University Of Jordan

Faculty of Engineering and Technology

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Chemical Engineering Principles 2

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Balances on Nonreactive Processes

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Introduction

- For open system in which shaft work and kinetic and potential energy changes can be neglected

$$\dot{Q} = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i$$

where the $\hat{H}_i$'s are the specific enthalpies of the inlet and outlet stream components at their respective process conditions (temperatures, pressures, and states of aggregation) relative to those components at some reference conditions.

For an integral balance on a closed constant volume system ($W = 0$), n (amount) would replace $\dot{n}$ (flow rate) in this equation. U (internal energy) would replace $\dot{H}$ (rate of enthalpy transport) and $\hat{U}$ (specific internal energy) would replace $\hat{H}$ (specific enthalpy).

Short Review

- The value of $\Delta\hat{U}$ and $\Delta\hat{H}$ is known for specified changes of state, not as absolute value
- An arbitrarily **reference state for a species can be chosen** and then,

$$\Delta\hat{U} = \hat{U} - \hat{U}_{\text{ref}}$$

for the transition from the reference state to a series of other states

If $\hat{U}_{\text{ref}}$ equal to zero, then $\hat{U}(= \Delta\hat{U})$ for a specified state is the *specific internal energy at that state relative to the reference state.*

- The reference state for liquid water is at the triple point [H_2O(l, 0.01°C, 0.00611 bar)]
- For water vapor at 400°C and 10.0 bar, $\hat{U} = 2958$ kJ/kg.

This means that $\hat{U}$ of water vapor at 400°C and 10.0 bar is 2958 kJ/kg *relative to water at the reference state,*

$$H_2O(\text{l}, 0.01°\text{C}, 0.00611\ \text{bar}) \longrightarrow H_2O(\text{v}, 400°\text{C}, 10.0\ \text{bar}), \quad \Delta\hat{U} = 2958\ \text{kJ/kg}$$

Short Review

Relative to water at the same reference state, the specific enthalpy of water vapor at 400°C and 10.0 bar is

$$\hat{H} = \hat{U} + P\hat{V}$$

$$= 2958\ \text{kJ/kg} + \frac{10\ \text{bar}}{} \left| \frac{0.307\ \text{m}^3}{\text{kg}} \right| \frac{10^3\ \text{L}}{1\ \text{m}^3} \left| \frac{8.314 \times 10^{-3}\ \text{kJ/(mol·K)}}{0.08314\ \text{L·bar/(mol·K)}} \right.$$

$$= 3264\ \text{kJ/kg}$$

Hypothetical Process Paths

$\hat{V}$ $\hat{U}$ and $\hat{H}$ are **state properties** of a species:

- Their values depend only on the state of the species-primarily on its temperature and state of aggregation (solid, liquid, or gas) and,
- To a lesser extent, on its pressure and
- For mixtures of some species, on its mole fraction in the mixture).
- A state property does not depend on how the species reached its state. Consequently,
- When a species passes from one state to another, both $\Delta\hat{U}$ *and* $\Delta\hat{H}$ for the process are independent of the path taken from the first state to the second one.
- For a process, the change on internal energy or enthalpy depend on the initial and final state.

Hypothetical Process Paths

Type of processes

1. ***Changes in P at constant T and state of aggregation***

   Compressing hydrogen gas from 1 atm to 300 atm at 25°C

2. ***Changes in T at constant P and state of aggregation***

   Heating the liquid water at 0°C to 30°C, at 1 atm

3. ***Phase changes at constant T and P***—melting, solidifying, vaporizing, condensing, sublimating

   Melting ice at 0°C at 1 atm

4. ***Mixing of two liquids or dissolving of a gas or a solid in a liquid at constant T and P***

   Mixing sulfuric acid and water at a constant temperature of 20°C and a constant pressure of 1 atm

5. ***Chemical reaction at constant T and P***

Hypothetical Process Paths

- To calculate $\Delta\hat{U}$ and $\Delta\hat{H}$ for any process,
  - Construct a hypothetical process path from the initial state to the final state consisting of a series of steps of the given five types
  - Calculate $\Delta\hat{H}$ for each of the steps,
  - Added the $\Delta\hat{H}$'s for the steps to calculate $\Delta\hat{H}$ for the total process.

The same procedure can be followed to calculate $\Delta\hat{U}$ for any process.

Example

Calculate $\Delta\hat{H}$ for a process in which solid phenol at 25°C and 1 atm is converted to phenol vapor at 300°C and 3 atm.

Hypothetical Process Paths

Hypothetical Process Paths

the first, third, and fifth steps	change in T at constant P
the second and fourth steps	change in phase at constant T and P
the sixth step	change in P at constant T

$$\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2 + \Delta\hat{H}_3 + \Delta\hat{H}_4 + \Delta\hat{H}_5 + \Delta\hat{H}_6$$

Change in pressure at constant temperature

- It has been observed experimentally that internal energy is nearly independent of pressure for solids and liquids at a fixed temperature, as is specific volume.
- If the pressure of a solid or liquid changes at constant temperature,

$$\Delta\hat{U} \approx 0 \qquad \text{and} \qquad \Delta\hat{H}\ [= \Delta\hat{U} + \Delta(P\hat{V})] \approx \hat{V}\,\Delta P.$$

Change in pressure at constant temperature

Both $\hat{U}$ and $\hat{H}$ are independent of pressure for ideal gases.

➡ $\Delta\hat{U} \approx 0$ and $\Delta\hat{H} \approx 0$ *for a gas undergoing an isothermal pressure change unless gases at temperatures well below* 0°C *or well above 1 atm are involved.*

- If gases are far from ideal or if they undergo large pressure changes, you must either
  - Use tables of thermodynamic properties (such as the steam tables for water) or
  - Thermodynamic correlations. good source for such correlations is Chapter 5 of Reid, Prausnitz, and Poling

- H.W: Try to get such tables for some gases

Change temperature

Sensible Heat and Heat Capacities

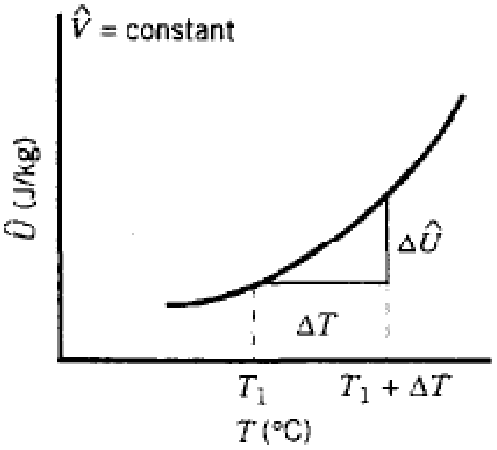
- **Sensible heat** it is the heat that must be transferred to raise or lower the temperature of a substance or mixture of substances.
- The quantity of heat required to produce a temperature change in a system can be determined from

$$Q = \Delta U \quad \text{(closed system)} \qquad\qquad \dot{Q} = \Delta\dot{H} \quad \text{(open system)}$$

- The specific internal energy of a substance depends strongly on temperature.

Sensible Heat and Heat Capacities

- If the temperature is raised or lowered in such a way that the system volume remains constant, the specific internal energy might vary as shown,



and $$C_v(T) = \left\{ \lim_{\Delta T \to 0} \frac{\Delta\hat{U}}{\Delta T} \right\} = \left(\frac{\partial\hat{U}}{\partial T} \right)_V$$

is the heat capacity at constant volume

Since the plot of $\hat{U}$ versus T is not generally a straight line, C_v (the slope of the curve) is a function of temperature.

The change in $\hat{U}$ for a temperature rise from T to $T + dT$ at constant volume is

$$d\hat{U} = C_v(T)\, dT$$

Sensible Heat and Heat Capacities

the change $\Delta\hat{U} = \hat{U}_2 - \hat{U}_1$ associated with a temperature change from T_1 to T_2 at constant volume is,

$$\Delta\hat{U} = \int_{T_1}^{T_2} C_v(T)\, dT$$

Ideal gas: exact

Solid or liquid: good approximation

Nonideal gas: valid only if V is constant

- If both the temperature and the volume of a substance change

break the process into two steps—a change in $\hat{V}$ at constant T followed by a change in T at constant $\hat{V}$.

$$\begin{tikzcd} A(T_1, \hat{V}_1) \arrow[r, "\Delta\hat{U}_1"] \arrow[d, dash] & A(T_1, \hat{V}_2) \arrow[r, "\Delta\hat{U}_2"] & A(T_2, \hat{V}_2) \\ {} \arrow[rr] & & {} \arrow[u] \end{tikzcd}$$

$$\Delta\hat{U} = \Delta\hat{U}_1 + \Delta\hat{U}_2$$

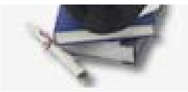
Example

Evaluation of an Internal Energy Change from Tabulated Heat Capacity

Calculate the heat required to raise 200 kg of nitrous oxide from 20°C to 150°C in a constant-volume vessel. The constant-volume heat capacity of N_2O in this temperature range is given by the equation

$$C_v\,(\text{kJ/kg}\cdot{}^\circ\text{C}) = 0.855 + 9.42 \times 10^{-4}T$$

where T is in °C.



Sensible Heat and Heat Capacities

- Similar to the internal energy, the enthalpy depends strongly on temperature.
- If substance is heated at constant pressure, then the **heat capacity at constant pressure**

$$C_p(T) = \left[\lim_{\Delta T \to 0} \frac{\Delta \hat{H}}{\Delta T}\right] = \left(\frac{\partial \hat{H}}{\partial T}\right)_P$$

$$\Rightarrow \quad d\hat{H} = C_p(T)\,dT$$

for a change from T_1 to T_2 at constant pressure

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT$$

For a process $A(T_1, P_1) \rightarrow A(T_2, P_2)$, we may construct a two-step process path

$$\begin{tikzcd} A(T_1, P_1) \arrow[r, "\Delta\hat{H}_1"] \arrow[rr, bend right, "\Delta\hat{H}"'] & A(T_1, P_2) \arrow[r, "\Delta\hat{H}_2"] & A(T_2, P_2) \end{tikzcd}$$

Sensible Heat and Heat Capacities

- For a change in pressure at constant temperature (step 1),

$$\Delta\hat{H}_1 = 0 \quad \text{(ideal gas)}$$

$$\Delta\hat{H}_1 \approx \hat{V}\,\Delta P \quad \text{(solid or liquid)}$$

- For a change in temperature at constant pressure (step 2),

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT$$

Ideal gas: exact
Nonideal gas: exact only if P is constant

$$\Delta\hat{H} = \hat{V}\,\Delta P + \int_{T_1}^{T_2} C_p(T)\,dT$$

Solid or liquid

Sensible Heat and Heat Capacities

- Generally, the heat capacity is a function of temperature,

$$C_p = a + bT + cT^2 + dT^3$$

The polynomial expressions for C_p in Table B.2 are based on experimental data

- For liquids and Solids $C_p \approx C_v$

- For ideal gas $C_p = C_v + R$ Try to prove it

where R is the gas constant.

Example ***Cooling of an Ideal Gas***

Assuming ideal gas behavior, calculate the heat that must be transferred in each of the following cases.

1. A stream of nitrogen flowing at a rate of 100 mol/min is heated from 20°C to 100°C.
2. Nitrogen contained in a 5-liter flask at an initial pressure of 3 bar is cooled from 90°C to 30°C.

Example Cont.

Example Cont.

Example

Evaluation of $\Delta\dot{H}$ Using Heat Capacities and Tabulated Enthalpies

Fifteen kmol/min of air is cooled from 430°C to 100°C. Calculate the required heat removal rate using (1) heat capacity formulas from Table B.2 and (2) specific enthalpies from Table B.8.

Example Cont.

Example Cont.

Estimation of Heat Capacities

- Several approximate methods follow for estimating heat capacities in the absence of tabulated formulas

Kopp's rule

- A simple empirical method for estimating the heat capacity of a solid or liquid at or near 20°C.
- C_p for a molecular compound is the sum of contributions for each element in the compound.

Estimation of Heat Capacities

Example

Find the heat capacity of solid calcium hydroxide, $Ca(OH)_2$

- For a mixture of gases or liquids,

$$(C_p)_{\text{mix}}(T) = \sum_{\substack{\text{all}\\ \text{mixture}\\ \text{components}}} y_i C_{pi}(T)$$

where

$(C_p)_{\text{mix}}$ = heat capacity of the mixture
y_i = mass or mole fraction of the ith component
C_{pi} = heat capacity of the ith component

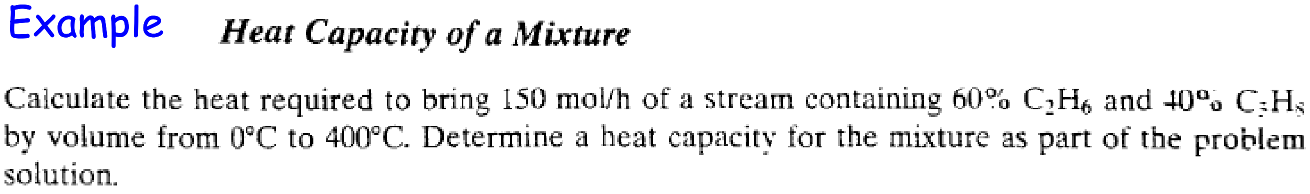
Estimation of Heat Capacities

- For highly dilute solutions of solids or gases in liquids, neglect the enthalpy change of the solute

$$\Delta\hat{H} = \int_{T_1}^{T_2} (C_p)_{\text{mix}}(T)\, dT$$

valid to the extent that enthalpies of mixing may be neglected

Example



Heat Capacity of a Mixture

Calculate the heat required to bring 150 mol/h of a stream containing 60% C_2H_6 and 40% C_3H_8 by volume from 0°C to 400°C. Determine a heat capacity for the mixture as part of the problem solution.

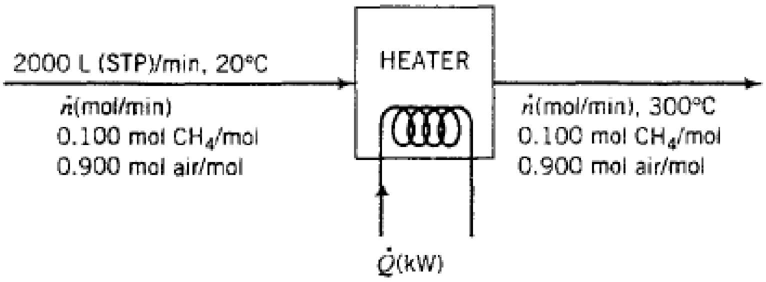
Estimation of Heat Capacities

Energy Balances on Single-Phase Systems

Example

Energy Balance on a Gas Preheater

A stream containing 10% CH_4 and 90% air by volume is to be heated from 20°C to 300°C. Calculate the required rate of heat input in kilowatts if the flow rate of the gas is 2.00×10^3 liters (STP)/min.



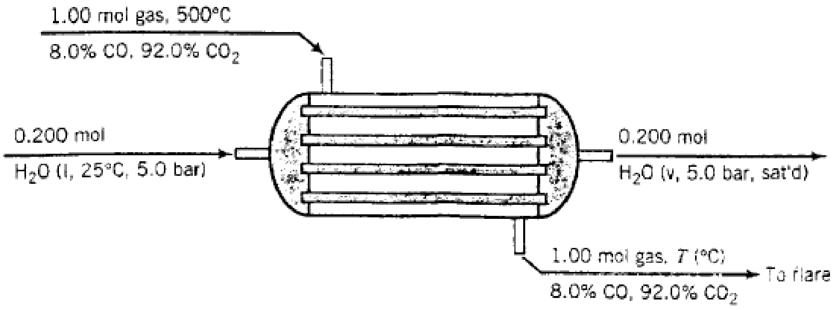
Example Cont.

Example Cont.

Example

Energy Balance on a Waste Heat Boiler

A gas stream containing 8.0 mole% CO and 92.0 mole% CO_2 at 500°C is fed to a **waste heat boiler,** a large metal shell containing a bundle of small-diameter tubes. The hot gas flows over the outside of the tubes. Liquid water at 25°C is fed to the boiler in a ratio 0.200 mol feedwater/mol hot gas and flows inside the tubes. Heat is transferred from the hot gas through the tube walls to the water, causing the gas to cool and the water to heat to its boiling point and evaporate to form saturated steam at 5.0 bar. The steam may be used for heating or power generation in the plant or as the feed to another process unit. The gas leaving the boiler is flared (burned) and discharged to the atmosphere. The boiler operates adiabatically—all the heat transferred from the gas goes into the water, as opposed to some of it leaking through the outside boiler wall. The flowchart for an assumed basis of 1.00 mol feed gas is shown below. What is the temperature of the exiting gas?



Example Cont.

Example Cont.

Example Cont.

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