Computer Applications in Chemical Engineering
Priv.-Doz. Dr. Roland Dittmeyer
Karl-Winnacker-Institut der DECHEMA e.V., Frankfurt am Main
Summer 2003

<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>Lecturer</th>
<th>Topic: Reactor Modelling in AspenPlus</th>
</tr>
</thead>
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<tr>
<td></td>
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<td>Unit 1</td>
</tr>
<tr>
<td>1.</td>
<td>April 8</td>
<td>Wenzel</td>
<td>Material and energy balances, basic definitions</td>
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<td></td>
<td>April 15</td>
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<td>Implementation in AspenPlus</td>
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<td>Exercise 1: Simple reactors</td>
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<td>June 3</td>
<td>Dittmeyer</td>
<td></td>
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<td>June 10</td>
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<td>June 17</td>
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<td>Stirred tank and tubular reactors</td>
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<td>July 1</td>
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<td>Implementation in AspenPlus</td>
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<td>12.</td>
<td>July 8</td>
<td>Test</td>
<td>Exercise 2: Cyclohexanol dehydrogenation</td>
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<td>Batch reactor operations</td>
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<td>Implementation in AspenPlus</td>
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<tr>
<td></td>
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<td>Trouble shooting for Exercise 2</td>
</tr>
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Required knowledge:

- Chemical Engineering Thermodynamics
- Unit Operations
- Chemical Reaction Engineering

Books:

Unit 1  Material Balances

1. The Material Balance

In words: \[
\left\{ \text{accumulation within the system} \right\} = \left\{ \text{input through system boundaries} \right\} - \left\{ \text{output through system boundaries} \right\} + \left\{ \text{generation within the system} \right\} - \left\{ \text{consumption within the system} \right\}
\]

General Principle:
Conservation of:  
Requirements:
1. Total mass  no nuclear reactions !  
2. Total moles  no net change of moles due to chemical reactions !  
3. Mass of an atomic species 
4. Moles of an atomic species see 1.  
5. Moles of a chemical compound  
6. Mass of a chemical compound no chemical reactions !  

Task:
Find mathematical expressions for these terms that accurately describe the particular situation  
Solve the resulting system of equations (linear, nonlinear)
Unit 1  Material Balances

2. Determining the Number of Independent Equations

**General Example:**
- steady state
- no chemical reactions

**Rule:**
The number of variables whose values are unknown equals the number of independent equations!

**Systems of Linear Equations:**
The rank of the coefficient matrix equals the number of independent variables!

rank = order of the largest nonzero determinant in a matrix (can be determined by Gauss-Jordan method)

**Total Mole Balance:**
0 = F – P – W

**Component Mole Balances:**
- EtOH: \(0 = F \cdot x_{1F} - P \cdot x_{1P} - W \cdot x_{1W}\)
- H\(_2\)O: \(0 = F \cdot x_{2F} - P \cdot x_{2P} - W \cdot x_{2W}\)
- MeOH: \(0 = F \cdot x_{3F} - P \cdot x_{3P} - W \cdot x_{3W}\)

**Balance of Mole Fractions:**
\(\Sigma x_{iF} = 1\)
\(\Sigma x_{iP} = 1\)
\(\Sigma x_{iW} = 1\)

**Component Mole Balances in Matrix Form:**
\[
\begin{bmatrix}
F \cdot x_{1F} - P \cdot x_{1P} \\
F \cdot x_{2F} - P \cdot x_{2P} \\
F \cdot x_{3F} - P \cdot x_{3P}
\end{bmatrix}
= \begin{bmatrix}
W & 0 & 0 \\
0 & W & 0 \\
0 & 0 & W
\end{bmatrix}
\times \begin{bmatrix}
x_{1W} \\
x_{2W} \\
x_{3W}
\end{bmatrix}
\]
3. Number of Degrees of Freedom

\[
f = n - r
\]

<table>
<thead>
<tr>
<th>( f )</th>
<th>Problem is</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>properly specified</td>
<td>unique solution exists</td>
</tr>
<tr>
<td>&lt; 0</td>
<td>underspecified</td>
<td>infinite number of solutions</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>overspecified</td>
<td>no solution, equations are inconsistent</td>
</tr>
</tbody>
</table>

Nonlinear Equations:

more than one solution may exist even for \( f = 0 \)

if so, the physics of the process tell which solution (s) is (are) relevant

no general statement can be made

LOOKING BACK

- 12 variables in total
- 7 equations, of which 1 is not independent
- 6 variables have to be specified
- choice of these independent variables is not at will
  → selection must leave a number of independent material balances equal to the number of unknown variables
**Unit 1  Material Balances**

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### General Strategy for Analyzing Material Balance Problems

1. Read the problem and clarify what is to be accomplished.

2. Draw a sketch of the process; define the system by a boundary.

3. Label with symbols the flow of each stream and the associated compositions and other information that is unknown.

4. Put all the known values of compositions and stream flows on the figure by each stream; calculate additional compositions from the given data as necessary. Or, at least initially identify the known parameters in some fashion.

5. Select a basis.

6. Make a list by symbols for each of the unknown values of the stream flows and compositions, or at least mark them distinctly in some fashion, and count them.

7. Write down the names of an appropriate set of balances to solve; write the balances down with type of balance listed by each one. Do not forget the implicit balances for mass or mole fractions.

8. Count the number of independent balances that can be written; ascertain that a unique solution is possible. If not, look for more information or check your assumptions.

9. Solve the equations. Each calculation must be made on a consistent basis.

10. Check your answers by introducing them, or some of them, into any redundant material balances. Are the equations satisfied? Are the answers reasonable?
**Unit 1  Material Balances**

**Distillation Unit:**

Feed $F = 1000 \ kg$
10 % EtOH
90 % H$_2$O

Heat

Vapor

System Boundary

Reflex

Cooling Water

Distillate $D = 0.1 \cdot F$
60 % EtOH
40 % H$_2$O

Bottoms (Waste) $B = \ kg$
EtOH = ?
H$_2$O = ?

**Task:**

Calculate composition of bottoms and mass of lost alcohol

**Steps 1–3:** Symbols and data placed in flow sheet

**Step 4:** Evaluate $D = 0.1 \cdot F = 100 \ kg$

**Step 5:** Select as the basis the given feed $F = 1000 \ kg$

**Steps 6–8:** The remaining unknowns are $w_{EtOH,B}$, $w_{H2O,B}$ and $B$. Two components exist, yielding two independent component mass balances, and $w_{EtOH,B} + w_{H2O,B} = 1$, so that the problem has a unique solution.

**Step 9:** The total mass balance yields:

$B = F - D = 100 \ kg$

The solution for the composition of the bottoms can be computed directly by subtraction:

<table>
<thead>
<tr>
<th>Component</th>
<th>kg in Feed</th>
<th>kg Distillate out</th>
<th>kg Bottoms</th>
<th>percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH</td>
<td>$0.1 \cdot 1000$</td>
<td>$- 0.6 \cdot 100$</td>
<td>= 40</td>
<td>4.4</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$0.9 \cdot 1000$</td>
<td>$- 0.4 \cdot 100$</td>
<td>= 860</td>
<td>95.6</td>
</tr>
</tbody>
</table>

| Total     | 900         | 100.0          |
Material Balance Problem Involving Chemical Reactions

\[
\begin{align*}
\left\{ \text{accumulation} \right\} & = \left\{ \text{input through system boundaries} \right\} - \left\{ \text{output through system boundaries} \right\} \\
& + \left\{ \text{generation within the system} \right\} - \left\{ \text{consumption within the system} \right\}
\end{align*}
\]

Coal Composition

<table>
<thead>
<tr>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Gas Composition

<table>
<thead>
<tr>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂+ SO₂</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>O₂</td>
</tr>
<tr>
<td>N₂</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Refuse Composition

<table>
<thead>
<tr>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C+H+O+N+S</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Combustion of Coal:

- Steady state
- Coal elemental composition is given
- Moisture content of the coal is 3.9 %
- Moisture content of the air is 0.0048 lb H₂O/lb dry air
- Stack gas analysis is given on a dry basis
- Refuse shows 14 % unburned coal with the remainder being ash

Tasks:

Check data for consistency

Determine the average percentage excess air used
Unit 1  Material Balances

Steps 1–4:

Coal

<table>
<thead>
<tr>
<th>Element</th>
<th>Quantity (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>83.05</td>
</tr>
<tr>
<td>H</td>
<td>4.45</td>
</tr>
<tr>
<td>O</td>
<td>3.36</td>
</tr>
<tr>
<td>N</td>
<td>1.08</td>
</tr>
<tr>
<td>S</td>
<td>0.7</td>
</tr>
<tr>
<td>Ash</td>
<td>7.36</td>
</tr>
</tbody>
</table>

Added H₂O 3.9 lb

Furnace

Stack Gas

Air

Refuse

Step 5: Pick a basis of $F = 100$ lb as convenient.

Added H₂O 0.0048 lb/lb Air
**Unit 1 Material Balances**

**Steps 1–4:**

\[
\begin{align*}
\text{C} & \quad 83.05 \\
\text{H} & \quad 4.45 \\
\text{O} & \quad 3.36 \\
\text{N} & \quad 1.08 \\
\text{S} & \quad 0.7 \\
\text{Ash} & \quad 7.36 \\
\frac{\text{Added H}_2\text{O}}{100} & \quad 3.9 \text{ lb}
\end{align*}
\]

Coal: \( W \) (lb mol)

\[
\begin{align*}
\text{Coal} & \quad \text{Furnace} \\
\text{Stack Gas} & \quad \text{Air} \\
\text{Refuse} & \quad \text{R}
\end{align*}
\]

**Step 5:** Pick a basis of \( F = 100 \text{ lb} \) as convenient.

**Step 6:** \( A, W, P, R \) remain unknown. Mass balance on the elements in \( \text{lb mol} \).

\[
\begin{align*}
\text{Added H}_2\text{O} & \quad 0.0048 \text{ lb/lb Air} \\
\text{Containing} & \quad \left\{ \begin{array}{l}
\text{H}: 0.0154 \text{ lb mol/mol A} \\
\text{O}: 0.0077 \text{ lb mol/mol A}
\end{array} \right.
\end{align*}
\]

\[
\begin{align*}
\text{lb air} & \quad 29 \text{ lb} \\
\text{lb mol air} & \quad 1 \text{ lb mol} \\
\text{lb mol H}_2\text{O} & \quad 18 \text{ lb H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
0.0048 \text{ lb H}_2\text{O} & \quad 1 \text{ lb mol H}_2\text{O} \\
& \quad 18 \text{ lb H}_2\text{O} = 0.0077 \frac{\text{lb mol H}_2\text{O}}{\text{lb mol air}}
\end{align*}
\]
Unit 1 Material Balances

Steps 1–4:

Coal:
- C: 83.05 lb
- H: 4.45 lb
- O: 3.36 lb
- N: 1.08 lb
- S: 0.7 lb
- Ash: 7.36 lb

Stack Gas:
- 3.9 lb H₂O
- 1 lb mol H₂O
- 2 lb mol H

W (lb mol):
- H₂O(g) 100%

H₂O(g) 100%

CO₂ + SO₂ 15.4%
- CO: 0.0%
- O₂: 4.0%
- N₂: 80.6%

Refuse R (lb):
- 7.36 lb = R·0.86

Step 5: Pick a basis of F = 100 lb as convenient.


Added H₂O 0.0048 lb/lb Air

Containing:
- H: 0.0154 lb mol/mol A
- O: 0.0077 lb mol/mol A

Added H₂O 0.0048 lb/lb Air

Air:
- N₂: 0.79
- O₂: 0.21

100

0.0048 lb H₂O 29 lb air 1 lb mol H₂O 18 lb H₂O

lb air 1 lb mol air = 0.0077 lb mol H₂O lb mol air

Ash Material Balance

7.36 lb = R·0.86

→ R = 8.56 lb
### Unit 1 Material Balances

#### C, H, O, N, S in unburned coal (assumption: proportions may not change)

Mass of unburned coal: \(0.14\cdot R = 1.2 \text{ lb}\)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass %*</th>
<th>lb</th>
<th>lb mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>89.65</td>
<td>1.076</td>
<td>0.0897</td>
</tr>
<tr>
<td>H</td>
<td>4.8</td>
<td>0.058</td>
<td>0.0537</td>
</tr>
<tr>
<td>O</td>
<td>3.63</td>
<td>0.0436</td>
<td>0.0027</td>
</tr>
<tr>
<td>N</td>
<td>1.17</td>
<td>0.014</td>
<td>0.0010</td>
</tr>
<tr>
<td>S</td>
<td>0.76</td>
<td>0.009</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

*on an ash-free basis

**Step 6 (repeated):** \(A, W, P\) remain unknown. Only four mole balances on the elements can be written, because \(S + C\) must be combined as these elements are linked in the stack gas analysis \((\text{SO}_2 + \text{CO}_2)\).

<table>
<thead>
<tr>
<th></th>
<th>Input</th>
<th>Output</th>
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</thead>
<tbody>
<tr>
<td>1.</td>
<td>(F)</td>
<td>(A)</td>
</tr>
<tr>
<td>C+S</td>
<td>(83.05/12 + 0.70/32)</td>
<td>+ 0</td>
</tr>
<tr>
<td>3.</td>
<td>(H)</td>
<td>(4.45/1.008 + 0.433)</td>
</tr>
<tr>
<td>Test</td>
<td>(O)</td>
<td>(3.36/16 + 0.217)</td>
</tr>
<tr>
<td>2.</td>
<td>(N)</td>
<td>(1.08/14)</td>
</tr>
</tbody>
</table>

\(C+S \rightarrow P = 50 \text{ lb mol} \quad N \rightarrow A = 45.35 \text{ lb mol} \quad H \rightarrow W = 2.746 \text{ lb mol} \quad O \rightarrow 19.8 \approx 20\)
Unit 1  Material Balances

Average percentage excess air:

\[ \% \text{ excess air} = 100 \times \frac{O_2 \text{ entering} - O_2 \text{ required}}{O_2 \text{ required}} \]

\( O_2 \text{ required} \) is calculated from reaction stoichiometry:

<table>
<thead>
<tr>
<th>Component</th>
<th>Reaction</th>
<th>lb</th>
<th>lb mol</th>
<th>Required O₂ (lb mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>( \text{C} + O_2 \rightarrow \text{CO}_2 )</td>
<td>83.05</td>
<td>6.921</td>
<td>6.921</td>
</tr>
<tr>
<td>H</td>
<td>( \text{H}_2 + 0.5 \text{O}_2 \rightarrow \text{H}_2\text{O} )</td>
<td>4.45</td>
<td>4.415</td>
<td>1.104</td>
</tr>
<tr>
<td>O</td>
<td>-</td>
<td>3.36</td>
<td>0.210</td>
<td>-0.105</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>1.08</td>
<td>0.077</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>( \text{S} + O_2 \rightarrow \text{SO}_2 )</td>
<td>0.70</td>
<td>0.022</td>
<td>0.022</td>
</tr>
</tbody>
</table>

\( O_2 \) coming with the coal!

\( O_2 \) entering with the air: 45.35 lb mol \( \times \) 0.21 = 9.524 lb mol.

\[ \% \text{ excess air} = 100 \times \frac{9.524 - 7.942}{7.942} = 19.9\% \]
Extent of Reaction, Reaction Rate and Fractional Conversion in Single Reactions:

**Batch Reactor:**

**Reaction:**

\[ \nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D \]

**Molar extent:**

\[ \xi = \frac{n_A - n_A^0}{\nu_A} \text{ [kmol]} \quad \Rightarrow \quad n_A = n_A^0 + \nu_A \xi \]

\[ \lambda = \frac{\xi}{V_R} \left[ \frac{\text{kmol}}{m^3} \right] \quad \Rightarrow \quad c_A = c_A^0 + \nu_A \lambda \]

**Rate of Consumption:**

\[ R_A = -r_A = -\frac{1}{V_R} \frac{dn_A}{dt} \left[ \frac{\text{kmol}}{m^3 \text{s}} \right] \]

**Rate of Reaction:**

\[ \nu_A = -1 \]

**Fractional Conversion of A:**

\[ X_A = \frac{n_A^0 - n_A}{n_A^0} = 1 - \frac{n_A}{n_A^0} = -\frac{\nu_A \xi}{n_A^0} [-] \]

\[ = 1 - \frac{c_A}{c_A^0} = -\frac{\nu_A \lambda}{c_A^0} [-] \quad \text{for } V_R = \text{const.} \]
Unit 1  Basic definitions

Rate of Consumption/Formation, Yield and Selectivity in Multiple Reactions:

\[ \dot{n}_i^0 \quad i = 1...n \]

\[ \dot{n}_i \quad i = 1...n \]

- **Fractional Conversion of A:**
  \[ X_A = \frac{\dot{n}_A - \dot{n}_A}{\dot{n}_A^0} = 1 - \frac{\dot{n}_A}{\dot{n}_A^0} \]
  
  Same definition, but more than one reaction contribute to the consumption of A.

- **Matrix Form:**
  \[ \dot{n} = \dot{n}_0 + V_R \mathbf{v}_\xi \]

- **Rate of Consumption/Formation:**
  \[ R_i = \sum_{j=1}^{m} \nu_{ij} \dot{r}_j \quad \left[ \frac{\text{kmol}}{\text{m}^3 \text{s}} \right] \]
  
  stoichiometric coefficient of compound i in reaction j
Unit 1 Basic definitions

Rate of Consumption/Formation, Yield and Selectivity in Multiple Reactions:

Yield of Product P based on consumption of A:

\[ Y_{P,A} = \frac{P \text{ formed} - P \text{ supplied with feed}}{A \text{ supplied with feed}} \times \left( \text{moles of P formed when all moles of A are converted to P} \right) \]

\[ Y_{P,A} = \frac{\dot{n}_P - \dot{n}_P^0}{\dot{n}_A^0} \times \frac{\beta_{A,\text{ref}}}{\beta_{P,\text{ref}}} \]

Stoichiometric ratio between A and P based on a common reference, e.g. an atomic species

(\( \beta = \text{matrix of chemical compounds vs. atomic species} \))
Unit 1 Basic definitions

Example:

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \]
\[ CH_4 + CO_2 \rightarrow CO + 2H_2 \]

<table>
<thead>
<tr>
<th></th>
<th>CH4</th>
<th>O2</th>
<th>CO2</th>
<th>H2O</th>
<th>CO</th>
<th>H2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ \beta = \frac{\beta_{CO,C}}{\beta_{CH4,C}} \]

Yield of CO either based on CH4 or on O2:

\[ Y_{CO,CH4} = \frac{\dot{n}_{CO} - \dot{n}_{CO}^0}{\dot{n}_{CH4}^0} \times \frac{\beta_{CO,C}}{\beta_{CH4,C}} \]

\[ Y_{CO,O2} = \frac{\dot{n}_{CO} - \dot{n}_{CO}^0}{\dot{n}_{O2}^0} \times \frac{\beta_{CO,O}}{\beta_{O2,O}} \]

ATTENTION

The definitions based on moles – as given here – is convenient for most applications in chemical reaction engineering, but an analogous definition of extent of reaction, reaction rate, rate of formation/consumption, conversion, yield and selectivity based on mass* is used frequently as well.

Sometimes even mixed definitions, e.g. moles produced per mass of feed.
Unit 1  Energy Balances

1. The Energy Balance

General Principle:
Conservation of total energy

Careful choice of system boundary!

In words:
\[ \begin{align*}
\text{accumulation} & \quad \text{transfer of energy} \\
\text{of energy} & \quad \text{into system} \\
\text{within the} & \quad \text{through system} \\
\text{system} & \quad \text{boundary} \\
\end{align*} \]

\[ = \begin{align*}
\text{transfer of energy} & \quad \text{transfer of energy} \\
\text{into system} & \quad \text{out of system} \\
\text{through system} & \quad \text{through system} \\
\text{boundary} & \quad \text{boundary} \\
\end{align*} \]

\[ \begin{align*}
\text{energy} & \quad \text{energy} \\
\text{generation} & \quad \text{consumption} \\
\text{within the} & \quad \text{within the} \\
\text{system} & \quad \text{system} \\
\end{align*} \]

Six Types of Energy

<table>
<thead>
<tr>
<th>Type</th>
<th>Symbol</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work</td>
<td>( W = \int F \cdot ds )</td>
<td>[kJ] Path</td>
</tr>
<tr>
<td>Heat</td>
<td>( Q = k \cdot A \cdot \Delta T )</td>
<td>[kJ] Path</td>
</tr>
<tr>
<td>Kinetic Energy</td>
<td>( K = \frac{1}{2} \cdot m \cdot v^2 )</td>
<td>[kJ] State</td>
</tr>
<tr>
<td>Potential Energy</td>
<td>( P = m \cdot g \cdot h )</td>
<td>[kJ] State</td>
</tr>
<tr>
<td>Internal Energy</td>
<td>( \hat{U} = \hat{U}(T,p) )</td>
<td>[kJ/kg] State</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>( \hat{H} = \hat{U} + p \cdot \hat{V} = \hat{H}(T,p) )</td>
<td>[kJ/kg] State</td>
</tr>
</tbody>
</table>

Task:
Find mathematical expressions for these terms that accurately describe the particular situation

Solve the resulting system of equations (linear, nonlinear)
Unit 1  Energy Balances

1. Closed System (without Chemical Reactions)

**SYSTEM**

\[
\Delta E = E_2 - E_1 \quad \text{Total Energy}
\]

\[
\Delta P = P_2 - P_1 \quad \text{Potential Energy}
\]

\[
\Delta K = K_2 - K_1 \quad \text{Kinetic Energy}
\]

\[
\Delta U = U_2 - U_1 \quad \text{Internal Energy}
\]

<table>
<thead>
<tr>
<th>Energy Inventory</th>
<th>Acumulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Energy</td>
<td>( \Delta U = U_2 - U_1 )</td>
</tr>
<tr>
<td>Kinetic Energy</td>
<td>( \Delta K = K_2 - K_1 )</td>
</tr>
<tr>
<td>Potential Energy</td>
<td>( \Delta P = P_2 - P_1 )</td>
</tr>
<tr>
<td>Total Energy</td>
<td>( \Delta E = E_2 - E_1 )</td>
</tr>
</tbody>
</table>

Energy Balance:

\[
\Delta E = E(t_2) - E(t_1) = \Delta U + \Delta P + \Delta K = Q + W
\]
Unit 1  Energy Balances

2. Open System (without Chemical Reactions)

SURROUNDINGS

\[ \Delta E = E(t_2) - E(t_1) = (\hat{U}_2 + \hat{K}_2 + \hat{P}_2) m_2 - (\hat{U}_1 + \hat{K}_1 + \hat{P}_1) m_1 \]

\[ = (\hat{U}_a + \hat{K}_a + \hat{P}_a) m_a - (\hat{U}_b + \hat{K}_b + \hat{P}_b) m_b + Q + W + p_a \hat{V}_a m_a - p_b \hat{V}_b m_b \]

\[ \Delta E = E(t_2) - E(t_1) = Q + W - \Delta[H + K + P] \]

\[ \Delta \text{ means } "t_2 \text{ vs. } t_1" \]

\[ \Delta \text{ means } "a \text{ minus } b" \]

\[ \Delta \text{ means } "a \text{ minus } b" \]
### Summary of the Symbols to be Used in the General Energy Balance

<table>
<thead>
<tr>
<th>Accumulation term</th>
<th>At time $t_1$</th>
<th>At time $t_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type of Energy</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Internal</td>
<td>$U_a$</td>
<td>$U_b$</td>
</tr>
<tr>
<td>Kinetic</td>
<td>$K_a$</td>
<td>$K_b$</td>
</tr>
<tr>
<td>Potential</td>
<td>$P_a$</td>
<td>$P_b$</td>
</tr>
<tr>
<td>Mass</td>
<td>$m_1$</td>
<td>$m_2$</td>
</tr>
<tr>
<td><strong>Energy accompanying mass transport</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type of Energy</td>
<td>Transport in</td>
<td>Transport out</td>
</tr>
<tr>
<td>Internal</td>
<td>$U_a = \hat{U} \cdot m_a$</td>
<td>$U_b = \hat{U} \cdot m_b$</td>
</tr>
<tr>
<td>Kinetic</td>
<td>$K_a = \hat{K} \cdot m_a$</td>
<td>$K_b = \hat{K} \cdot m_b$</td>
</tr>
<tr>
<td>Potential</td>
<td>$P_a = \hat{P} \cdot m_a$</td>
<td>$P_b = \hat{P} \cdot m_b$</td>
</tr>
<tr>
<td><strong>Net heat input to system</strong></td>
<td>$Q$</td>
<td></td>
</tr>
<tr>
<td><strong>Net work done on system by surroundings</strong></td>
<td>$W$</td>
<td></td>
</tr>
<tr>
<td><strong>Work to introduce material into system, or work recovered on removing material from system</strong></td>
<td>$m_a(p_a \hat{V}_a)$</td>
<td>$-m_b(p_b \hat{V}_b)$</td>
</tr>
</tbody>
</table>
**Unit 1  Energy Balances**

**Air Compressor:**

100 kg/hr air

225 K

100 kPa

\( \Delta H_a = 489 \text{ kJ/kg} \)

\( v_a = 0 \text{ m/s} \)

100 kg/hr air

278 K

1000 kPa

\( \Delta H_b = 509 \text{ kJ/kg} \)

\( v_b = 60 \text{ m/s} \)

**System Boundary**

**Task:**

determine the required power in kW for the compressor

**Steps 1 – 4:** Steady state flow process (open system) without chemical reactions. Available data and unknowns listed.

**Step 5:** Basis 100 kg/hr of air

**Steps 6 – 7:** Simplification of the general energy balance.

\[
\Delta E = E(t_2) - E(t_1) = Q + W - \Delta[H + K + P]
\]

(1) The process is at steady state, hence \( \Delta E = 0 \).
(2) \( m_a = m_b = m \).
(3) Potential Energy is not changed: \( \Delta P = 0 \).
(4) \( Q = 0 \) by assumption (insulation).
(5) \( v_a = 0 \) by assumption (unknown but will be small)

**Result:** \( 0 = W - \Delta H - \Delta K \)

**Steps 6 (repeated):** We have one equation and one unknown \( W \) (\( \Delta H \) and \( \Delta K \) can be calculated), hence a unique solution exists.

\[
\Delta H = \frac{(509-489) \text{ kJ}}{100 \text{ kg}} = 2000 \text{ kJ/kg}
\]

\[
\Delta K = \frac{1}{2} m(v_b^2 - v_a^2) = 50 \text{ kg} \times 3600 \text{ (m/s)^2} = 180 \text{ kJ}
\]

\[ W = 2180 \text{ kJ} \]

**Required Power:**

\[
2180 \text{ kJ} / 3600 \text{ s} = 0.61 \text{ kW}
\]
An iron pyrite ore containing 85 % FeS₂ and 15 % inert dirt, rock, etc. (gangue) is roasted with an amount of air equal to 200 % excess air according to the reaction:

\[ 4 \text{FeS}_2 + 11 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 + 8 \text{SO}_2 \]

In order to produce SO₂. All the gangue plus the Fe₂O₃ end up in the solid waste product (cinder), which analyses 4% FeS₂.

**Task:**

*Determine the heat transferred per kg of ore to keep the product stream at 25°C if the entering streams are at 25°C*

**Material balance:**

**Steps 1 – 4:** Steady state flow process (open system) with reaction. The system is the reactor. Available data and unknowns listed.

**Step 5:** Basis 100 kg of pyrite ore.

**Step 6:** Six unknowns exist. We can write 5 component mass balances (O, N, S, gangue, and Fe). With the information on FeS₂ in the gangue six equations are available, hence the problem should have a unique solution.
Roasting of Iron Ore:

The excess air is calculated based on the stated reaction as if all the FeS₂ reacted to Fe₂O₃ even though some FeS₂ will not.

**Required O₂:**
\[
0.85 \cdot \frac{100}{120} \cdot \frac{11}{4} = 1.9479 \text{ kg mol}
\]

**Excess O₂:**
\[
2 \cdot 1.9479 = 3.8958 \text{ kg mol}
\]

**Total O₂:**
5.8438 kg mol

**Total N₂:**
5.8438 \cdot \frac{21}{79} = 21.983 kg mol
**Unit 1  Material and Energy Balances**

**Roasting of Iron Ore:**

- **Ore:** Fe
- **Gangue:** 15.0 kg
- **FeS₂:** 85.0 wt %
- **Total:** 100.0

**Product:** 2SO₂

**Cinder:** C

**200 % excess Air:** A

- **N₂:** 79.0 mol %
- **O₂:** 21.0
- **Total:** 100.0

**Step 7 – 9:** The component mass balances are:

<table>
<thead>
<tr>
<th>Component</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gangue (kg)</td>
<td>15.0</td>
<td>x₁</td>
</tr>
<tr>
<td>Fe (kg mol)</td>
<td>0.85·100/120</td>
<td>2·x₂/159.7 + x₃/120</td>
</tr>
<tr>
<td>O₂ (kg mol)</td>
<td>5.8437</td>
<td>x₄ + x₅ + 1.5·x₂/159.7</td>
</tr>
<tr>
<td>N₂ (kg mol)</td>
<td>21.983</td>
<td>x₆</td>
</tr>
<tr>
<td>S (kg mol)</td>
<td>0.85·100/120·2</td>
<td>x₄ + 2·x₃/120</td>
</tr>
</tbody>
</table>

Together with

\[
0.04 = \frac{x₃}{15 + x₂ + x₃}
\]

**the solution is:**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x₁</td>
</tr>
<tr>
<td></td>
<td>x₂</td>
</tr>
<tr>
<td></td>
<td>x₃</td>
</tr>
<tr>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x₄</td>
</tr>
<tr>
<td></td>
<td>x₅</td>
</tr>
<tr>
<td></td>
<td>x₆</td>
</tr>
</tbody>
</table>

**Energy Balance:**

With \( \Delta E = 0 \), \( \Delta K = 0 \), \( \Delta P = 0 \) and \( W = 0 \), the general energy balance

\[
\Delta E = E(t₂) - E(t₁) = Q + W - \Delta[H + K + P]
\]

reduces to: \( Q = \Delta H \)
Roasting of Iron Ore:

<table>
<thead>
<tr>
<th></th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore: F</td>
<td></td>
</tr>
<tr>
<td>FeS₂</td>
<td>85.0</td>
</tr>
<tr>
<td>gangue</td>
<td>15.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Steps 7 – 9: Gangue goes completely to Cinder, hence:

\[ x_1 = 100 \times 0.15 \text{ kg} = 15 \text{ kg} \]

To determine \( x_2 \) and \( x_3 \) we use the Fe component mass balance and the information that the FeS₂ content in C is 4%.

\[
\frac{0.85 \times 100}{120} = \frac{2 \cdot x_2 + x_3}{159.7} \quad \text{and} \quad 0.04 = \frac{x_3}{15 + x_2 + x_3}
\]

The equations can be solved easily by substitution, which gives:

\[ x_2 = 57.7455 \text{ kg} \]
\[ x_3 = 3.0311 \text{ kg} \]

Step 6 (repeated): We have 3 unknowns left and 3 component mass balances.

The excess air is calculated from the stated reaction while taking into account that not all the FeS₂ will react to Fe₂O₃.

Required \( O_2 \):

\[
(0.85 \times 100 - 3.0311)/120 \cdot 11/4 = 1.8785 \text{ kg mol}
\]

Excess \( O_2 \): 2 \cdot 1.8785 = 3.7569 kg mol

Total \( O_2 \):

5.6354 kg mol

Total \( N_2 \): 5.7023 \cdot 0.21/0.79 = 21.200 kg mol

Calculating excess oxygen the exact way (1)
Roasting of Iron Ore:

Step 7 – 9: The component mass balances are:

<table>
<thead>
<tr>
<th>Component</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$ (kg mol)</td>
<td>5.6354</td>
<td>$x_4 + x_5 + 1.5\cdot57.7445/159.7$</td>
</tr>
<tr>
<td>$N_2$ (kg mol)</td>
<td>21.200</td>
<td>$x_6$</td>
</tr>
<tr>
<td>S (kg mol)</td>
<td>0.85·100/120·2</td>
<td>$x_4 + 3.0311/120·2$</td>
</tr>
</tbody>
</table>

The solution is:

<table>
<thead>
<tr>
<th>kg mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_4$</td>
</tr>
<tr>
<td>$x_5$</td>
</tr>
<tr>
<td>$x_6$</td>
</tr>
</tbody>
</table>

Energy Balance:

Since $\Delta E = 0$, $\Delta K = 0$, $\Delta P = 0$ and $W = 0$, the general energy balance

$\Delta E = E(t_2) - E(t_1) = Q + W - \Delta[H + K + P]$

reduces to: $Q = \Delta H$
Reactants and products are at the same temperature and pressure of 25°C and 1 atm. Hence this is chosen as reference state, so that the temperature dependent term becomes zero.

\[
\Delta H_{\text{mixture}} = \left( \sum_i n_i \Delta H^0_{fi} + \int_{T_{\text{ref}}}^T \sum_i n_i c_p,i dT \right)
\]

\[
Q = \sum_{\text{products}} n_i \Delta H^0_{fi} - \sum_{\text{reactants}} n_i \Delta H^0_{fi}
\]

<table>
<thead>
<tr>
<th>Component</th>
<th>(10^{-3} \times \text{g mol})</th>
<th>(\Delta H_i^0) (kJ/g mol)</th>
<th>(n_i \Delta H_i^0) (kJ)</th>
<th>(10^{-3} \times \text{g mol})</th>
<th>(\Delta H_i^0) (kJ)</th>
<th>(n_i \Delta H_i^0) (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS(_2)</td>
<td>0.0253</td>
<td>-177.9</td>
<td>-4.494</td>
<td>0.7083</td>
<td>-177.9</td>
<td>-126.007</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.3616</td>
<td>-822.156</td>
<td>-297.281</td>
<td>0</td>
<td>-822.156</td>
<td>0</td>
</tr>
<tr>
<td>N(_2)</td>
<td>21.200</td>
<td>0</td>
<td>0</td>
<td>21.200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(_2)</td>
<td>3.7269</td>
<td>0</td>
<td>0</td>
<td>5.6354</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>1.3661</td>
<td>-296.60</td>
<td>-405.185</td>
<td>0</td>
<td>-296.90</td>
<td>0</td>
</tr>
</tbody>
</table>

**Result:**

\[
Q = \left[ -706.96 - (-126.007) \right] \times 10^3 = -580.953 \times 10^3 \text{ kJ} / 100 \text{ kg ore} = -5.801 \times 10^3 \text{ kJ/kg ore}
\]

The negative sign indicates that heat is removed from the process.
Many more instructive examples are contained in the book by D.M. Himmelblau (Basic Principles and Calculations in Chemical Engineering), which is an excellent textbook for self-instruction.

The last wisdom:

Take care of your units and they will take care of you!