
MOLE BALANCES

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Learning Outcomes

- Set up and solve time-dependent mole and energy balances for releasing gases or liquids.
- Calculate source terms for dispersion modeling, including evaporation rates from liquid pools.
- Estimate concentration profiles in a workspace over time to assess flammability or toxicity risks.

Reading

- Foundations of Spiritual and Physical Safety: with Chemical Processes; Chapter VI.3 through VI.3.1 (Mass and Energy Balance Review)

Mass (mole) and energy balance problems are fundamental to chemical engineering. It takes practice to understand how to set up and solve these problems. These problems are part of multiple courses in chemical engineering, and they are also part of the Fundamentals of Engineering (FE) exam and proficiency exams given by chemical engineering departments. This course is the 2nd or 3rd time reviewing these principles. Example exam results demonstrating that more practice is needed are shown below.

1 Mass and Energy Balances

Helpful sheet: [General Mass and Balance Equations](#)

2 Why?: Concentration Estimates for Assessing Risk

Prior to implementing control techniques, it can be important to quantify the risk of exposure from a spill scenario of other toxic gas/ vapor release.

2.1 Total Mole (Mass) and Component Mole Balances

Given a control volume and:

- A release of toxic gas or vapor at a constant rate

Winter 2024

	Correct	Incorrect
Points	9	0
Percent of all students who selected option	29%	71%
Percent of high-scoring students (Q4) who selected option	86%	14%
Percent of low-scoring students (Q1) who selected option	0%	100%
Mean test score of students who selected option	96.01	81.13

Winter 2025

	Correct	Incorrect
Points	9	0
Percent of all students who selected option	38%	62%
Percent of high-scoring students (Q4) who selected option	94%	6%
Percent of low-scoring students (Q1) who selected option	11%	89%
Mean test score of students who selected option	79.55	71.66

Figure 1: Mass Balance Example Exam Results

- Addition of air at a constant rate
- Exit of the gasses based on the inlet conditions and assuming that the exit rate can be achieved without pressurization of the control volume
- Steady state conditions

Total molar balance:

$$\text{Rate of accumulation} = \text{Rate of inlet} - \text{Rate of exit} + \text{Generation rate} \quad (1)$$

$$\frac{dn_{tot}}{dt} = n_{in} - n_{out} + n_{gen} \quad (2)$$

Component balances:

$$\frac{dn_i}{dt} = n_{in,i} - n_{out,i} + n_{gen,i} \quad (3)$$

At steady state, the accumulation terms ($\frac{dn_{tot}}{dt}$ and $\frac{dn_i}{dt}$) are zero.

Other assumptions/ notation:

- concentration of interest, $C_i = n_i/V$,
- the exit rate of the total gases is Q_v^n , mol//time,
- the inlet rate of the composition of interest is Q^e , mol//time,
- $C_{ppm} = C_i RT/P \cdot 10^6$, where C_{ppm} is the concentration in parts per million (ppm), R is the ideal gas constant, T is the temperature, and P is the pressure.
- $n_{gen,i} = 0$, for the case of a spill or release of a toxic gas or vapor (new species are not generated).
- Perfect mixing of the gases in the control volume (no concentration gradients).

As such, the mole balance for the component of interest i is

$$0 = Q^e - C_i Q_v^n RT / P \quad (4)$$

$$C_i = \frac{Q^e}{Q_v^n RT / P} \quad (5)$$

If however, there are concentration gradients, the concentration could deviate significantly from the above estimate (larger or smaller).

2.2 Inlet composition from vaporization of a liquid

The inlet rate of the species of interest, Q^e , can be estimated from the vapor pressure of the liquid and the rate of vaporization and a mass transfer coefficient according to:

$$Q^e = k_m A (C_{sat} - C) \quad (6)$$

where k_m is the mass transfer coefficient, C_{sat} is the saturation concentration of the species close to the liquid surface, and C is the concentration of the species in the air, and A is the area of the spill.

k_m can be estimated from correlations or from experimental data or by comparison to another component with a known mass transfer coefficient (e.g. water, k_m^0):

$$k_m = k_m^0 \left(\frac{M}{M_0} \right)^{0.33} \quad (7)$$

where M is the molecular weight of the species of interest and M_0 is the molecular weight of water. k_m^0 is typically in the range of $0.1 - 10.0 \text{ cm/s}$ depending on the conditions.

C_{sat} can be estimated from the Antoine equation:

$$\log_{10} P_{sat} = A - \frac{B}{T + C} \quad (8)$$

where P_{sat} is the saturation pressure of the species of interest, and A , B , and C are constants that can be found in the literature. Where $C_{sat} = P_{sat}/RT$.

Incorporating those into the mole balance, we have:

$$0 = k_m A (C_{sat} - C_i) - C_i Q_v^n RT / P \quad (9)$$

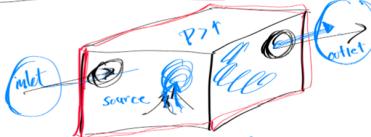
$$C_i = \frac{k_m A}{Q_v^n RT / P + k_m A} C_{sat} \quad (10)$$

How would you solve the above if you would like the unsteady state concentration as a function of time? And there by obtain the Time Weighted Average (TWA) for a worker directly after a spill?

See [here](#) to view a video on a mole (mass) balance for a spill scenario. This video can be helpful for the homework. You can download the sheet used in the video here: [physical/supportfiles/Balance.pdf](#)

Example 2: Leak inside room one species

$$\boxed{\begin{aligned} \text{total } & \stackrel{?}{=} \text{ accm} = \text{in-out} + \text{gen/loss} \\ \frac{d}{dt} & \\ \text{Species } & \stackrel{?}{=} \text{ accm}_i = \text{in}_i - \text{out}_i + \text{gen}_i \end{aligned}}$$



how do we calculate concentration of species City changing inside room?

Method: No leak ($C_{\text{CH}_4} = 0$)
 $t=0 \rightarrow$ scale starts (constant krate)

• Total balance (mol)

$$\frac{dn}{dt} = \dot{n}_{\text{CH}_4}^{\text{in}} + \dot{n}_{\text{air}}^{\text{in}} - \dot{n}_{\text{CH}_4}^{\text{out}} + \dot{n}_{\text{air}}^{\text{out}}$$

$n = \text{moles inside room}$

no generation inside room
flow rate in
flow rate out

• Molar mole balance

$$\frac{dn_{\text{CH}_4}}{dt} = \dot{n}_{\text{CH}_4}^{\text{in}} - y_m \cdot \dot{n}_{\text{out}}$$

$\dot{n}_{\text{CH}_4}^{\text{in}} = \text{moles inside room}$

fraction of CH₄ flowing out assuming perfect mixing
flow rate in

$$y_m = \frac{\text{moles of CH}_4}{\text{total moles } n} = \frac{n_{\text{CH}_4}}{n}$$

$$\frac{dn_{\text{CH}_4}}{dt} = \frac{d(n \cdot y_m)}{dt} = n \frac{dy_m}{dt} + y_m \frac{dn}{dt}$$

- Assuming that the room doesn't get pressurized from leak, $P = \text{constant}$
 thus, n is constant given T is constant
 so $\frac{dn}{dt} = 0$ given T, P, V are constant

Component (CH₄) balance

$$\frac{d(n \cdot y_m)}{dt} = n \frac{dy_m}{dt} + y_m \frac{dn}{dt} = \dot{n}_{\text{CH}_4}^{\text{in}} - y_m \dot{n}_{\text{out}} = \dot{n}_{\text{CH}_4}^{\text{in}} - y_m (\dot{n}_{\text{CH}_4}^{\text{out}} + \dot{n}_{\text{air}}^{\text{out}})$$

$$\begin{aligned} \frac{dy_m}{dt} &= \frac{1}{n} \cdot \dot{n}_{\text{CH}_4}^{\text{in}} - y_m \cdot \frac{(\dot{n}_{\text{CH}_4}^{\text{out}} + \dot{n}_{\text{air}}^{\text{out}})}{n} \\ \frac{dy_m}{dt} &= A - y_m B \quad A = \frac{\dot{n}_{\text{CH}_4}^{\text{in}}}{n} \quad B = \frac{(\dot{n}_{\text{CH}_4}^{\text{out}} + \dot{n}_{\text{air}}^{\text{out}})}{n} \end{aligned}$$

Analytical Solution

$$\int_0^t \frac{dy_m}{A - By_m} = \int_0^t dt$$

$$-\frac{1}{B} \ln(A - By_m) \Big|_0^t = t$$

$$-\frac{1}{B} \left[\ln(A - By_m) - \ln(A) \right] = t$$

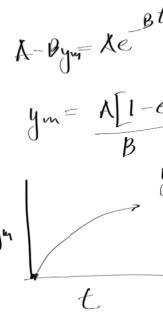
$$\ln \left[\frac{A - By_m}{A} \right] = Bt$$

$$\frac{A - By_m}{A} = e^{-Bt}$$

$$A - By_m = Ae^{-Bt}$$

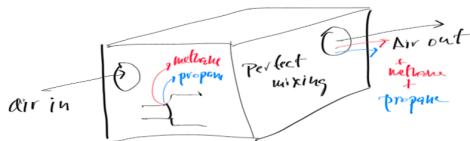
$$y_m = \frac{A[1 - e^{-Bt}]}{B}$$

$$y_m(t=0) = \frac{A}{B}$$

$$y_m(t=0) = 0$$


Could also solve numerically with Euler or ode int

Example 3: Leak inside room 2 species



Problem: how does the propane/methane concentration/mole fractions change with time?

$$\frac{dn}{dt} = \dot{n}_{in} - \dot{n}_{out}$$

control volume = room

Total mole balance:

$$\frac{dn}{dt} = \dot{n}_{in} + \dot{n}_{leak} - \dot{n}_{out}$$

total moles in control volume

Propane mole balance:

$$\frac{dn_p}{dt} = \dot{n}_{in} \cdot y_p^L - y_p^R \cdot \dot{n}_{out}$$

\rightarrow fraction of propane in perfectly mixed room
 \rightarrow fraction of propane in leaking gases

Methane mole balance:

$$\frac{dn_m}{dt} = \dot{n}_{in} \cdot y_m^L - y_m^R \cdot \dot{n}_{out}$$

\rightarrow fraction of methane in leaking gases

Assume constant pressure & constant temperature.

$$\text{So } \frac{dn}{dt} = 0$$

Also $y_m^L + y_p^L = 1$ (only mixture of propane)

$$y_m^R + y_p^R + y_{\text{air}}^R = 1 \quad (\text{air, propane, methane in room})$$

Methane Balance

$$\frac{dn_m}{dt} = \dot{n}_{\text{in}}^{\text{leak}} \cdot y_m^L - y_m^R \cdot (\dot{n}_{\text{in}}^{\text{leak}} + \dot{n}_{\text{in}}^{\text{air}})$$

$$\frac{dn_m}{dt} = \cancel{y_m^R} \frac{dn}{dt} + \cancel{n} \frac{dy_m^R}{dt} \quad (\text{product rule})$$

$$\textcircled{1} \quad \left(\frac{ndy_m^R}{dt} = \underbrace{\dot{n}_{\text{in}}^{\text{leak}} \cdot y_m^L}_{\substack{\text{these given in problem} \\ \text{n found from ideal gas}}} - \underbrace{y_m^R (\dot{n}_{\text{in}}^{\text{leak}} + \dot{n}_{\text{in}}^{\text{air}})}_{\substack{\text{V.T.P given usually} \\ \frac{PV}{RT}}}\right)$$

Propane Balance

$$\frac{dn_p}{dt} = \dot{n}_{\text{in}}^{\text{leak}} \cdot y_p^L - y_p^R \cdot (\dot{n}_{\text{in}}^{\text{leak}} + \dot{n}_{\text{in}}^{\text{air}})$$

$$\frac{dn_p}{dt} = \cancel{y_p^R} \frac{dn}{dt} + \cancel{n} \frac{dy_p^R}{dt} \quad (\text{product rule})$$

$$\textcircled{2} \quad \left(\frac{ndy_p^R}{dt} = \underbrace{\dot{n}_{\text{in}}^{\text{leak}} \cdot y_p^L}_{\substack{\text{usually given in problem statement}}} - \underbrace{y_p^R (\dot{n}_{\text{in}}^{\text{leak}} + \dot{n}_{\text{in}}^{\text{air}})}_{\substack{\text{V.T.P given usually}}} \right)$$

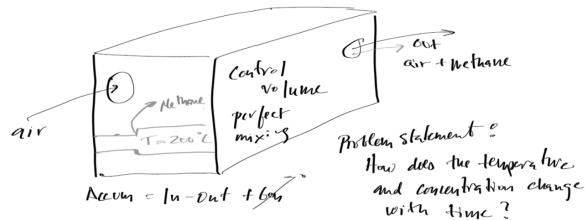
These two equations $\textcircled{1}$ & $\textcircled{2}$ above are independent so each could be solved independently.

They're independent as variables that change with time for methane aren't in the propane balance (some constants are present in both).

y_p^R & y_m^R can be solved analytically or numerically as a function of time given the initial conditions.

Example 4: Leak inside room 2 species with Temperature change

In this scenario, the pressure in the room is constant but flow of air and the temperature is changing.



Total mole balance:

$$(1) \frac{dn}{dt} = \dot{n}_{\text{air}}^{\text{in}} + \dot{n}_{\text{methane}}^{\text{in}} - \dot{n}^{\text{out}}$$

Methane balance

$$(2) \frac{dn_m}{dt} = \dot{n}_{\text{methane}}^{\text{in}} - \dot{y}_m \dot{n}^{\text{out}}$$

$\dot{y}_m = \frac{\dot{n}_{\text{methane}}^{\text{in}}}{\dot{n}_{\text{in}}} \xrightarrow{\text{layer with inner}}$

Energy balance:

$$\frac{d\bar{U}}{dt} = \dot{n}_{\text{air}}^{\text{in}} \bar{H}_{\text{air}} + \dot{n}_{\text{methane}}^{\text{in}} \bar{H}_{\text{methane}} - \dot{n}^{\text{out}} \bar{H}_{\text{standard temperature}}$$

For gases: $\bar{H} = \text{molar enthalpy} = \frac{C_p(T - T^\circ)}{C_v + C_p V}$

$$\bar{U} = \text{molar internal energy} = C_v(T - T^\circ)$$

We'll assume constant properties $C_v \neq f(t), C_p \neq f(t) \leftarrow$ usually not true

$$\frac{d\bar{U}}{dt} = \frac{d[\dot{n} C_v (T - T^\circ)]}{dt} = \dot{n} \frac{d[C_v (T - T^\circ)]}{dt} + C_v (T - T^\circ) \frac{dn}{dt} = \dot{n} C_v \frac{dT}{dt} + C_v (T - T^\circ) \frac{dn}{dt}$$

$\xrightarrow{\text{assumed constant}}$

3 Additional Mass Balance Examples

4 Mass and Energy Balance Example

#Mass and energy balance solution for Example 4

air flow into room at 20C, methane flow into room at 200C, air/methane mixture leaves the room
determine the fraction of methane and air temperature as a function of time

```
import numpy as np
import matplotlib.pyplot as plt
from scipy.integrate import odeint
```

Parameters

```
Cv_m = 27 # J/mol -K specific heat of methane, (estimate) assumed constant but is a function of temperature
Cv_air = 29 # J/mol -K specific heat of air, (estimated) assumed constant but is a function of temperature
# stream flow rates
n_in_air = 1 # mol/s air flow rate
n_in_m = 1/7 # mol/s methane flow rate
# stream temperatures
Pairin = 101425 # Pa, pressure of air stream entering the room
```

```

Tairin = 20 + 273.15 # K, temperature of air entering the room
Tmin = 200 + 273.15 # K, temperature of methane entering the room
#room parameters
orifice_diameter = 0.2 # m (outlet diameter)
Cd = 0.6 # discharge coefficient
Pext = 101325 # Pa, external pressure
P_initial = Pext # Pa, constant pressure
T_initial = 20 + 273.15 # K, initial temperature of room
n_initial = 1000 # total moles in room, can be found from the volume and initial temperature and pressure
nm_initial = 0 # initial moles of methane in room

Rg = 8.314 # J/mol -K
T0 = 20 + 273.15 # K, reference temperature
Pref = 101325 # Pa, constant pressure

Vol = n_initial * Rg* T_initial/P_initial # m^3, volume of room
print(f'Volume of room = {Vol} m^3')
print(f'Air flow rate into room = {nin_air*Rg*Tairin/Pairin} m3/s')
print(f'Air flow rate into room = {nin_air} mol/s')

def derivatives(p,t):
    # changing parameters
    n, nm, T = p
    ym = nm/n
    Cv = ym * Cv_m + (1 -ym) * Cv_air # J/mol -K, specific heat of the mixture
    Mw = ym * 0.016 + (1 -ym) * 0.029 # kg/mol, molecular weight of the mixture
    P = n*Rg*T/Vol # Pa, pressure in the room
    rho = P*Mw/Rg/T # kg/m^3, density of the mixture

    # flow rate out, assume flow out is incompressible
    nout = Cd * np.pi/4 * orifice_diameter**2 * np.sqrt(2*(P -Pext)*rho)/Mw # mol/s

    # Mass balance
    # first total mass balance
    dndt = nin_air + nin_m - nout
    # then component balance
    dnmdt = nin_m - nout * ym

    # Energy balance
    dTdt = 1/(n*Cv)*(- Cv*(T -T0)*dndt + nin_air*(Cv_air+Rg)*(Tairin -T0) + nin_m*(Cv_m+Rg)*(Tmin -T0))

    return [dndt, dnmdt, dTdt]

# time points
t = np.linspace(0,1000,1000) # seconds

# solve ODE
n0 = [n_initial, nm_initial, T_initial]
sol = odeint(derivatives, n0, t)

# plot results in a grid of subplots
fig, ax = plt.subplots(4, 1, figsize=(8, 6))
ax[0].plot(t, sol[:, 0], 'b', label='n')

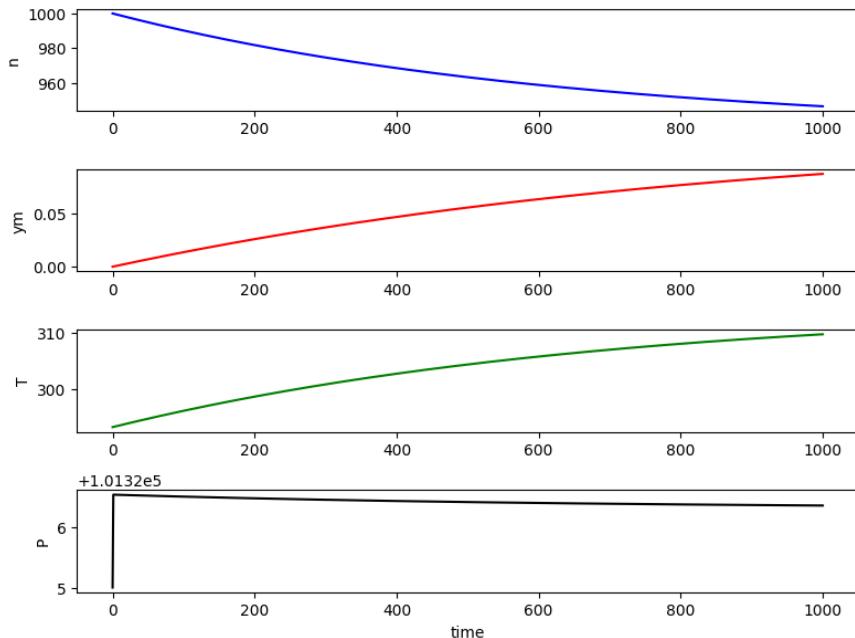
```

```

ax[0].set_ylabel('n')
ax[1].plot(t, sol[:, 1]/sol[:,0], 'r', label='ym')
ax[1].set_ylabel('ym')
ax[2].plot(t, sol[:, 2], 'g', label='T')
ax[2].set_ylabel('T')
ax[3].plot(t, sol[:, 0]*Rg*sol[:,2]/Vol, 'k', label='P')
ax[3].set_ylabel('P')
ax[3].set_xlabel('time')
fig.tight_layout(pad = 1.0)
plt.show()

```

Volume of room = 24.053778435726617 m³
Air flow rate into room = 0.024030062607838305 m³/s
Air flow rate into room = 1 mol/s



Action Items

- For each of the groupings of terms in Eq. VI.14([Guymon, 2025](#)), verify that the units are consistent. In other words, write out the units of each term and ensure that the units agree for each side of the equation.
- Derive Eq. VI.20([Guymon, 2025](#)) from the assumption and relationships given in the text. What is the steady-state fraction of benzene in the air?
- Write the mass balance equations for an H₂S leak into a pump house with passive ventilation and determine how many minutes it will take for the concentration to reach 100 ppm given an initial 10 ppm concentration. Solve the problem analytically.
- Solve Problem 3 numerically.
- Explain in words how the overall energy balance in Example 2([Guymon, 2025](#)), Page 171-172, simplifies down to Eq. VI.22.

References

C. Guymon. *Foundations of Spiritual and Physical Safety: with Chemical Processes*. 2025.