Laboratory of
Computational
Systems
Biotechnology

EPFL

Introduction to Chemical Engineering

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Office hours: Mondays 16h-19h (CH H4 625) or schedule by email

Fridays, 14h15 - 17h00
2024-2025

Course Schedule

Date	Subject
13-Sep	**1. Fundamentals of Material Balances** 1.1. Process definition and classification 1.2. Material balance calculations
20-Sep	1.3. Balances on multiple-unit processes
27-Sep	**Review on Mass Balances (non-reactive)**
04-Oct	1.4. Chemical reaction stoichiometry **1.5.1 Balances on reactive processes (part 1)**
11-Oct	**1.5.2 Balances on reactive processes (part 2)** **1.6. Balances on multiple unit reactive processes** **Review on Mass Balances (non-reactive & reactive)**
18-Oct	**2. Fundamentals of Energy and Energy Balances** 2.1. Energy balances on closed systems 2.2. Open systems at steady state **3. Balances on Non-Reactive Processes** 3.1. Energy balance calculation 3.2. Changes in Pressure, Temperature, Phases
01-Nov	**4. Balances on Reactive Processes** 4.1. Introduction to the Enthalpy of Reaction 4.2. Heat of Reaction Method 4.3. Heat of Formation Method 4.4 General Procedure to solve energy balance in reactive systems
08-Nov	**Review on Balances on Non-Reactive Processes** Problems: Mass and Energy Balances on non-Reactive Systems
15-Nov	**Midterm Exam: Mass & Energy Balances non-Reactive Systems**
22-Nov	**Review Midterm**

Date	Subject
29-Nov	Review on Heat of Reaction vs Heat of Formation Methods 4.5 Hess's Law to compute the Heat of Reaction 4.6 Heat of Combustion
06-Dec	5. Energy balances on mixing processes 5.1 Distinction between ideal and real solutions 5.2 Heat of Solution
13-Dec	**Review and Study Session** • **Material balances** • **Energy balances**

Recommended textbook:
Elementary Principles of Chemical Processes, Richard M. Felder & Ronald W. Rousseau

Session IX: Friday 13 December 2024

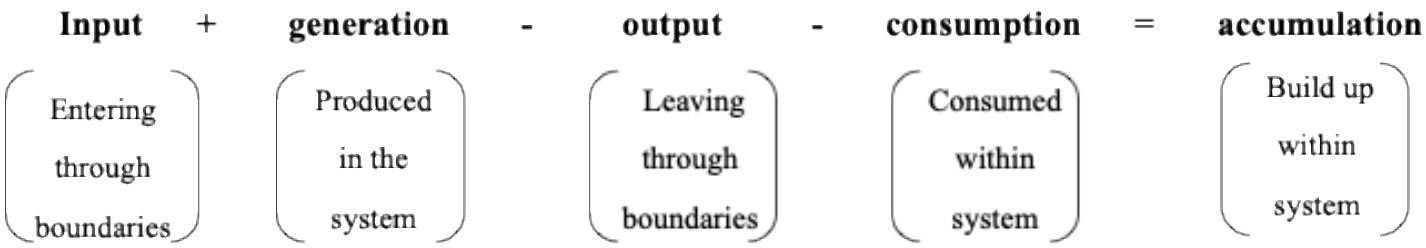
During this session, we will review the following concepts

1. Material balances
2. Energy balances

Material Balances

Material Balances: overview

It all starts with the mother of all equations:



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It all starts with the mother of all equations:

Input	+	**generation**	-	**output**	-	**consumption**	=	**accumulation**
Entering through boundaries		Produced in the system		Leaving through boundaries		Consumed within system		Build up within system

(Almost) all the systems we study represent **steady-state continuous processes:**

Input	+	**generation**	-	**output**	-	**consumption**	=	**0**
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From there, we have seen 2 possible methods:

Species Material Balances

We perform balances for each molecular species

Atom Material Balances

We perform balances for each element

Material Balances: species vs atom balances

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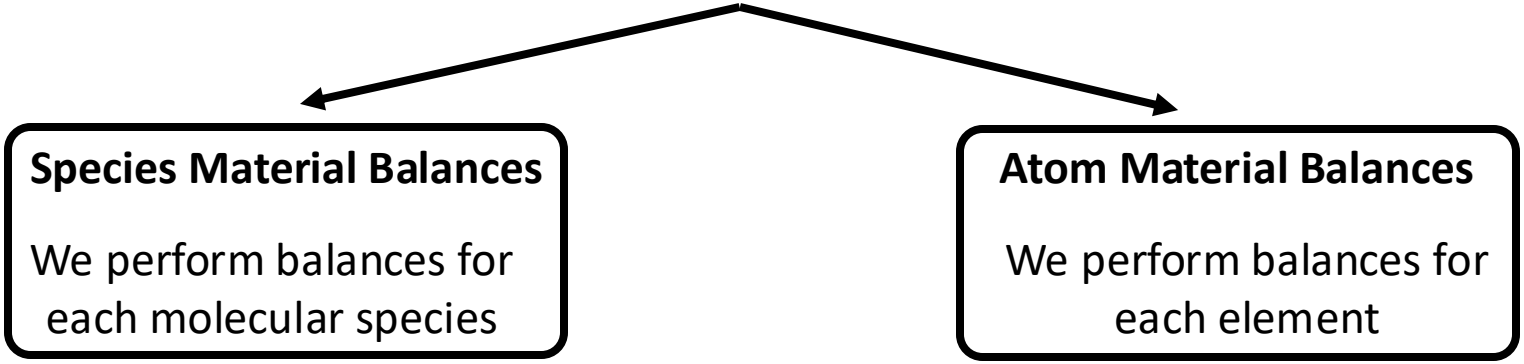

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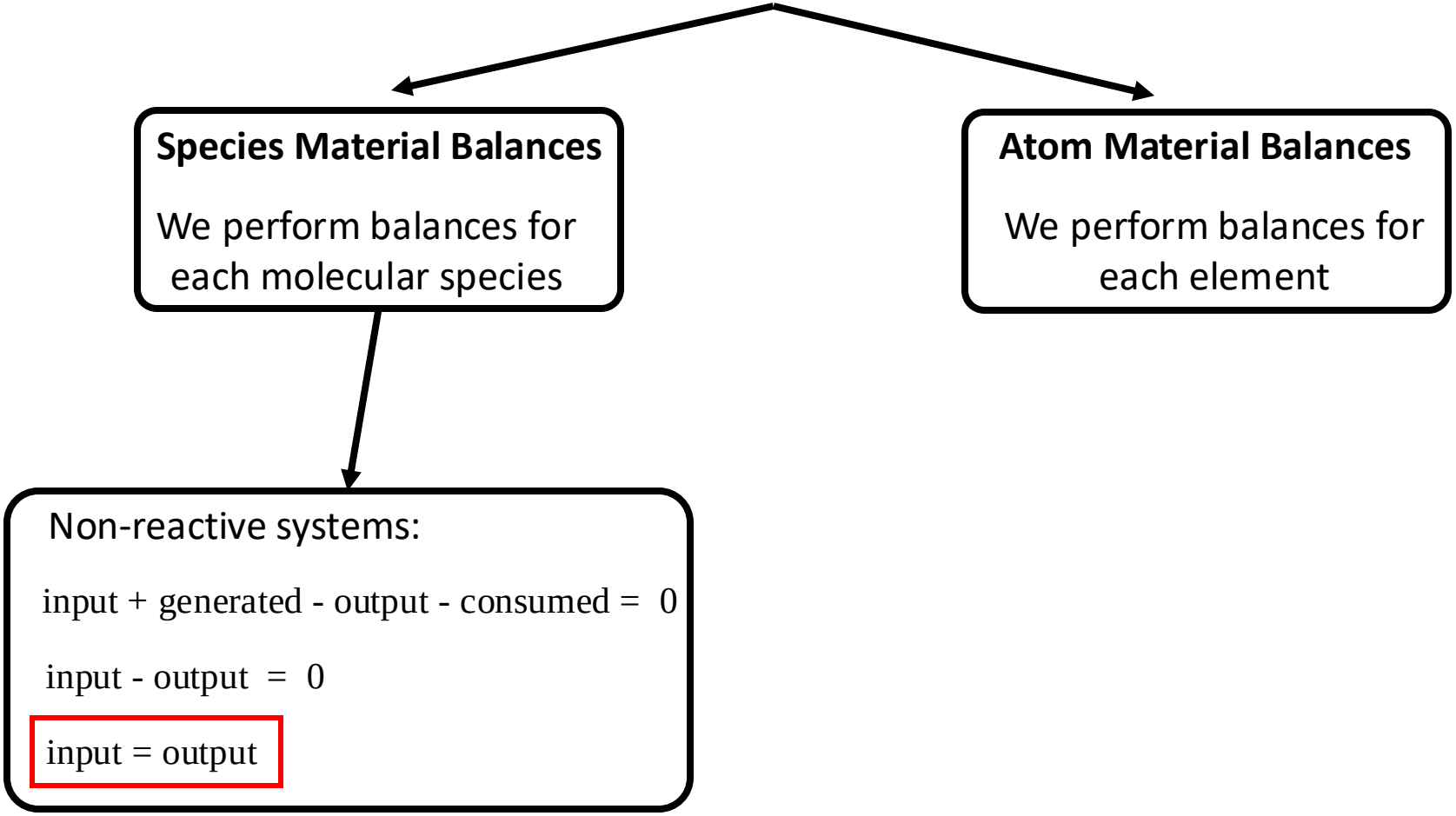

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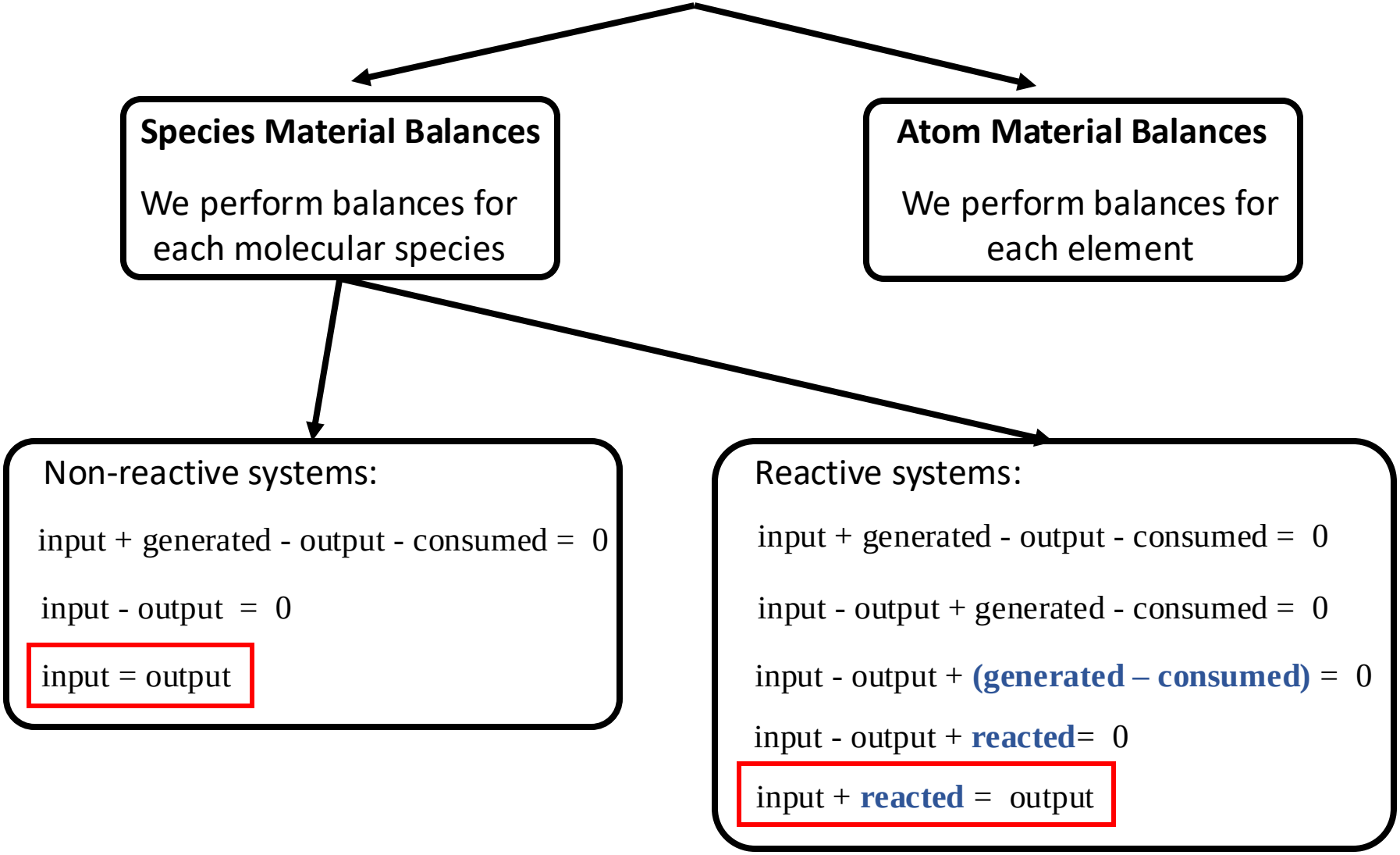


Material Balances: species vs atom balances

From there, we have seen 2 possible methods:

Species Material Balances

We perform balances for each molecular species

Atom Material Balances

We perform balances for each element

Non-reactive systems:

input = output

$$n_{CH4,in} = n_{CH4,out}$$

Reactive systems:

input + **reacted** = output

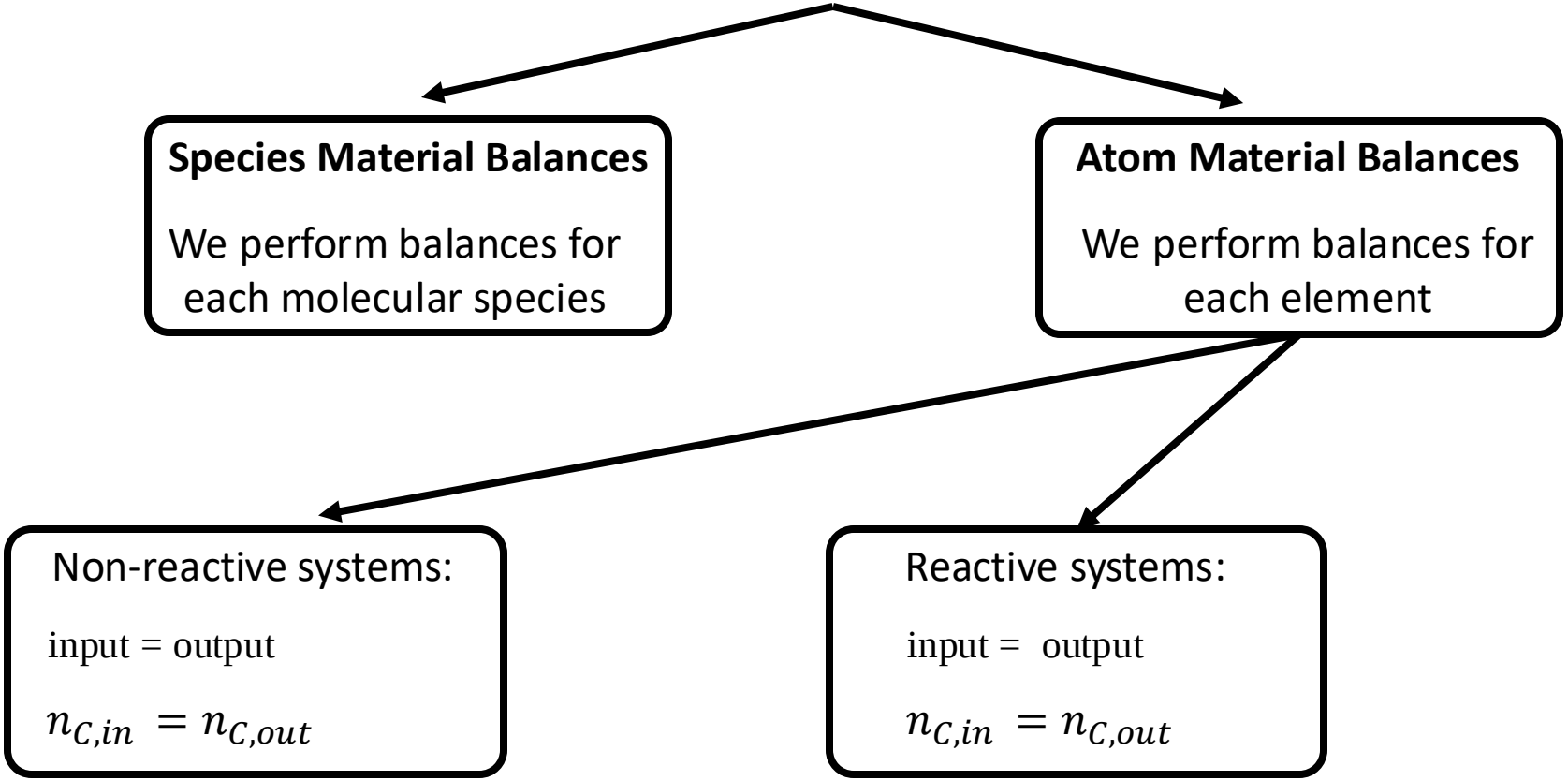
$$n_{CH4,in} + \boldsymbol{\nu_{CH4}} \cdot \boldsymbol{\xi} = n_{CH4,out}$$

Reactant: $\boldsymbol{\xi < 0}$ consumed

Product: $\boldsymbol{\xi > 0}$ generated

Material Balances: species vs atom balances

From there, we have seen 2 possible methods:



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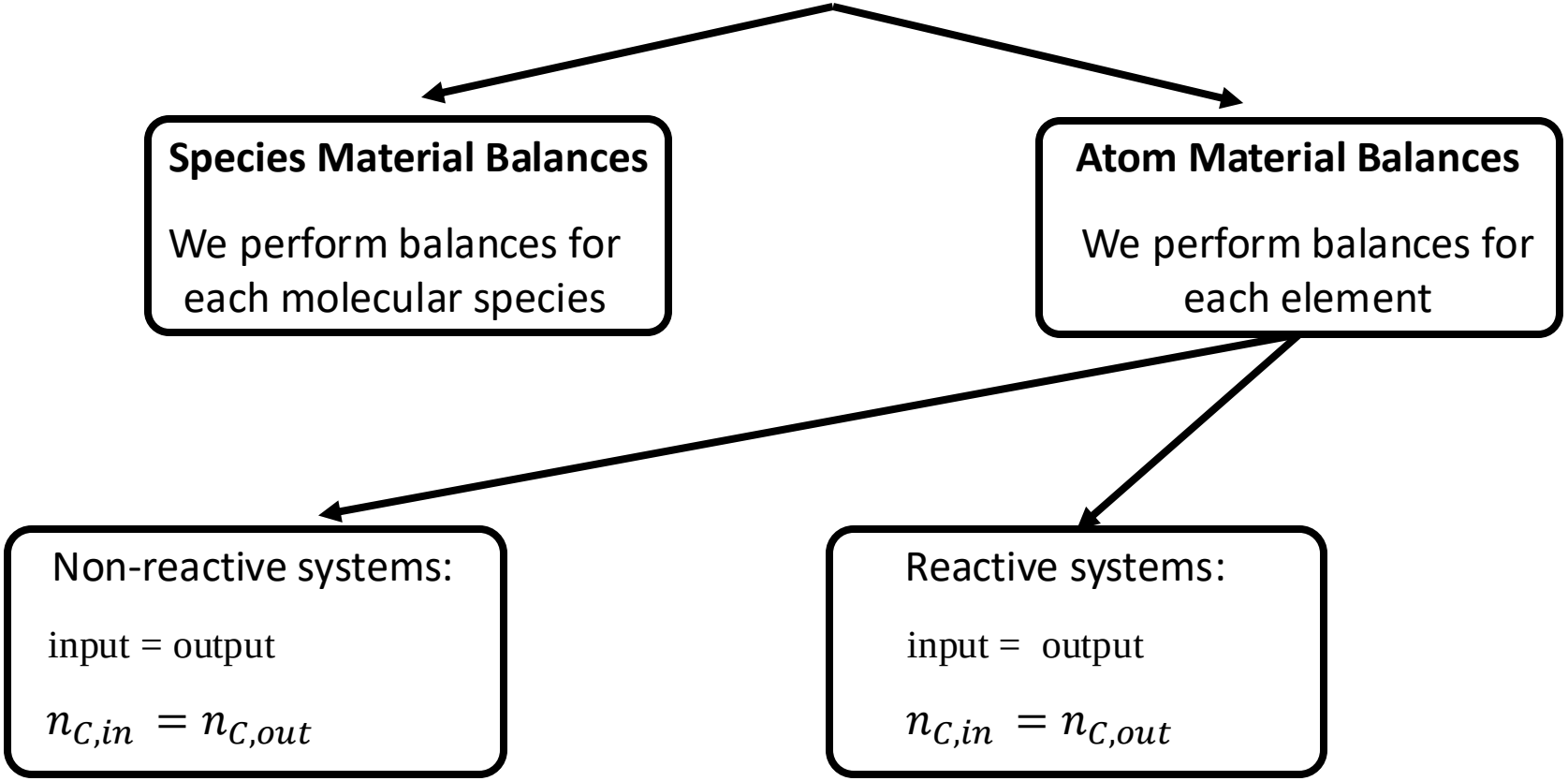

- No consideration of the extent of reaction with atom balance
- However, do not forget to multiply by the stoichiometric coefficient, e.g, in 1 mole of CH4, there is 1 mole of Carbon BUT 4 moles of Hydrogen!

Material Balances: Considerations on Reactive Systems

Multiple reactions → multiple extents of reactions (species material balance)

$$\left.\begin{array}{ll} R_1: 2\,CO_2 \rightarrow 2\,CO + O_2 & \longrightarrow \xi_1 \\ R_2: O_2 + N_2 \rightarrow 2NO & \longrightarrow \xi_2 \end{array}\right\} \quad n_i = n_{i0} + \sum_j \nu_{ij}\xi_j$$

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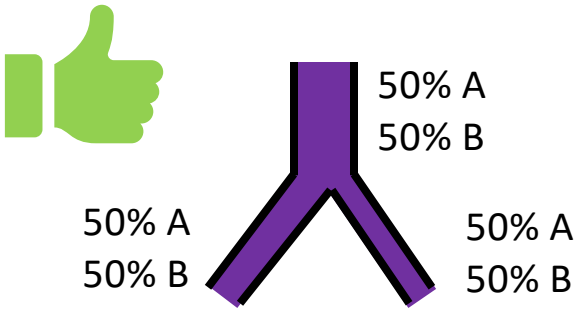
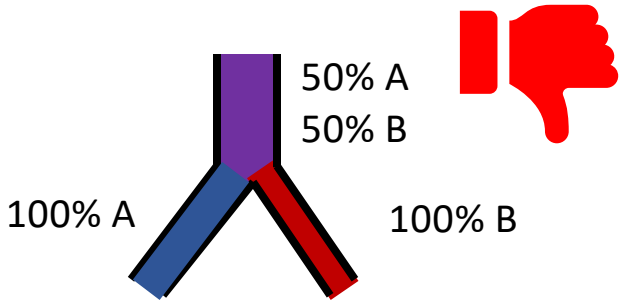
In **reactive systems, moles of species are not conserved** (look at reaction 1, we start with a total of 2 moles (CO2) and ends up with a total of 3 moles (2 moles CO and 1 mole O2). HOWEVER, the moles of elements are conserved → if we use the molecular species balance method**, do not forget to convert the moles to mass when solving your material balances!**

Material Balances: General Considerations

At a splitting point, the composition of the stream is maintained (unless mentioned otherwise)





Material Balances: Limiting and Excess Reactants

Limiting reactant in reactive process = reactant that would be **completely consumed if the reaction proceeded to completion**.

All other reactants must either be fed in (1) stoichiometric proportion to the limiting reactant (the feed rates are in the ratio of the stoichiometric coefficients) or (2) in excess of the limiting reactant (in greater than stoichiometric proportion to it).

$$\%\ excess = \frac{amount\ fed\ - amount\ theoretically\ required}{amount\ theoretically\ requied}$$

Material Balances: Procedure for Calculations

1. Choose **as basis of calculation** an amount or flow rate of one of the process streams
    1. Basis can already be given in the problem
    2. If no stream amount or flow rate is specified, take as a basis an arbitrary amount or flow rate of a stream with known composition
2. **Draw a flowchart** and fill in all known variable values, including the basis of calculation, then label the unknown stream variables on the chart
3. Express what the **problem statement asks you** to determine in terms of the labeled variables
4. If you are given mixed mass and mole units for a stream**, convert all quantities to one basis or the other**.
5. OPTIONNAL: Perform a degree-of-freedom analysis
6. OPTIONNAL: If the number of unknowns equals the number of equations relating them, write the equation in an efficient order (minimizing simultaneous equations), and circle the variables for which you will solve
7. **Solve the equations**
8. **Calculate the quantities requested in the problem statement** if they have not already been calculated
9. OPTIONNAL: Scale if you chose a different basis than the one initially suggested.

Energy Balances

Energy Balances: overview

Again, with the mother of all equations:

$$E_{accumulated} = E_{input} - E_{output} + E_{gen} + E_{transferred}$$

Where $E_{transferred} = Q - W$

Conventions:

- $Q > 0$ when heat is transferred **from the surrounding to the system**
- $W > 0$ when work is **done by the system on the surroundings** *

* The opposite convention is sometimes used. The choice is arbitrary, **if it is used consistently**

Energy Balances: overview

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$$E_{accumulated} = E_{input} - E_{output} + E_{gen} + E_{transferred}$$

Closed

$$\Delta U + \Delta E_k + \Delta E_p = Q - W$$

- Δ : final – initial

Open

$$\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} - \dot{W}_s$$

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Non-reactive

Reactive $(\dot{\Delta H} = ?)$

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Energy Balances: considerations for non-reactive system

Reference state

Arbitrarily designate a reference state for substance at which $\widehat{U}$ or $\widehat{H}$ is declared to equal zero.

Tabulate $\widehat{U}$ or $\widehat{H}$ for the substance relative to the reference state

Energy Balances: Hypothetical Process Paths

In the systems we study, there are internal energy and **enthalpy changes associated with key processes**. We are specifically interested in the following:

- Changes in P at constant T and state of aggregation
- Changes in T at constant P and state of aggregation
- Phase changes at constant T and P
- Mixing of 2 liquids or dissolving of a gas or a solid in a liquid at constant T and P
- Chemical reaction at constant T and P

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- Chemical reaction at constant T and P

The ones you are expected to know

* For the processes and species seen in this class, we can neglect the enthalpy changes associated with changes in P(ressure).

** Enthalpy changes due to mixing were briefly covered in the last lecture. These will not be subject to examination

Changes in T at constant P and state of aggregation

There are 2 ways to calculate the enthalpy change associated to a change of temperature from T1 (initial temperature) to T2 (final temperature).

Let's take an example: 15 kmol/min of air is cooled from 430 C to 100C. Calculate the required heat removal rate.

Changes in T at constant P and state of aggregation

There are 2 ways to calculate the enthalpy change associated to a change of temperature from T1 (initial temperature) to T2 (final temperature).

Let's take an example: 15 kmol/min of air is cooled from 430 C to 100C. Calculate the required heat removal rate.

Most common (harder) way: Integrate the heat capacity formula from table B2

$$\Delta\hat{H}\,(\mathrm{kJ/mol}) = \int_{430^\circ C}^{100^\circ C} C_p(T)\,dT$$

$$C_p(T) = 0.02894 + (0.4147 \times 10^{-5})T + (0.3191 \times 10^{-8})T^2 - (1.965 \times 10^{-12})T^3$$

The integral expands to:

$$\Delta\hat{H} = \left[0.02894(T) + \frac{0.4147 \times 10^{-5}}{2}(T^2) + \frac{0.3191 \times 10^{-8}}{3}(T^3) - \frac{1.965 \times 10^{-12}}{4}(T^4)\right]_{430^\circ C}^{100^\circ C}$$

Plugging in the limits of integration ($T = 100^\circ C$ and $T = 430^\circ C$):

$$\Delta\hat{H} = \left[0.02894(100 - 430) + \frac{0.4147 \times 10^{-5}}{2}(100^2 - 430^2) + \frac{0.3191 \times 10^{-8}}{3}(100^3 - 430^3) - \frac{1.965 \times 10^{-12}}{4}(100^4 - 430^4)\right]$$

This evaluates to:

$$\Delta\hat{H} = (-9.5502 - 0.3627 - 0.0835 + 0.0167)\,\mathrm{kJ/mol} = -9.98\,\mathrm{kJ/mol}.$$

Changes in T at constant P and state of aggregation

There are 2 ways to calculate the enthalpy change associated to a change of temperature from T1 (initial temperature) to T2 (final temperature).

Let's take an example: 15 kmol/min of air is cooled from 430 C to 100C. Calculate the required heat removal rate.

Easy way (not always possible): Use tabulated enthalpies (with linear interpolation)

Initial

$$\widehat{H}(400\ C) = 11.24\frac{kJ}{mol}$$

$$\widehat{H}(430\ C) = 11.24 + 0.3\ (14.37\ - 11.24) = 12.17$$

$$\widehat{H}(500\ C) = 14.37\frac{kJ}{mol}$$

Final

$$\widehat{H}(100\ C) = 2.19\frac{kJ}{mol}$$

$$\Delta\widehat{H} = \widehat{H_{final}} - \widehat{H_{initial}} = 2.19\ - 12.17 = -9.98\frac{kJ}{mol}$$

Table B.8 Specific Enthalpies of Selected Gases: SI Units

$\hat{H}$(kJ/mol)
Reference state: Gas, P_{ref} = 1 atm, T_{ref} = 25°C

T	Air	O_2	N_2	H_2	CO	CO_2	H_2O
0	−0.72	−0.73	−0.73	−0.72	−0.73	−0.92	−0.84
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	2.19	2.24	2.19	2.16	2.19	2.90	2.54
200	5.15	5.31	5.13	5.06	5.16	7.08	6.01
300	8.17	8.47	8.12	7.96	8.17	11.58	9.57
400	11.24	11.72	11.15	10.89	11.25	16.35	13.23
500	14.37	15.03	14.24	13.83	14.38	21.34	17.01
600	17.55	18.41	17.39	16.81	17.57	26.53	20.91
700	20.80	21.86	20.59	19.81	20.82	31.88	24.92
800	24.10	25.35	23.86	22.85	24.13	37.36	29.05
900	27.46	28.89	27.19	25.93	27.49	42.94	33.32
1000	30.86	32.47	30.56	29.04	30.91	48.60	37.69
1100	34.31	36.07	33.99	32.19	34.37	54.33	42.18
1200	37.81	39.70	37.46	35.39	37.87	60.14	46.78
1300	41.34	43.38	40.97	38.62	41.40	65.98	51.47
1400	44.89	47.07	44.51	41.90	44.95	71.89	56.25
1500	48.45	50.77	48.06	45.22	48.51	77.84	61.09

Note on interpolating from tabulated values

$$H(T) = H(T_1) + \frac{(T - T_1)}{(T_2 - T_1)} \times [H(T_2) - H(T_1)]$$

Where:

- $H(T)$ is the enthalpy at the desired temperature T,
- T_1 and T_2 are the temperatures between which the interpolation is performed,
- $H(T_1)$ and $H(T_2)$ are the enthalpy values at T_1 and T_2, respectively.

For the example

- $T = 430°C$,
- $T_1 = 400°C$,
- $T_2 = 500°C$,
- $H(T_1) = 11.24\,\text{kJ/mol}$,
- $H(T_2) = 14.37\,\text{kJ/mol}$.

$$H(430°C) = 11.24 + \frac{(430 - 400)}{(500 - 400)} \times (14.37 - 11.24)$$

$$H(430°C) = 11.24 + 0.30 \times 3.13$$

$$H(430°C) = 11.24 + 0.939 = 12.17\,\text{kJ/mol}.$$

Phase changes at constant T and P

Latent Heat:
The specific enthalpy change ($\Delta\hat{H}$) during a phase transition (e.g., melting, vaporization) at constant temperature and pressure is called the **latent heat**. It is distinct from **sensible heat**, which involves temperature changes without a phase change (that we have just seen).

Heat of Vaporization (from liquid to gas):
- For water at 100°C and 1 atm, the latent heat of vaporization is 40.6 kJ/mol.
- The **heat of condensation** is the negative of the heat of vaporization (-40.6 kJ/mol) because condensation is the reverse process of vaporization.

Heat of Fusion (from solid to liquid):
The **heat of fusion** (or melting) is the enthalpy difference between the solid and liquid forms of a substance at a given T and P.
Similarly, the **heat of solidification** is the negative of the heat of fusion.

Tabulated Values:
Standard heats of fusion and vaporization are typically provided at the melting or boiling points of a substance at 1 atm. **These values can be found in Table B1 (more on this later)**

Energy Balances: overview

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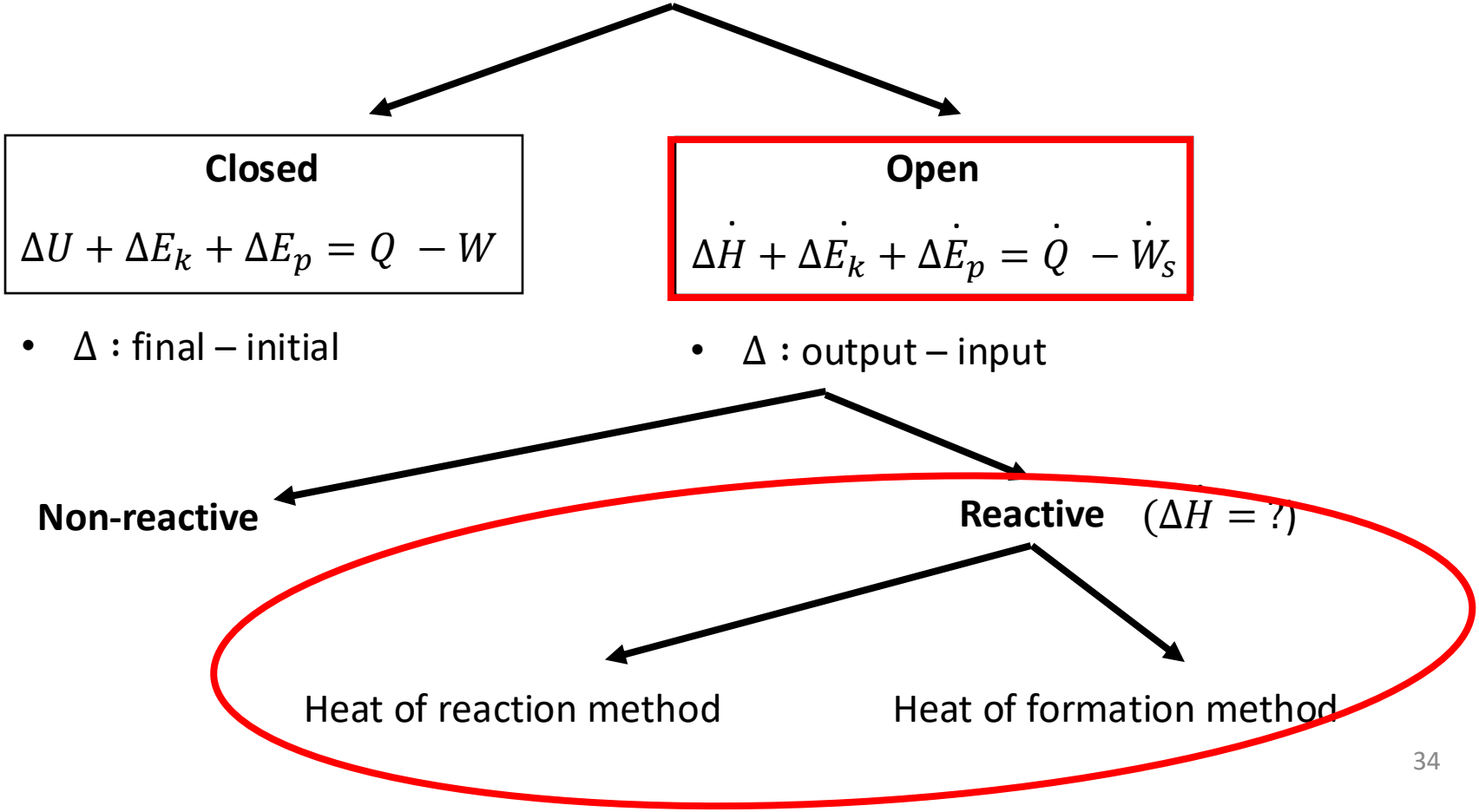

Energy Balances: Heat of Formation vs Heat of Reaction

Reactive $(\Delta\dot{H} = ?)$

Heat of reaction method

$$\Delta\dot{H} = \dot{\xi}\Delta H_r{}^0 + \sum_{out} \dot{n}_i\widehat{H_i} - \sum_{in} \dot{n}_i\widehat{H_i}$$

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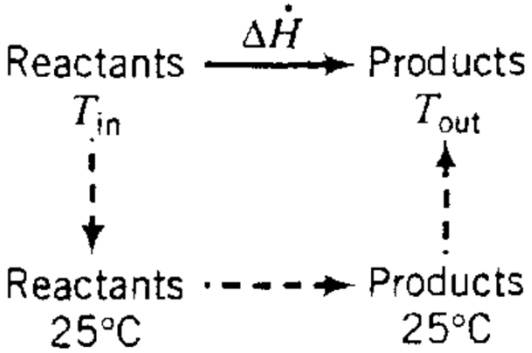
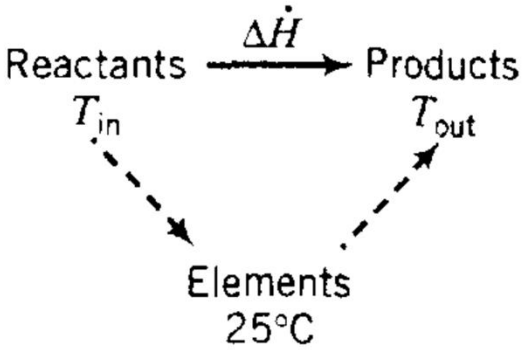


(*a*) Process path for heat of reaction method

Reference states: reactants and products species at 25 C at 1 atm in the phases (solid, liquid or gas) for which the heat of reaction is known

Heat of formation method

$$\Delta\dot{H} = \sum_{out} n_i\widehat{H_i} - \sum_{in} n_i\widehat{H_i}$$



(*b*) Process path for heat of formation method

Reference states: elemental species that constitute the reactants and products at 25 C at 1 atm

In both methods, reference states for nonreactive species may be chosen for convenience

Energy Balances: Heat of Formation vs Heat of Reaction

Reactive $(\Delta\dot{H} = ?)$

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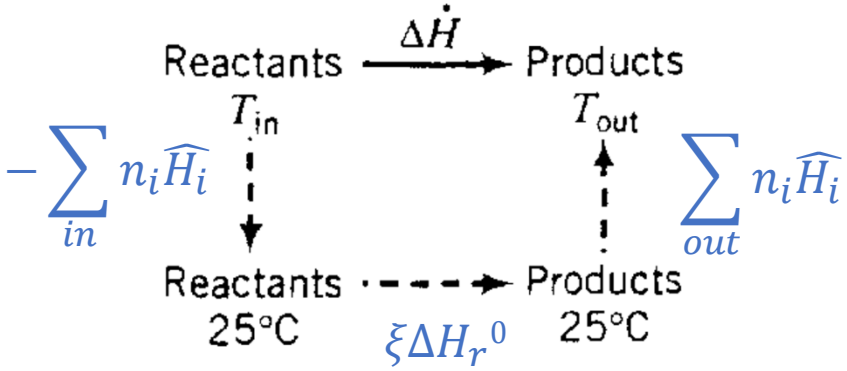

Heat of formation method

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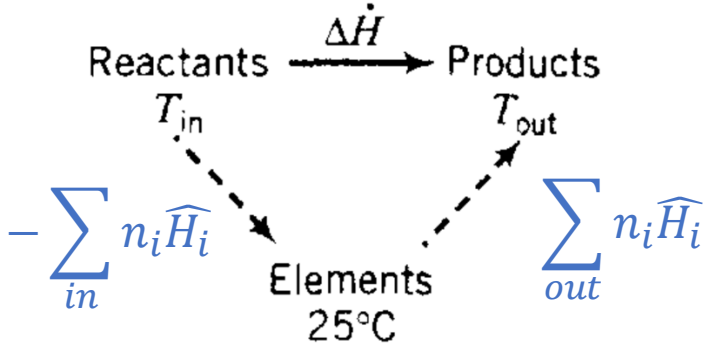

Hess's Law

$$\Delta\hat{H}_r^\circ = \sum_i \nu_i\Delta\hat{H}_{fi}^\circ = \sum_{\text{products}} |\nu_i|\Delta\hat{H}_{fi}^\circ - \sum_{\text{reactants}} |\nu_i|\Delta\hat{H}_{fi}^\circ$$

Know Thy Tables

Appendix B

Physical Property Tables

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B.1 Selected Physical Property Data

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[b]	$\Delta\hat{H}_m(T_m)$[c,j] kJ/mol	T_b(°C)[d]	$\Delta\hat{H}_v(T_b)$[e,j] kJ/mol	T_c(K)[f]	P_c(atm)[g]	$(\Delta\hat{H}_f°)$[h,j] kJ/mol	$(\Delta\hat{H}_c°)$[i,j] kJ/mol
Acetaldehyde	CH_3CHO	44.05	0.783[18°]	−123.7	—	20.2	25.1	461.0	—	−166.2(g)	−1192.4(g)
Acetic acid	CH_3COOH	60.05	1.049	16.6	12.09	118.2	24.39	594.8	57.1	−486.18(l)	−871.69(l)
										−438.15(g)	−919.73(g)
Acetone	C_3H_6O	58.08	0.791	−95.0	5.69	56.0	30.2	508.0	47.0	−248.2(l)	−1785.7(l)
										−216.7(g)	−1821.4(g)
Acetylene	C_2H_2	26.04	—	—	—	−81.5	17.6	309.5	61.6	+226.75(g)	−1299.6(g)
Ammonia	NH_3	17.03	—	−77.8	5.653	−33.43	23.351	405.5	111.3	−67.20(l)	
										−46.19(g)	−382.58(g)

(latent) heat of fusion/melting H_m : specific enthalpy from solid to liquid stage = - latent heat of solidification

(latent) heat of vaporization H_v: specific enthalpy change from liquid to gaseous stage = - latent heat of condensation

[b] Melting point at 1 atm.
[c] Heat of fusion at T_m and 1 atm.
[d] Boiling point at 1 atm.
[e] Heat of vaporization at T_b and 1 atm.
[f] Critical temperature.
[g] Critical pressure.
[h] Heat of formation at 25°C and 1 atm.
[i] Heat of combustion at 25°C and 1 atm. Standard states of products are CO_2(g), H_2O(l), SO_2(g), HCl(aq), and N_2(g). To calculate $\Delta\hat{H}_c°$ with H_2O(g) as a product, $44.01n_w$ to the tabulated value, where n_w = moles H_2O formed/mole fuel burned.

Know Thy Tables

B.2 Heat Capacities

Table B.2 Heat Capacities[a]

Form 1: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^2 + dT^3$
Form 2: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^{-2}$

Example: $(C_p)_{\text{acetone(g)}} = 0.07196 + (20.10 \times 10^{-5})T - (12.78 \times 10^{-8})T^2 + (34.76 \times 10^{-12})T^3$, where T is in °C.

Note: The formulas for gases are strictly applicable at pressures low enough for the ideal gas equation of state to apply.

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Acetone	CH_3COCH_3	58.08	l	1	°C	123.0	18.6			−30–60
			g	1	°C	71.96	20.10	−12.78	34.76	0–1200
Acetylene	C_2H_2	26.04	g	1	°C	42.43	6.053	−5.033	18.20	0–1200
Air		29.0	g	1	°C	28.94	0.4147	0.3191	−1.965	0–1500
			g	1	K	28.09	0.1965	0.4799	−1.965	273–1800
Ammonia	NH_3	17.03	g	1	°C	35.15	2.954	0.4421	−6.686	0–1200
Ammonium sulfate	$(NH_4)_2SO_4$	132.15	c	1	K	215.9				275–328
Benzene	C_6H_6	78.11	l	1	°C	126.5	23.4			6–67
			g	1	°C	74.06	32.95	−25.20	77.57	0–1200
Isobutane	C_4H_{10}	58.12	g	1	°C	89.46	30.13	−18.91	49.87	0–1200
n-Butane	C_4H_{10}	58.12	g	1	°C	92.30	27.88	−15.47	34.98	0–1200
Isobutene	C_4H_8	56.10	g	1	°C	82.88	25.64	−17.27	50.50	0–1200
Calcium carbide	CaC_2	64.10	c	2	K	68.62	1.19	-8.66×10^{10}	—	298–720
Calcium carbonate	$CaCO_3$	100.09	c	2	K	82.34	4.975	-12.87×10^{10}	—	273–1033
Calcium hydroxide	$Ca(OH)_2$	74.10	c	1	K	89.5				276–373
Calcium oxide	CaO	56.08	c	2	K	41.84	2.03	-4.52×10^{10}		273–1173
Carbon	C	12.01	c	2	K	11.18	1.095	-4.891×10^{10}		273–1373

Know Thy Tables

Some specific enthalpies are already computed for you → Gain of time during the exam!

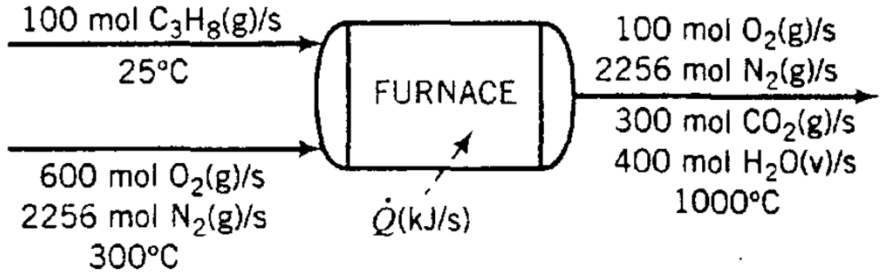
Table B.8 Specific Enthalpies of Selected Gases: SI Units

$\hat{H}$(kJ/mol)
Reference state: Gas, P_{ref} = 1 atm, T_{ref} = 25°C

T	Air	O_2	N_2	H_2	CO	CO_2	H_2O
0	−0.72	−0.73	−0.73	−0.72	−0.73	−0.92	−0.84
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	2.19	2.24	2.19	2.16	2.19	2.90	2.54
200	5.15	5.31	5.13	5.06	5.16	7.08	6.01
300	8.17	8.47	8.12	7.96	8.17	11.58	9.57
400	11.24	11.72	11.15	10.89	11.25	16.35	13.23
500	14.37	15.03	14.24	13.83	14.38	21.34	17.01
600	17.55	18.41	17.39	16.81	17.57	26.53	20.91
700	20.80	21.86	20.59	19.81	20.82	31.88	24.92
800	24.10	25.35	23.86	22.85	24.13	37.36	29.05
900	27.46	28.89	27.19	25.93	27.49	42.94	33.32
1000	30.86	32.47	30.56	29.04	30.91	48.60	37.69
1100	34.31	36.07	33.99	32.19	34.37	54.33	42.18
1200	37.81	39.70	37.46	35.39	37.87	60.14	46.78
1300	41.34	43.38	40.97	38.62	41.40	65.98	51.47
1400	44.89	47.07	44.51	41.90	44.95	71.89	56.25
1500	48.45	50.77	48.06	45.22	48.51	77.84	61.09

Energy Balances: Heat of Formation vs Heat of Reaction

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l): \quad \Delta\hat{H}_r^\circ = -2220\ \text{kJ/mol}$$



$$\dot{\xi} = \frac{|(\dot{n}_{C_3H_8})_{out} - (\dot{n}_{C_3H_8})_{in}|}{|\nu_{C_3H_8}|}$$

$$= \frac{|0 - 100|\ \text{mol/s}}{1} = 100\ \text{mol/s}$$

Heat of reaction method

References: $C_3H_8(g)$, $O_2(g)$, $N_2(g)$, $CO_2(g)$, $H_2O(l)$ at 25°C and 1 atm

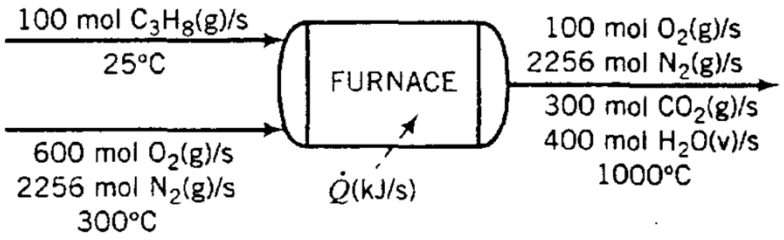
Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C_3H_8	100	0	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

Heat of formation method

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	100	$\hat{H}_1$	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

Energy Balances: Heat of Formation vs Heat of Reaction



$$\Delta\hat{H}_r^\circ = -2220 \text{ kJ/mol} \quad \dot{\xi} = 100 \text{ mol/s}$$

Know your tables!

Heat of reaction method

References: $C_3H_8(g)$, $O_2(g)$, $N_2(g)$, $CO_2(g)$, $H_2O(l)$ 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	100	0	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

$\hat{H}_2 = \Delta\hat{H}$ for $O_2(25°C) \rightarrow O_2(300°C) = 8.47$ kJ/mol (from Table B.8)

$\hat{H}_3 = 8.12$ kJ/mol

$\hat{H}_4 = 32.47$ kJ/mol

$\hat{H}_6 = 48.60$ kJ/mol

$\hat{H}_7 = \Delta\hat{H}$ for $H_2O(l, 25°C) \rightarrow H_2O(g, 1000°C)$

$$\int_{25°C}^{100°C} C_{pl}\,dT + \Delta\hat{H}_v(100°C) + \int_{100°C}^{1000°C} C_{pv}\,dT.$$

Table B.1 (Continued)

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[b]	$\Delta\hat{H}_m(T_m)$[c,j] kJ/mol	T_b(°C)[d]	$\Delta\hat{H}_v(T_b)$[e,j] kJ/mol	T_c(K)[f]	P_c(atm)[g]	$(\Delta\hat{H}_f^\circ)$[h,j] kJ/mol	$(\Delta\hat{H}_c^\circ)$[i,j] kJ/mol
Sodium thiosulfate	$Na_2S_2O_3$	158.11	1.667	—	—	—	—	—	—	−1117.1(c)	—
Sulfur (rhombic)	S_8	256.53	2.07	113	10.04	444.6	83.7	—	—	0(c)	—
Sulfur (monoclinic)	S_8	256.53	1.96	119	14.17	444.6	83.7	—	—	+0.30(c)	—
Sulfur dioxide	SO_2	64.07	—	−75.48	7.402	−10.02	24.91	430.7	77.8	−296.90(g)	—
Sulfur trioxide	SO_3	80.07	—	16.84	25.48	43.3	41.80	491.4	83.8	−395.18(g)	—
Sulfuric acid	H_2SO_4	98.08	1.834[18°]	10.35	9.87	Decomposes at 340°C		—	—	−811.32(l)	—
										−907.51(aq)	—
Toluene	C_7H_8	92.13	0.866	−94.99	6.619	110.62	33.47	593.9	40.3	+12.00(l)	−3909.9(l)
										+50.00(g)	−3947.9(g)
Water	H_2O	18.016	1.00[4°]	0.00	6.0095	100.00	40.656	647.4	218.3	−285.84(l)	—
										−241.83(g)	—
m-Xylene	C_8H_{10}	106.16	0.864	−47.87	11.569	139.10	36.40	619	34.6	−25.42(l)	−4551.9(l)
										+17.24(g)	−4594.5(g)
o-Xylene	C_8H_{10}	106.16	0.880	−25.18	13.598	144.42	36.82	631.5	35.7	−24.44(l)	−4552.9(l)
										+18.99(g)	−4596.3(g)
p-Xylene	C_8H_{10}	106.16	0.861	13.26	17.11	138.35	36.07	618	33.9	−24.43(l)	−4552.91(l)
										17.95(g)	−4595.2(g)
Zinc	Zn	65.38	7.140	419.5	6.674	907	114.77	—	—	0(c)	—

2 different Cps for 2 different phases

Table B.2 Heat Capacities[a]

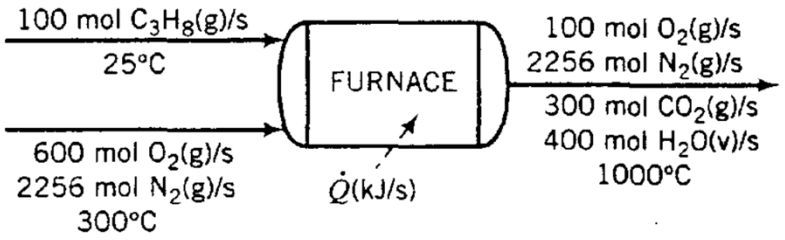
Form 1: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^2 + dT^3$
Form 2: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^{-2}$

Example: $(C_p)_{acetone(g)} = 0.07196 + (20.10 \times 10^{-5})T - (12.78 \times 10^{-8})T^2 + (34.76 \times 10^{-12})T^3$, where T is in °C.

Note: The formulas for gases are strictly applicable at pressures low enough for the ideal gas equation of state to apply.

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Water	H_2O	18.016	l	1	°C	75.4				0–100
			g	1	°C	33.46	0.6880	0.7604	−3.593	0–1500

Energy Balances: Heat of Formation vs Heat of Reaction



$$\Delta\hat{H}_r^\circ = -2220 \text{ kJ/mol} \quad \dot{\xi} = 100 \text{ mol/s}$$

Heat of reaction method

Know your tables!

References: $C_3H_8(g)$, $O_2(g)$, $N_2(g)$, $CO_2(g)$, $H_2O(l)$ 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	100	0	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

Table B.1 (Continued)

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[b]	$\Delta\hat{H}_m(T_m)$[c,j] kJ/mol	T_b(°C)[d]	$\Delta\hat{H}_v(T_b)$[e,j] kJ/mol	T_c(K)[f]	P_c(atm)[g]	$(\Delta\hat{H}_f^\circ)$[h,j] kJ/mol	$(\Delta\hat{H}_c^\circ)$[i,j] kJ/mol
Sodium thiosulfate	$Na_2S_2O_3$	158.11	1.667	—	—	—	—	—	—	−1117.1(c)	—
Sulfur (rhombic)	S_8	256.53	2.07	113	10.04	444.6	83.7	—	—	0(c)	—
Sulfur (monoclinic)	S_8	256.53	1.96	119	14.17	444.6	83.7	—	—	+0.30(c)	—
Sulfur dioxide	SO_2	64.07	—	−75.48	7.402	−10.02	24.91	430.7	77.8	−296.90(g)	—
Sulfur trioxide	SO_3	80.07	—	16.84	25.48	43.3	41.80	491.4	83.8	−395.18(g)	—
Sulfuric acid	H_2SO_4	98.08	1.834[18°]	10.35	9.87	Decomposes at 340°C		—	—	−811.32(l)	—
										−907.51(aq)	—
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										+50.00(g)	−3947.9(g)
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										−241.83(g)	—
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										+18.99(g)	−4596.3(g)
p-Xylene	C_8H_{10}	106.16	0.861	13.26	17.11	138.35	36.07	618	33.9	−24.43(l)	−4552.91(l)
										17.95(g)	−4595.2(g)
Zinc	Zn	65.38	7.140	419.5	6.674	907	114.77	—	—	0(c)	—

$\hat{H}_2 = \Delta\hat{H}$ for $O_2(25°C) \rightarrow O_2(300°C) = 8.47$ kJ/mol (from Table B.8)

$\hat{H}_3 = 8.12$ kJ/mol

$\hat{H}_4 = 32.47$ kJ/mol

$\hat{H}_6 = 48.60$ kJ/mol

$\hat{H}_7 = \Delta\hat{H}$ for $H_2O(l, 25°C) \rightarrow H_2O(g, 1000°C)$

$$\Delta\dot{H} = \dot{\xi}\,\Delta\hat{H}_r^\circ + \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in} = -1.26 \times 10^5 \text{ kJ/s}$$

2 different Cps for 2 different phases

Table B.2 Heat Capacities[a]

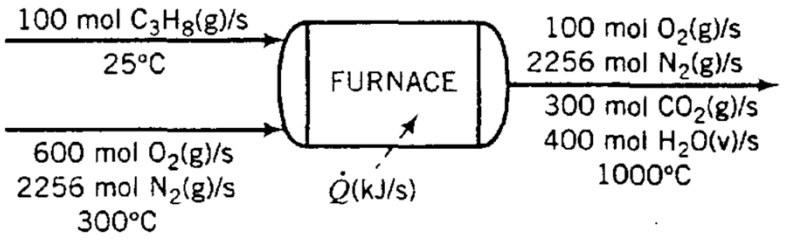
Form 1: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^2 + dT^3$
Form 2: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^{-2}$

Example: $(C_p)_{acetone(g)} = 0.07196 + (20.10 \times 10^{-5})T - (12.78 \times 10^{-8})T^2 + (34.76 \times 10^{-12})T^3$, where T is in °C.

Note: The formulas for gases are strictly applicable at pressures low enough for the ideal gas equation of state to apply.

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Water	H_2O	18.016	l	1	°C	75.4				0–100
			g	1	°C	33.46	0.6880	0.7604	−3.593	0–1500

Energy Balances: Heat of Formation vs Heat of Reaction



$$\Delta\hat{H}_r^\circ = -2220 \text{ kJ/mol} \quad \dot{\xi} = 100 \text{ mol/s}$$

Heat of reaction method

References: C_3H_8(g), O_2(g), N_2(g), CO_2(g), H_2O(l) 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	100	0	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

$\hat{H}_2 = \Delta\hat{H}$ for O_2(25°C) → O_2(300°C) = 8.47 kJ/mol (from Table B.8)

$\hat{H}_3 = 8.12$ kJ/mol

$\hat{H}_4 = 32.47$ kJ/mol

$\hat{H}_6 = 48.60$ kJ/mol

$\hat{H}_7 = \Delta\hat{H}$ for H_2O(l, 25°C) → H_2O(g, 1000°C)

$$\Delta\dot{H} = \dot{\xi}\,\Delta\hat{H}_r^\circ + \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in} = -1.26 \times 10^5 \text{ kJ/s}.$$

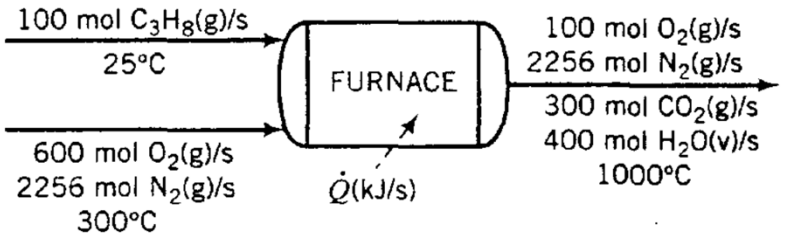
Heat of formation method

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	100	$\hat{H}_1$	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

For a reactant or product, start with the elemental species at 25°C and 1 atm (the references) and form 1 mol of the process species at 25°C and 1 atm at **gaseous stage** (from Table B.1). Then bring the species from 25°C and 1 atm to its process state, calculating using the appropriate heat capacities from Tables

Energy Balances: Heat of Formation vs Heat of Reaction



$$\Delta\hat{H}_r^\circ = -2220 \text{ kJ/mol} \quad \dot{\xi} = 100 \text{ mol/s}$$

Heat of formation method

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	100	$\hat{H}_1$	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

3 C(s)(25°C, 1 atm) + 4 H_2(g)(25°C, 1 atm) → C_3H_8(g)(25°C, 1 atm)

$$\Downarrow$$

$$\hat{H}_1 = (\Delta\hat{H}_f^\circ)_{C_3H_8(g)} = -103.8 \text{ kJ/mol (from Table B.1)}$$

This is the enthalpy of propane at 25°C (the process state) relative to C(s) and H2(g) at 25°C (the reference states). If the propane had entered at a temperature T_0 other than 25°C, a term of the form $\int_{25^\circ C}^{T0} C_p dT$ would be added to the heat of formation of propane.

Next, we calculate the specific enthalpy of O_2 at 300°C (the process state) relative to O_2 at 25°C (the reference state) as:

$$\hat{H}_2 = 8.47\,\text{kJ/mol (from Table B.8)}.$$

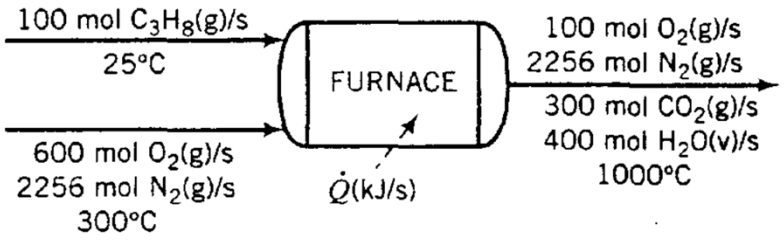
There is no heat of formation term since O_2 is an elemental species. We proceed in the same manner to calculate:

$\hat{H}_3 = 8.12\,\text{kJ/mol}$, $\hat{H}_4 = 32.47\,\text{kJ/mol}$, $\hat{H}_5 = 30.56\,\text{kJ/mol}$,

$\hat{H}_6 = -344.9\,\text{kJ/mol}$, and $\hat{H}_7 = -204.1\,\text{kJ/mol}$.

To calculate $\hat{H}_6$ and $\hat{H}_7$, we form the corresponding species ($CO_2(g)$ and $H_2O(v)$) at 25°C from their elements ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$), then heat them from 25°C to 1000°C ($\Delta\hat{H} = \hat{H}_{1000^\circ C}$ from Table B.8), and add the formation and heating terms.

Energy Balances: Heat of Formation vs Heat of Reaction



Next, we calculate the specific enthalpy of O_2 at 300°C (the process state) relative to O_2 at
(the reference state) as:

$$\hat{H}_2 = 8.47\,\text{kJ/mol (from Table B.8)}.$$

There is no heat of formation term since O_2 is an elemental species. We proceed in the sam
manner to calculate:

$\hat{H}_3 = 8.12\,\text{kJ/mol}$, $\hat{H}_4 = 32.47\,\text{kJ/mol}$, $\hat{H}_5 = 30.56\,\text{kJ/mol}$,

$\hat{H}_6 = -344.9\,\text{kJ/mol}$, and $\hat{H}_7 = -204.1\,\text{kJ/mol}$.

To calculate $\hat{H}_6$ and $\hat{H}_7$, we form the corresponding species ($CO_2(g)$ and $H_2O(v)$) at 25°C
from their elements ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$), then heat them from 25°C to 1000°C ($\Delta\hat{H} = \hat{H}_{1000^\circ C}$ f
Table B.8), and add the formation and heating terms.

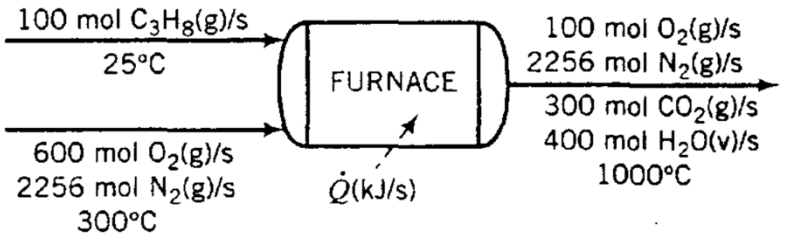
Table B.8 Specific Enthalpies of Selected Gases: SI Units

$\hat{H}$(kJ/mol)
Reference state: Gas, P_{ref} = 1 atm, T_{ref} = 25°C

T	Air	O_2	N_2	H_2	CO	CO_2	H_2O
0	−0.72	−0.73	−0.73	−0.72	−0.73	−0.92	−0.84
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	2.19	2.24	2.19	2.16	2.19	2.90	2.54
200	5.15	5.31	5.13	5.06	5.16	7.08	6.01
300	8.17	8.47	8.12	7.96	8.17	11.58	9.57
400	11.24	11.72	11.15	10.89	11.25	16.35	13.23
500	14.37	15.03	14.24	13.83	14.38	21.34	17.01
600	17.55	18.41	17.39	16.81	17.57	26.53	20.91
700	20.80	21.86	20.59	19.81	20.82	31.88	24.92
800	24.10	25.35	23.86	22.85	24.13	37.36	29.05
900	27.46	28.89	27.19	25.93	27.49	42.94	33.32
1000	30.86	32.47	30.56	29.04	30.91	48.60	37.69
1100	34.31	36.07	33.99	32.19	34.37	54.33	42.18
1200	37.81	39.70	37.46	35.39	37.87	60.14	46.78
1300	41.34	43.38	40.97	38.62	41.40	65.98	51.47
1400	44.89	47.07	44.51	41.90	44.95	71.89	56.25
1500	48.45	50.77	48.06	45.22	48.51	77.84	61.09

Water	H_2O	18.016	1.00[4°]	0.00	6.0095	100.00	40.656	647.4	218.3	−285.84(l) −241.83(g)	— —

Energy Balances: Heat of Formation vs Heat of Reaction



$$\Delta\hat{H}_r^\circ = -2220 \text{ kJ/mol} \quad \dot{\xi} = 100 \text{ mol/s}$$

Heat of reaction method

References: $C_3H_8(g)$, $O_2(g)$, $N_2(g)$, $CO_2(g)$, $H_2O(l)$ 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	100	0	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

$$\hat{H}_2 = 8.47 \text{ kJ/mol} \quad \hat{H}_5 = 30.56 \text{ kJ/mol}$$
$$\hat{H}_3 = 8.12 \text{ kJ/mol} \quad \hat{H}_6 = 48.60 \text{ kJ/mol}$$
$$\hat{H}_4 = 32.47 \text{ kJ/mol} \quad \hat{H}_7 = 81.71 \text{ kJ/mol}$$

$$\Delta H = \xi \Delta H_r{}^0 + \sum_{out} n_i \widehat{H_i} - \sum_{in} n_i \widehat{H_i} = -1.26 \times 10^5 \frac{kJ}{s}$$

Heat of formation method

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	100	$\hat{H}_1$	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

$$\hat{H}_1 = -103.8 \text{ kJ/mol} \quad \hat{H}_5 = 30.56 \text{ kJ/mol}$$
$$\hat{H}_2 = 8.47 \text{ kJ/mol} \quad \hat{H}_6 = -344.9 \text{ kJ/mol}$$
$$\hat{H}_3 = 8.12 \text{ kJ/mol} \quad \hat{H}_7 = -204.1 \text{ kJ/mol}$$
$$\hat{H}_4 = 32.47 \text{ kJ/mol}$$

$$\Delta H = \sum_{out} n_i \widehat{H_i} - \sum_{in} n_i \widehat{H_i} = -1.26 \times 10^5 \frac{kJ}{s}$$

Energy Balances: Procedure for Calculations

1. Perform all required material balances calculations (as much as possible)
2. Write the appropriate form of the energy balance (closed or open systems) and delete any of the terms that are either zero or negligible for the given process system
3. Choose a reference state (phase, temperature and pressure) for each species involved in the process
    1. If H or U for a species will be looked up in a table (such as the steam tables for water) choose the reference state used to generate the table
    2. Otherwise, choose one of the inlet or outlet steates as the reference states for the species (so that at least one H or U may be set equal to zero)
4. Construct a table with columns for number of species and specific enthalpies/internal energies) relative to the chosen reference states
5. Calculate all the required values
6. Use the final energy balance formula to find the desired quantities

Reminders

The Midterm grade (M) **only benefits** your Overall grade (O)

- Two cases, depending on your final exam grade (F):
  1. M > F: O = M*0.3 + F*0.7
  2. M < F: O = F

No electronic devices, except for calculators

- Print physical property tables

Plan for Q&A session before exam → **Class Reps?**

If more questions/clarifications needed, still Q&A session!