO_2(g)$	36.11	4.233	−2.887	7.464	1 (T in °C)
$H_2O(g)$	33.46	0.6880	0.7604	−3.593	1 (T in °C)

Styrene production:

$$\Delta \widehat{H}_{f, C_8 H_{10}(g)}^o = 29.92 \ kJ/mol$$
$$\Delta \widehat{H}_{f, C_8 H_8(g)}^o = 147.4 \ kJ/mol$$
$$\Delta \widehat{H}_{f, CO_2(g)}^o = -393.5 \ kJ/mol$$
$$\Delta \widehat{H}_{f, H_2 O(g)}^o = -241.83 \ kJ/mol$$

$$\Delta \widehat{H}_{v, C_8 H_{10}}(136.2°C) = 35.6 \ kJ/mol$$
$$\Delta \widehat{H}_{v, C_8 H_8}(145.1°C) = 37.05 \ kJ/mol$$

$$\widehat{H}_{H_2 O(g)}(700°C, 1 bar) = 3928 \ kJ/kg$$
$$\widehat{H}_{H_2 O(g)}(600°C, 1 \ bar) = 3705 \ kJ/kg$$

The reference state for $\widehat{H}_{H_2 O(g)}$ is the saturated liquid water at triple point (0.01 ℃ and 0.00611 bar).

Styrene production:

$$SOR_{mol} = \frac{87.9188}{5} = 17.5838 \; mol \; (steam)/mol \; (\text{ethylbenzene})$$

$$SOR_{mass} = \frac{87.9188 \times 18}{5 \times 106} = 2.9859 \; kg \; (steam)/kg \; (\text{ethylbenzene})$$

The lower limit of the steam to ethylbenzene molar ratio, SOR_{min}, is set at 7 to prevent coke formation on the catalyst surface and to remove coke deposits from the catalyst surface thereby regenerating it. However, if SOR is increased to a very large value, it will affect the economics of the process as extra energy is required to produce the excess steam and its subsequent condensation at the downstream of the reactor. Hence, it is common industrial practice to restrict SOR_{max} at 20. (A.K.Y. Yee et al., 2003, Multiobjective optimization of an industrial styrene reactor, Computers and Chemical Engineering, 27, 111-130.)