(905212)Chemical Engineering Principles (2)

CHAPTER 8:
Balances on Nonreactive Processes

Naim M. Faqir

JU Chemical Engineering

Objective:

After completion of this chapter we should be able to do the following:

1. Understand
    - Sensible heat
    - $C_v(T)$: Heat capacity at constant volume
    - Cp(T): Heat capacity at constant pressure
    - Phase change operations (latent heats)
    - ΔH_m= Heat of fusion or heat of melting
    - ΔH_v= Heat of vaporization
    - Mixing and ΔH_s= Heat of solution

Objective:

2. Understand

- Dry-bulb temperature
- Wet-bulb temperature
- Humid volume of humid air
- Psychometric chart (dry-bulb and wet-bulb temperature, absolute and relative humidity, dew point, humid volume)

Objectives:

3. Reference and state properties

4. Calculate ΔU, ΔH for the following changes (using tabulated values of H, U, CP, ΔH_m, ΔH_v ΔH_s and specific gravities)

- Isothermal changes in pressure
- Isobaric changes in temperature
- Isothermal isobaric phase changes and
- Isothermal isobaric mixing of two of more species

~~ Finally Energy balance calculations ~~

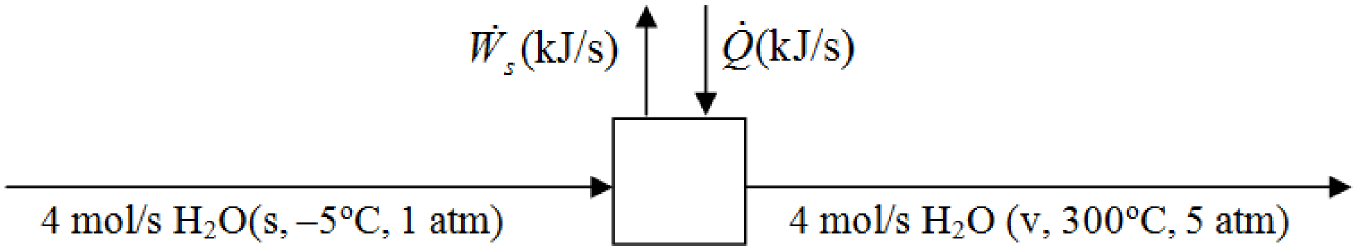
Reference States

- As we already learned that the absolute values of U and H for species at a given state we never be know.

- Fortunately, we never need to know the absolute values of U and H at specific states: we only need to know ΔU and ΔH for specific change of state, and we can determine these quantities experimentally.

- We may therefore arbitrarily choose a reference state for a species to determine ΔU= U-Uref. If we set Uref equal to zero, then U = (ΔU) for a specified state is the specific internal energy at the state relative to the reference state. Similarly, we can find H using H = U + PV formula.

Hypothetical process paths



$\dot{W}_s$(kJ/s)

$\dot{Q}$(kJ/s)

4 mol/s H_2O(s, –5°C, 1 atm)

4 mol/s H_2O (v, 300°C, 5 atm)

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

$\Delta\dot{E}_p = 0$ (Why? ______________________________)

Neglect $\Delta\dot{E}_k$ (Why? ______________________________)

$$\dot{Q} - \dot{W}_s \approx \Delta\dot{H} = \dot{n}_{out}\hat{H}_{out} - \dot{n}_{in}\hat{H}_{in} = 4\left(\frac{\text{mol}}{\text{s}}\right)\hat{H}_2\left(\frac{\text{kJ}}{\text{mol}}\right) - 4\hat{H}_1$$

$$\Downarrow$$

$$\dot{Q} - \dot{W}_s = 4\Delta\hat{H}$$

The problem is now to determine $\Delta\hat{H}$ for the given process.

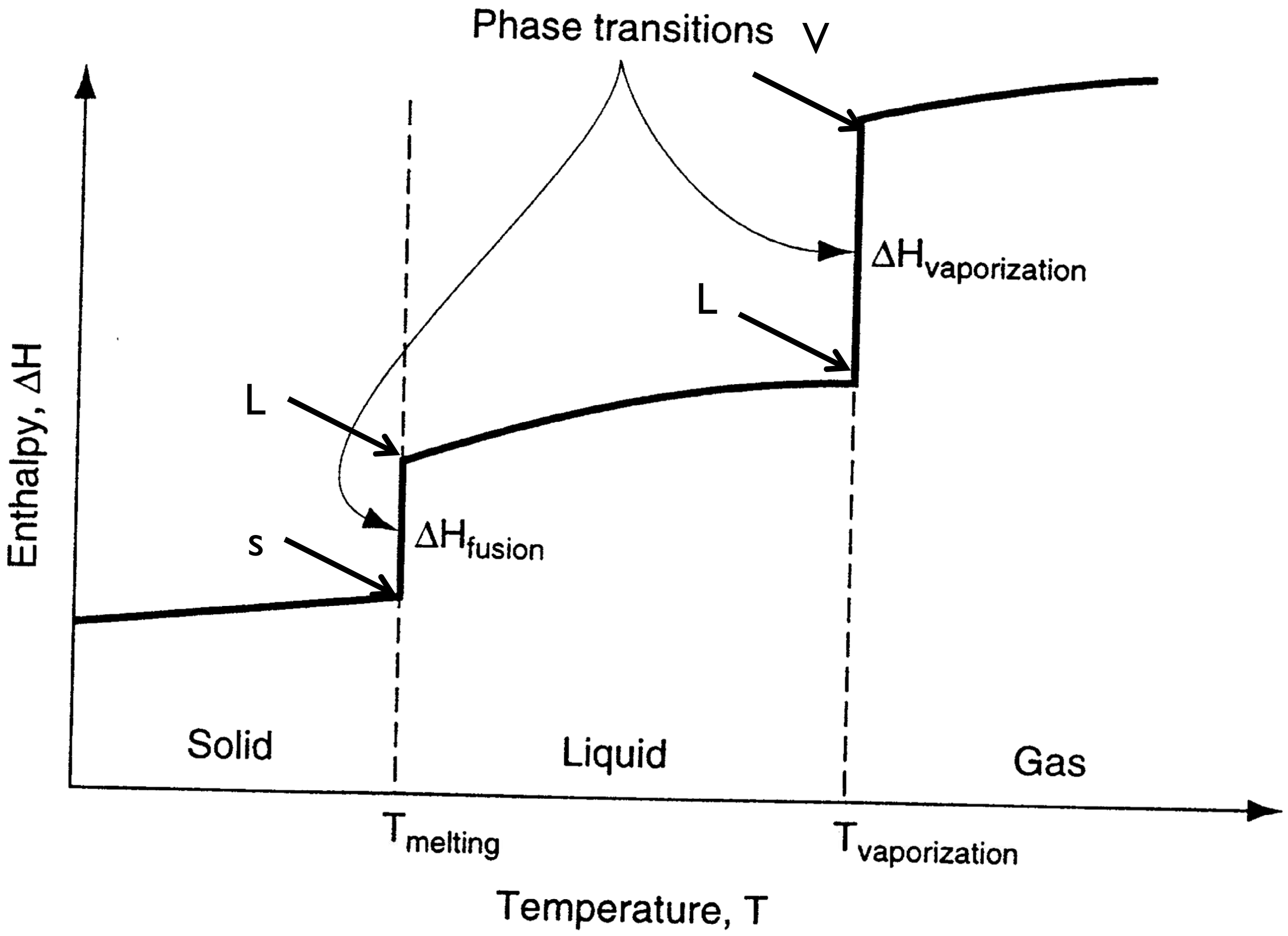
Can't use steam tables. (Why not? ____)

General procedure for calculating $\Delta\hat{H}$ for a specified change in state

- Construct a process path out of steps of 5 types:
  1. Change P at constant T and phase (Section 8.2 for calculation of ΔH and ΔU)
  2. Change T at constant P and phase (Section 8.3)
  3. Change phase at constant T,P (Section 8.4)
  4. Mix dissimilar liquid species (e.g. acid & water), absorb gas in liquid at constant T,P and phase (ΔH_{mix}) (Section 8.5)
  5. React at constant T,P (ΔH_{rxn}) (Chapter 9)
- Determine $\Delta\hat{H}$ for each step in the process path (formulas will be given for each of the 5 types)
- Calculate $(\Delta\hat{H})_{\substack{\text{overall}\\\text{process}}} = \sum_{\text{steps}} \Delta\hat{H}_i$ (follows since $\hat{H}$ is a state variable).
- Substitute in energy balance to calculate $\dot{Q} - \dot{W}_s$

- To calculate enthalpy changes, we need to construct a hypothetical pathway
  - Starting point: your defined reference state (T, P, phase)
  - End point: the conditions of the stream of interest (inlet or outlet)
- Since $\hat{U}$ and $\hat{H}$ are state properties (values are only dependent on the state of the species and not how they got there), any convenient process path from a reference state to a process state can be chosen

Enthalpy Versus Temperature for a Pure Component



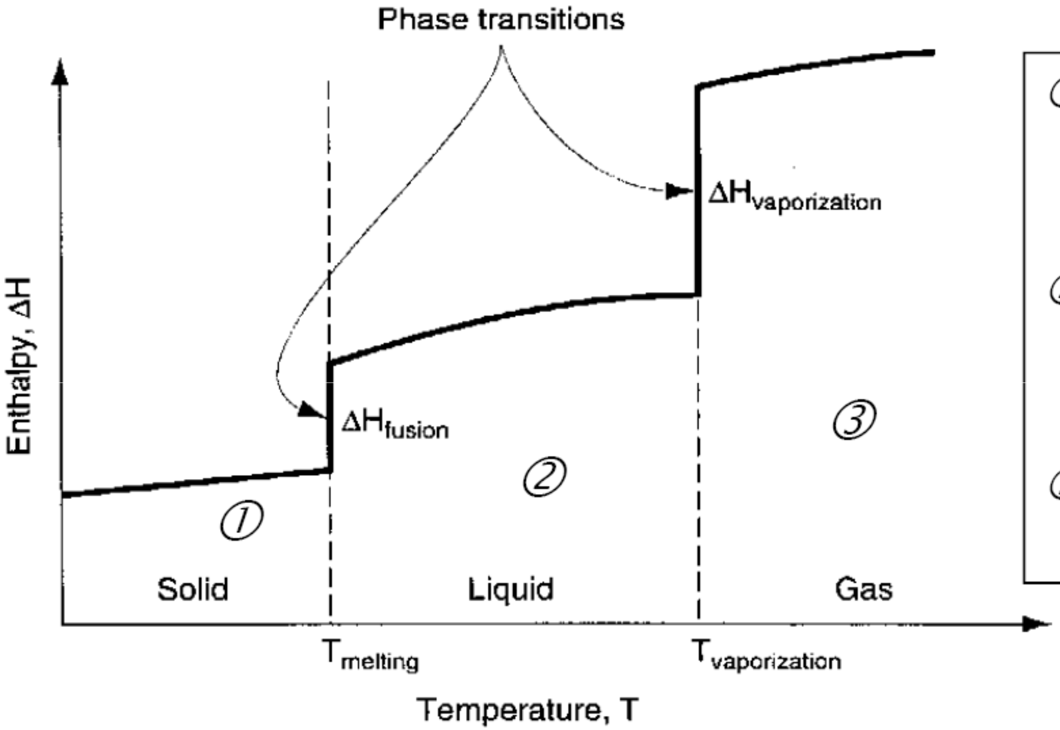
Calculating Enthalpy Changes

- The enthalpy changes associated with phase changes are called changes in **latent heat**.
- From the previous figure, it is clear that latent heat changes have a significant effect on the overall enthalpy change of a system.
- The heat of fusion indicates the heat required that must be remove from a liquid to freeze it or the heat added to a solid to melt it.
- The heat of vaporization is equal to the heat required to vaporize a liquid or the heat removed from a vapor to condense it.
- The heat of sublimation is the heat required to go from a solid directly to a vapor.

Calculating Enthalpy Changes for Sensible Heat Changes

- Enthalpy changes for a single phase involve temperature changes and are called changes in the **sensible heat.**
- The enthalpy for sensible heat changes can be determined by using
  - Enthalpy tables
  - Integrating heat capacities
  - Computer data bases

- **<u>Sensible Heat</u>** is heat that must be transferred to raise or lower T of a substance without change in phase



① Sensible heat of solid, $\Delta H\ (T_{initial} \leftrightarrow T_{melting})$

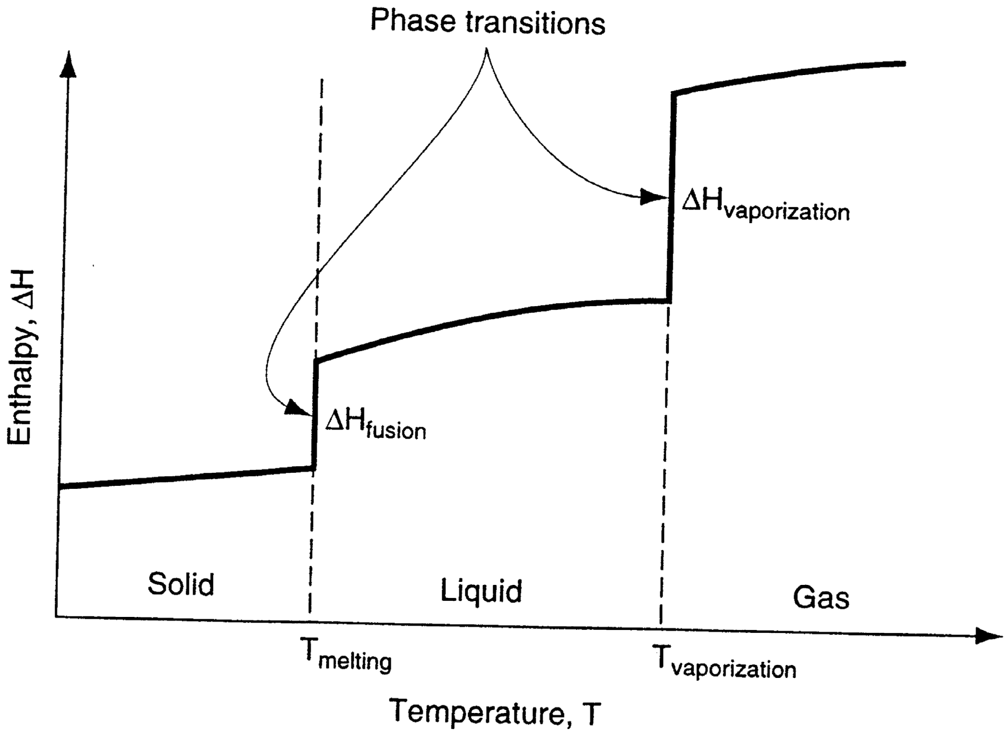
② Sensible heat of liquid, $\Delta H\ (T_{melting} \leftrightarrow T_{vapourization})$

③ Sensible heat of vapour, $\Delta H\ (T_{vapourization} \leftrightarrow T_{final})$

Reference States

Calculate the enthalpy change as 1 kg of ice at 0 °C is transformed to superheated steam at 400 °C and 3 atm.

$$\underset{0\ ^\circ\text{C},\ 1\ \text{atm}}{H_2O_{(s)}} \xrightarrow{\Delta\hat{H}=?} \underset{400\ ^\circ\text{C},\ 3\ \text{atm}}{H_2O_{(v)}}$$



First define a reference state: ice at 0 °C → $\Delta\hat{H}=\hat{H}_{\text{final}}-0$

$$\begin{tikzcd}
\boxed{\substack{H_2O_{(s)} \\ 0\ ^\circ\text{C},\ 1\ \text{atm}}} \arrow[r, "\Delta\hat{H}=?"] \arrow[d, "\Delta\hat{H}_1"] & \substack{H_2O_{(v)} \\ 400\ ^\circ\text{C},\ 3\ \text{atm}} \\
\substack{H_2O_{(l)} \\ 0\ ^\circ\text{C},\ 1\ \text{atm}} \arrow[d, "\Delta\hat{H}_2"] & \substack{H_2O_{(v)} \\ 400\ ^\circ\text{C},\ 1\ \text{atm}} \arrow[u, "\Delta\hat{H}_5"'] \\
\substack{H_2O_{(l)} \\ 100\ ^\circ\text{C},\ 1\ \text{atm}} \arrow[r, "\Delta\hat{H}_3"] & \substack{H_2O_{(v)} \\ 100\ ^\circ\text{C},\ 1\ \text{atm}} \arrow[u, "\Delta\hat{H}_4"']
\end{tikzcd}$$

$\Delta\hat{H}_1=\Delta\hat{H}_m$ at the normal freezing pt of H_2O (Table B.1)

$\Delta\hat{H}_5\approx 0$ (A reasonable assumption for small changes in P)

$$\Delta\hat{H}_2=\int_0^{100} C_p^{H_2O(l)}\,dT$$

(C_p expressions found in Table B.2)

$$\Delta\hat{H}_4=\int_{100}^{400} C_p^{H_2O(v)}\,dT$$

(C_p expressions found in Table B.2)

$\Delta\hat{H}_3=\Delta\hat{H}_v$ at the normal boiling pt of H_2O (Table B.1)

$$\Delta\hat{H}=\hat{H}_{\text{final}}-0=\Delta\hat{H}_1+\Delta\hat{H}_2+\Delta\hat{H}_3+\Delta\hat{H}_4+\Delta\hat{H}_5$$

Example

- The properties that do not depend on the how the species reached its state, i.e., the path chosen to reach a state from an initial state is immaterial.

Example:

(s, 25 °C, 1 atm) $\xrightarrow{\hspace{4cm}}$ C_6H_6OH **(v, 300 °C, 3 atm, H_f)**

Ph: Phenol (C_6H_6OH)

Construct Hypothetical process path?

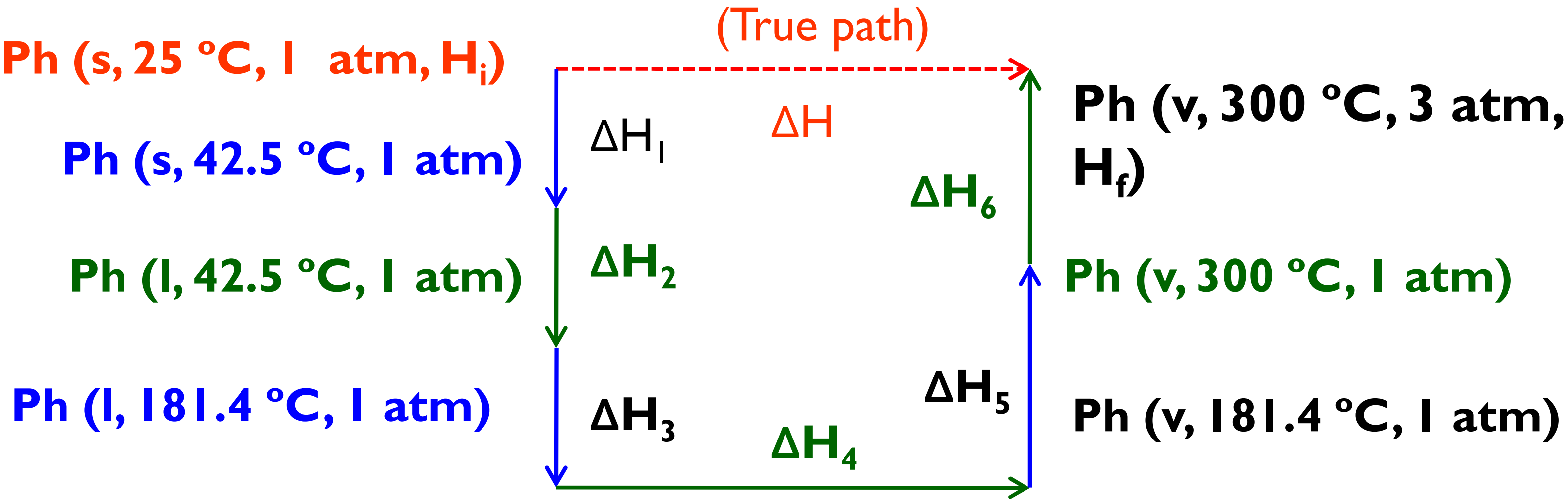
Example

- The properties that do not depend on the how the species reached its state, i.e., the path chosen to reach a state from an initial state is immaterial.

Example:

Ph: Phenol (C_6H_6OH)

$$\boxed{\begin{array}{l}\Delta H = H_f - H_i \\ \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6\end{array}}$$



Ph (s, 25 °C, 1 atm, H_i)

(True path)

ΔH

Ph (v, 300 °C, 3 atm, H_f)

Ph (s, 42.5 °C, 1 atm)

ΔH_1

ΔH_6

Ph (l, 42.5 °C, 1 atm)

ΔH_2

Ph (v, 300 °C, 1 atm)

Ph (l, 181.4 °C, 1 atm)

ΔH_3

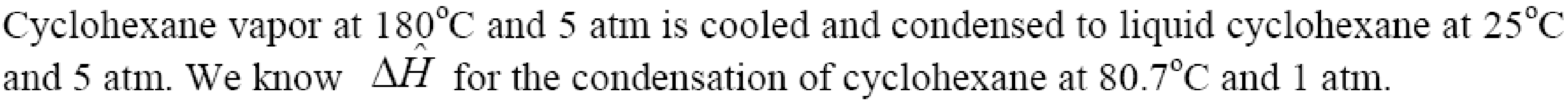
ΔH_4

ΔH_5

Ph (v, 181.4 °C, 1 atm)

Exercise

Construct a path that utilizes as many known enthalpy changes as possible:



Cyclohexane vapor at 180°C and 5 atm is cooled and condensed to liquid cyclohexane at 25°C and 5 atm. We know $\Delta\hat{H}$ for the condensation of cyclohexane at 80.7°C and 1 atm.

8.2 Changes in Pressure at constant T

Process Type 1: Change *P* at constant T and phase.

$$\Delta\hat{U} = 0 \quad \text{(Exact for ideal gas, approximate for solids and liquids)}$$

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

$$= \hat{V}\Delta P \quad \text{(Solid or liquid - } \hat{V} \text{ is constant)}$$

Find $\hat{V}$ for solids and liquids from specific gravity in Table B.1 (convert to density, $\boxed{\hat{V} = 1/\rho}$).

In a problem: State that changes in U or H with P are small and will be neglected (except for steam tables)

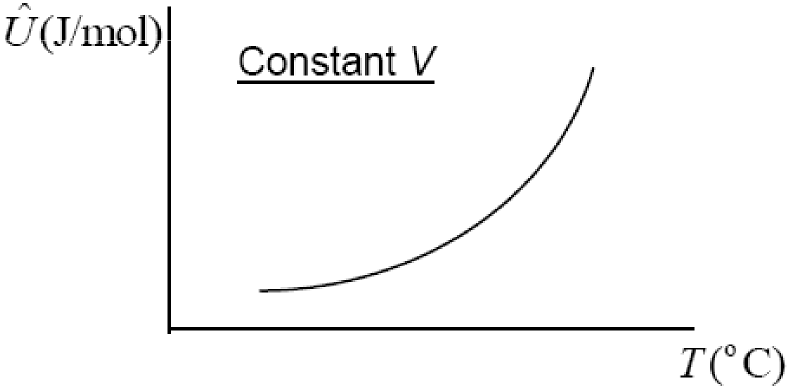
8.3 Changes in Temperature

- 8.3a Sensible Heat and Heat capacity:

Enthalpy changes for a single phase involve temperature changes and are called changes in the **sensible heat**

$\hat{U}$ depends strongly on T (molecules move faster at higher temperatures), and therefore so does $\hat{H}\ (= \hat{U} + P\hat{V})$.

Plot $\hat{U}$ vs. T for a process in which V is held constant.

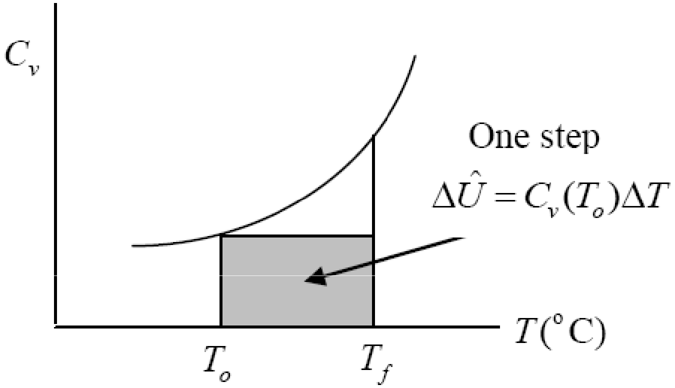


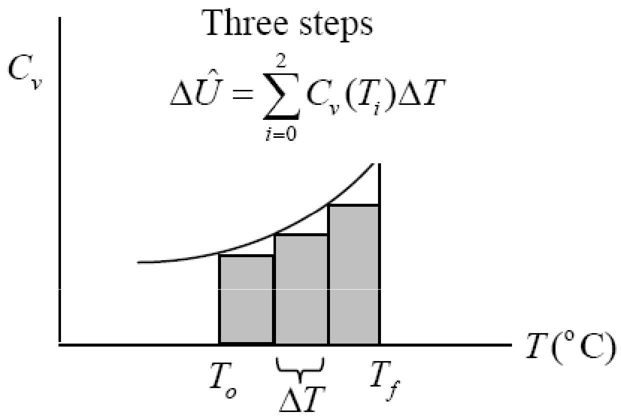
Define $\quad C_v(T)\left(\frac{\text{kJ}}{\text{mol}\cdot{}^\circ\text{C}}\right) = \frac{d\hat{U}}{dT} = \left(\frac{\partial \hat{U}}{\partial T}\right)_V \quad$ Constant volume heat capacity

C_V is the rate of increase of specific internal energy with temperature for a constant volume process. Graphically, it is the slope of the tangent to the plot of $\hat{U}$ vs. T.

We want to be able to calculate $\Delta\hat{U}$ for a change in T from T_o to T_f. It would be easy if the plot of $\hat{U}$ vs. T were linear.

In terms of the plot of C_v vs. T, we need to break the calculation into a series of temperature steps small enough for the curvature to be neglected (C_v constant) in each step. The procedure is easily seen in terms of the graphical calculation.





The values of C_v at each step in the second calculation are clearly much closer to the true values, so the estimated value of $\Delta\hat{U}$ would be more accurate. The smaller the value of ΔT (and the more steps between T_o and T_f), the closer the rectangles follow the curve and the more accurate the value of $\Delta\hat{U}$. To get complete accuracy, let $\Delta T \rightarrow dT \rightarrow 0$ & find the limiting value of the sum of the areas of the rectangles.

$$\Delta\hat{U} = \hat{U}_f - \hat{U}_o = \lim_{\Delta T \to 0} \sum_{T_i = T_o}^{T_f - \Delta T} C_v(T_i)\Delta T$$

$$\Rightarrow \Delta\hat{U} =$$

That expression strictly applies to processes that take place at constant volume; however, since $\hat{U}$ is almost independent of P for every species but real gases at high pressures, it can be applied to most processes in which volume changes occur as well. In short, *for processes with temperature changes but no phase changes*,

$$\boxed{\Delta\hat{U} = \int_{T_1}^{T_2} C_v(T)dT} \qquad (8.3\text{-}6)$$

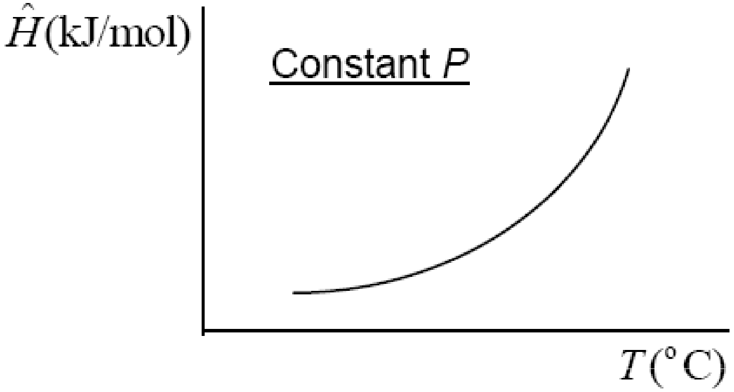
Equation 8.3-6:

- exact for ideal gases
- an excellent approximation for liquids and solids, even if volume and pressure change.
- For non-ideal gas: valid only if V is constant.

Remember not valid if there is phase change

Expressions for *Cv* (T) for many substances can be determined from data in the text, but we'll hold off on that until after we derive the expression for $\Delta\widehat{H}$

We do it the same way, starting by plotting $\Delta\widehat{H}$ vs. *T* for a process in which the temperature of a substance is raised holding the pressure constant.



Define $$C_p(T)\left(\frac{\mathrm{kJ}}{\mathrm{mol}\cdot{}^\circ\mathrm{C}}\right) = \frac{d\hat{H}}{dT} = \left(\frac{\partial\hat{H}}{\partial T}\right)_P$$

constant pressure heat capacity

Proceeding exactly as before, we can show that $\Delta\hat{H} = \int_{T_o}^{T_f} C_p(T)dT$ for a change in *T* at constant *P*. If we combine this result with the previous expressions for Type 1 processes (change *P* at constant *T*), we get

$$\boxed{\begin{aligned}\Delta\hat{H} &= \int_{T_1}^{T_2} C_p(T)dT \quad \text{[exact for ideal gases with varying } T\text{, any gas at constant } P\text{]} \quad (8.3\text{-}10a)\\ &= \int_{T_1}^{T_2} C_p(T)dT + \hat{V}\Delta P \quad \text{[liquids and solids]} \quad (8.3\text{-}10b)\end{aligned}}$$

- *Look up polynomial expressions for C_p at 1 atm in Table B.2.* For example Acetone

$$\text{Ac(l)}: \quad C_p\left(\frac{\mathrm{kJ}}{\mathrm{mol}\cdot{}^\circ\mathrm{C}}\right) = 0.123 + 18.6 \times 10^{-5}T$$

$$\text{Ac(v)}: \quad C_p\left(\frac{\mathrm{kJ}}{\mathrm{mol}\cdot{}^\circ\mathrm{C}}\right) = 0.07196 + 20.10 \times 10^{-5}T - 12.78 \times 10^{-8}T^2 + 34.76 \times 10^{-12}T^3$$

Different Empirical Forms for C_p for Liquids and Gases

$$C_p = a + bT + cT^2$$ (T in K, ºC, ºF or ºR)

$$\boxed{C_p = a + bT + cT^2 + dT^3}$$ (T in K, ºC, ºF or ºR)

$$\boxed{C_p = a + bT + cT^{-2}}$$ (T in K, ºC, ºF or ºR)

$$C_p = a + bT + c\sqrt{T}$$ (T in K, ºC, ºF or ºR)

The parameters (a, b, c, d) are determined by selecting the values that provide the best fit between the equation and experimental results.

These empirical functions are determined for a fixed range of temperatures. Don't extrapolate!

Example 8.3.1

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.

Solution

From Equation 8.3-6,

$$\Delta\hat{U}(\text{kJ/kg}) = \int_{20^\circ\text{C}}^{150^\circ\text{C}} (0.855 + 9.42 \times 10^{-4}T)\left(\frac{\text{kJ}}{\text{kg}\cdot{}^\circ\text{C}}\right) dT$$

$$= 0.855T\Big]_{20^\circ\text{C}}^{150^\circ\text{C}} + \frac{9.42 \times 10^{-4}T^2}{2}\Bigg]_{20^\circ\text{C}}^{150^\circ\text{C}}$$

$$= (111 + 10.4)\ \text{kJ/kg} = 121\ \text{kJ/kg}$$

The energy balance for this closed system is

$$Q = \Delta U = m(\text{kg})\ \Delta\hat{U}(\text{kJ/kg}) = (200\ \text{kg})(121\ \text{kJ/kg}) = \boxed{24{,}200\ \text{kJ}}$$

Procedure for energy balance calculation

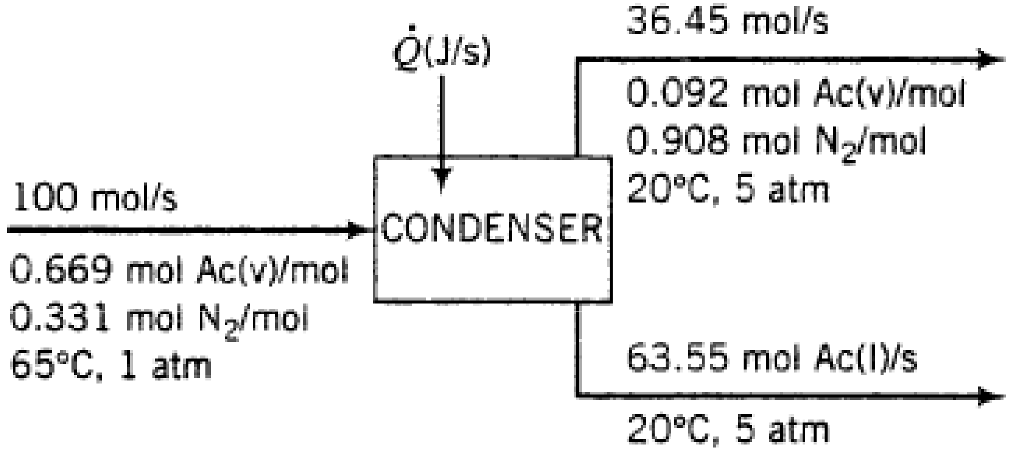
1. Draw and completely label a process flowchart
2. Perform all material balance calculations
3. Write the appropriate form of the energy balance equation and remove any negligible terms
4. Choose a reference state (phase, T, P) for each species involved
   - If using enthalpy tables, use reference state used to generate table
   - If no tables are available, choose one inlet or outlet condition as the reference state for the species
5. Construct an inlet-outlet enthalpy table
   - Columns for inlet and outlet amounts of each species along with their corresponding $\hat{U}_i$ or $\hat{H}_i$ values
   - Use a separate row for each phase of a species
   - Identify unknowns with variables (e.g., $\hat{H}_1$, $\hat{H}_2$, etc.)

Procedure for energy balance calculation

6. Calculate all required values of $\hat{U}_i$ or $\hat{H}_i$ and insert values into table
7. Calculate ΔU or ΔH (e.g., $\Delta H = \Sigma m_i \hat{H}_i - \Sigma m_i \hat{H}_i$)
8. Calculate any other terms in the energy balance equation (i.e., W, ΔE_k, ΔE_p)
9. Solve for the unknown quantity in the energy balance equation
    - Typically solve for Q but sometimes asked to solve for a mass (mole) flow or occasionally a T!

Example 8.1.1

Acetone (Ac) vapor is partially condensed out of a gas stream containing 66.9 mole % acetone vapor and the balance nitrogen. The process operates at stead-state. Calculate the require cooling rate.



1. Perform required material balance calculations
2. Write simplified energy balance

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

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

3. Chose reference state for Ac and N_2

- The reference states may be chosen for computational convenience, since the choice has no effect on the calculated value of ∆H.
- Specific enthalpies of N_2 available in Table B.8 relative to N_2 (g, 25 C, 1 atm)
- There are no tabulated data for acetone in the text, so we will chose one of the process stream condition, Ac(l, 20 C, 5 atm), as the reference state for this species, i.e. H = 0

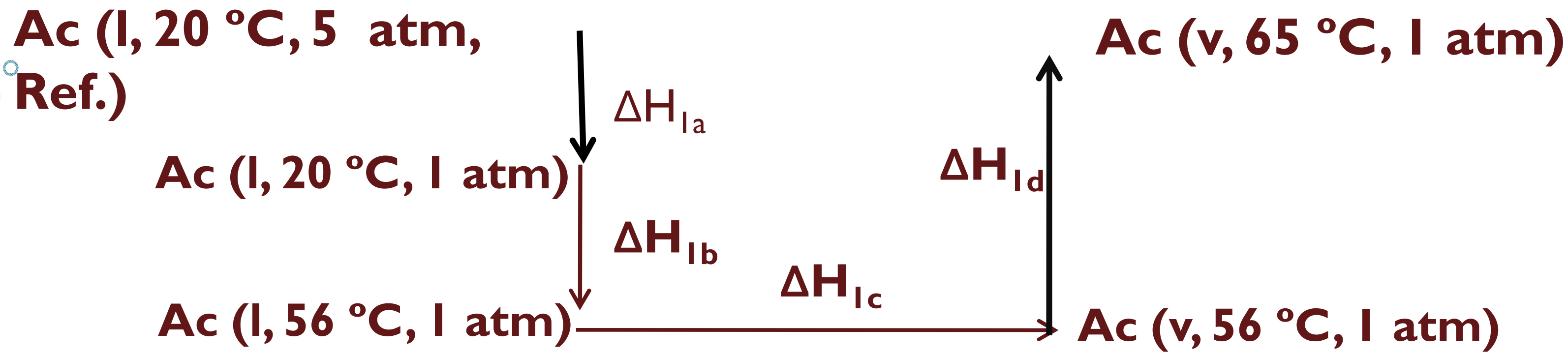
4. Construct an inlet-outlet enthalpy table

References: Ac(l, 20°C, 5 atm), N_2(g, 25°C, 1 atm)

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
Ac(v)	66.9	$\hat{H}_1$	3.35	$\hat{H}_3$
Ac(l)	—	—	63.55	0
N_2	33.1	$\hat{H}_2$	33.1	$\hat{H}_4$

$$\text{Ac(l)}: \quad C_p\left(\frac{\text{kJ}}{\text{mol}\cdot{}^\circ\text{C}}\right) = 0.123 + 18.6 \times 10^{-5}T$$

$$\text{Ac(v)}: \quad C_p\left(\frac{\text{kJ}}{\text{mol}\cdot{}^\circ\text{C}}\right) = 0.07196 + 20.10 \times 10^{-5}T - 12.78 \times 10^{-8}T^2 + 34.76 \times 10^{-12}T^3$$



Ac (l, 20 °C, 5 atm, Ref.)

ΔH_{1a}

Ac (l, 20 °C, 1 atm)

ΔH_{1b}

Ac (l, 56 °C, 1 atm)

ΔH_{1c}

Ac (v, 56 °C, 1 atm)

ΔH_{1d}

Ac (v, 65 °C, 1 atm)

$\Delta H_1 = \Delta H_{1a} + \Delta H_{1b} + \Delta H_{1c} + \Delta H_{1d}$

$= 0.02\,97 + 4.68 + 30.2 + 0.753$

$= 35.7$ **kJ/mol**

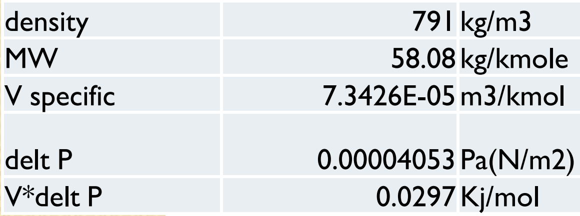
Similarly,

$\Delta H_2 = 1.16$ **kJ/mol;**

$\Delta H_3 = 32.0$ **kJ/mol**

$\Delta H_4 = -0.10$ **kJ/mol**

$$\hat{H}_1 = \hat{V}_{Ac}\,\Delta P + \int_{20}^{56} (C_P)_{Ac\,(l)}\,dT + \left(\Delta \hat{H}_v\right)_{Ac} + \int_{56}^{65} (C_P)_{Ac\,(v)}\,dT$$



density	791	kg/m3
MW	58.08	kg/kmole
V specific	7.3426E-05	m3/kmol
delt P	0.00004053	Pa(N/m2)
V*delt P	0.0297	Kj/mol

$$\hat{H}_1 = 35.7\,kJ\ /\ mol$$

Proceeding in a similar manner, we obtain the values for $\hat{H}_2$, $\hat{H}_3$, and $\hat{H}_4$ shown in the following revised enthalpy table:

References: Ac(l, 20°C, 5 atm), N_2(g, 25°C, 1 atm)

Substance	$\dot{n}_{\text{in}}$ (mol/s)	$\hat{H}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/s)	$\hat{H}_{\text{out}}$ (kJ/mol)
Ac(v)	66.9	35.7	3.35	32.0
Ac(l)	—	—	63.55	0
N_2	33.1	1.16	33.1	−0.10

6. *Calculate $\Delta\dot{H}$.*

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

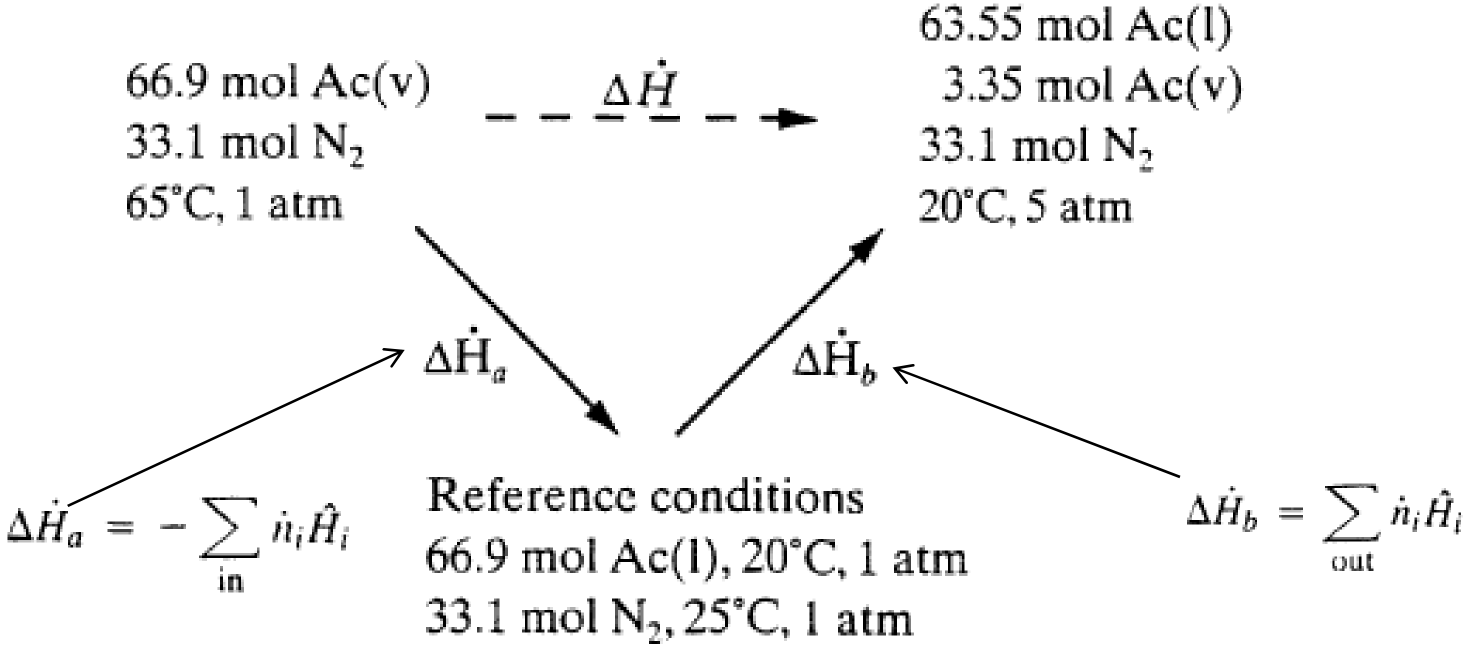
$$= (3.35\ \text{mol/s})(32.0\ \text{kJ/mol}) + [(63.55)(0) + (33.1)(-0.10) - (66.9)(35.7) - (33.1)(1.16)]\ \text{kJ/s}$$

$$= -2320\ \text{kJ/s}$$

1.16	using a only for Cp calculation
0.0017592	b only
0.000122091	c only
-1.83744E-06	d only
1.161879453	using a, b, c, d for Cp calculation

$$\begin{array}{l}66.9 \text{ mol Ac(v)}\\ 33.1 \text{ mol } N_2\\ 65^\circ\text{C, 1 atm}\end{array} \xrightarrow{\Delta\dot{H}} \begin{array}{l}63.55 \text{ mol Ac(l)}\\ \ \ 3.35 \text{ mol Ac(v)}\\ 33.1 \text{ mol } N_2\\ 20^\circ\text{C, 5 atm}\end{array}$$

To calculate $\Delta\dot{H}$, in effect we constructed the following process path:



66.9 mol Ac(v)
33.1 mol N_2
65°C, 1 atm

$\Delta\dot{H}$

63.55 mol Ac(l)
3.35 mol Ac(v)
33.1 mol N_2
20°C, 5 atm

$\Delta\dot{H}_a$

$\Delta\dot{H}_b$

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

Reference conditions
66.9 mol Ac(l), 20°C, 1 atm
33.1 mol N_2, 25°C, 1 atm

$$\Delta\dot{H}_b = \sum_{\text{out}} \dot{n}_i\hat{H}_i$$

$$\boxed{\Delta\dot{H} = \Delta\dot{H}_a + \Delta\dot{H}_b = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i}$$

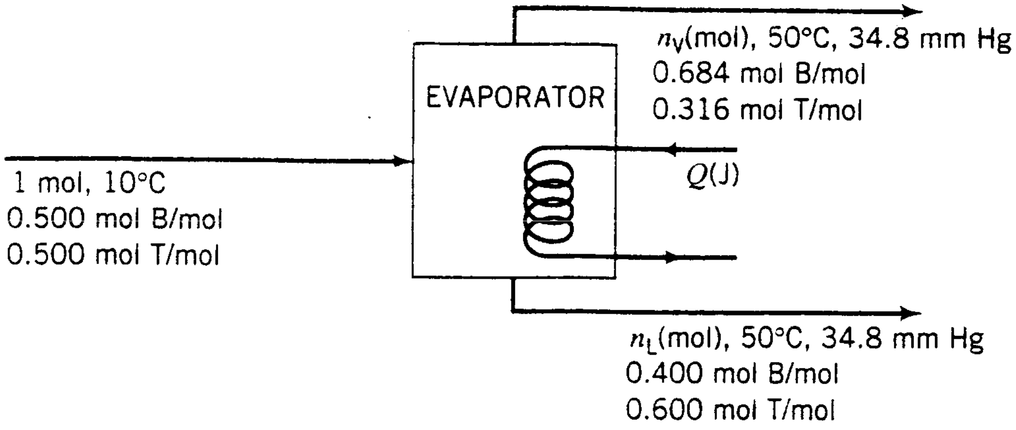
Take Home Examples:

- Solve Example: 8.3.5
- Solve Example: 8.4.4 (combined mass & energy balance)
- Look at Example: 8.3.6 (required excel sheet)

Example: 8.4.4

An equimolar liquid mixture of benzene (B) and toluene (T) at 10°C is fed continuously to a vessel in which the mixture is heated to 50°C. The liquid product is 40.0 mole% B, and the vapor product is 68.4 mole% B. How much heat must be transferred to the mixture per g-mole of feed?

Basis: 1 mol Feed



Solution

$$\left.\begin{aligned} &\textbf{\textit{Total Mass Balance:}} & 1.00\text{ mol} &= n_V + n_L \\ &\textbf{\textit{Benzene Balance:}} & 0.500\text{ mol} &= 0.684 n_V + 0.400\, n_L \end{aligned}\right\} \Longrightarrow \begin{aligned} n_V &= 0.352\text{ mol} \\ n_L &= 0.648\text{ mol} \end{aligned}$$

The energy balance for this process has the form $Q = \Delta H$. An enthalpy table for the process appears as follows:

References: B(l, 10°C, 1 atm), T(l, 10°C, 1 atm)

Substance	n_{in} mol	$\hat{H}_{in}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{out}$ (kJ/mol)
B(l)	0.500	0	0.259	$\hat{H}_1$
T(l)	0.500	0	0.389	$\hat{H}_2$
B(v)	—	—	0.241	$\hat{H}_3$
T(v)	—	—	0.111	$\hat{H}_4$

$$\hat{H}_1 = \int_{10°\mathrm{C}}^{50°\mathrm{C}} (C_p)_{C_6H_6(l)}\, dT = 5.332 \text{ kJ/mol}$$

$$\hat{H}_2 = \int_{10°\mathrm{C}}^{50°\mathrm{C}} (C_p)_{C_7H_8(l)}\, dT = 6.340 \text{ kJ/mol}$$

$$\hat{H}_3 = \int_{10°\mathrm{C}}^{80.1°\mathrm{C}} (C_p)_{C_6H_6(l)}\, dT + (\Delta\hat{H}_v)_{C_6H_6}(80.1°\mathrm{C}) + \int_{80.1°\mathrm{C}}^{50°\mathrm{C}} (C_p)_{C_6H_6(v)}\, dT$$
$$= 37.52 \text{ kJ/mol}$$

$$\hat{H}_4 = \int_{10°\mathrm{C}}^{110.62°\mathrm{C}} (C_p)_{C_7H_8(l)}\, dT + (\Delta\hat{H}_v)_{C_7H_8}(110.62°\mathrm{C}) + \int_{110.62°\mathrm{C}}^{50°\mathrm{C}} (C_p)_{C_7H_8(v)}\, dT$$
$$= 42.93 \text{ kJ/mol}$$

The energy balance is

$$Q = \Delta H = \sum_{\text{out}} n_i\hat{H}_i - \sum_{\text{in}} n_i\hat{H}_i \Longrightarrow \boxed{Q = 17.7 \text{ kJ}}$$

8.3b Heat Capacity Formulas

The heat capacities C_v and C_p are physical properties of materials and are tabulated in standard references such as *Perry's Chemical Engineers' Handbook.*[5] They may be expressed in any units of energy per unit amount per unit temperature interval—for example, J/(mol·K), or Btu/(lb_m·°F). The term **specific heat** is also used for this physical property.

Heat capacities are functions of temperature and are frequently expressed in polynomial form ($C_p = a + bT + cT^2 + dT^3$). Values of the coefficients *a, b, c,* and *d* are given in Table B.2 of Appendix B for a number of species at 1 atm, and listings for additional substances are given on pp. 2-161 to 2-186 of *Perry's Chemical Engineers' Handbook.*

- *Determination of C_v from C_p*

$$C_v = C_p - R \quad \text{(ideal gases)} \qquad \text{where } R = 8.314\times10^{-3}\ \text{kJ/(mol}\cdot\text{K)} \qquad (8.3\text{-}11)$$

$$\approx C_p \quad \text{(liquids and solids)} \qquad (8.3\text{-}12)$$

Example 8.3.2: 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.

1. From Table B.2, Appendix B, the heat capacity of N_2 at a constant pressure of 1 atm is

$$C_p[\text{kJ/(mol}\cdot{}^\circ\text{C)}] = 0.02900 + 0.2199 \times 10^{-5}T + 0.5723 \times 10^{-8}T^2 - 2.871 \times 10^{-12}T^3$$

$$\Delta\hat{H} = \int_{20^\circ\text{C}}^{100^\circ\text{C}} C_p(T)\,dT$$

$$\Downarrow$$

$$\Delta\hat{H}(\text{kJ/mol}) = 0.02900T\Big]_{20^\circ\text{C}}^{100^\circ\text{C}} + 0.2199 \times 10^{-5}\frac{T^2}{2}\Big]_{20^\circ\text{C}}^{100^\circ\text{C}} + 0.5723 \times 10^{-8}\frac{T^3}{3}\Big]_{20^\circ\text{C}}^{100^\circ\text{C}}$$

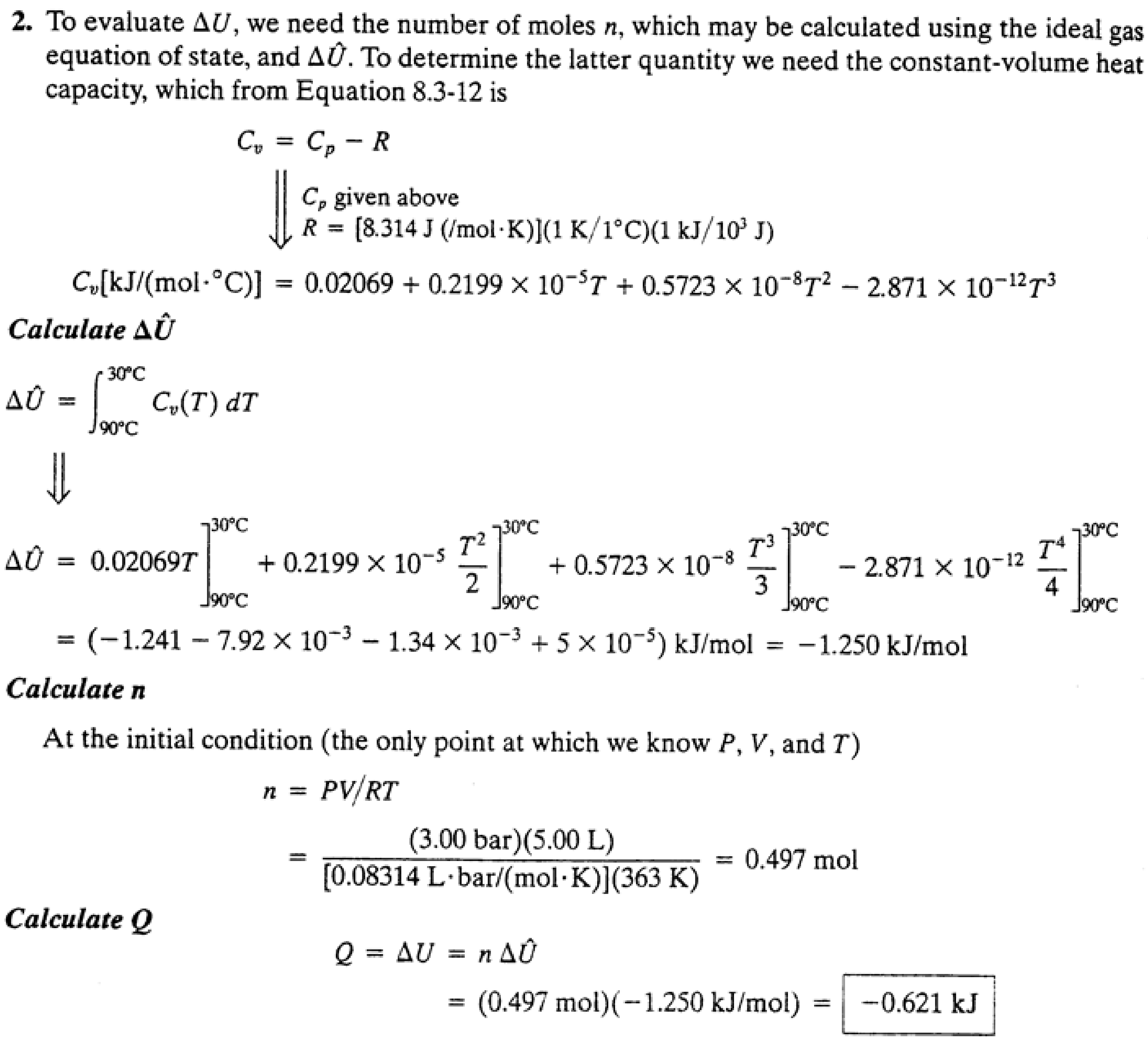
$$- 2.871 \times 10^{-12}\frac{T^4}{4}\Big]_{20^\circ\text{C}}^{100^\circ\text{C}}$$

$$= (2.320 + 0.0106 + 1.9 \times 10^{-3} - 7 \times 10^{-5})\ \text{kJ/mol} = 2.332\ \text{kJ/mol}$$

Finally,

$$\dot{Q} = \Delta\dot{H} = \dot{n}\,\Delta\hat{H}$$

$$= 100\ \frac{\text{mol}}{\text{min}}\left|\frac{2.332\ \text{kJ}}{\text{mol}}\right. = \boxed{233\ \text{kJ/min}}$$



2. To evaluate ΔU, we need the number of moles n, which may be calculated using the ideal gas equation of state, and $\Delta \hat{U}$. To determine the latter quantity we need the constant-volume heat capacity, which from Equation 8.3-12 is

$$C_v = C_p - R$$

$$\Bigg\Downarrow \begin{array}{l} C_p \text{ given above} \\ R = [8.314 \text{ J }(/\text{mol}\cdot\text{K})](1 \text{ K}/1^\circ\text{C})(1 \text{ kJ}/10^3 \text{ J}) \end{array}$$

$$C_v[\text{kJ}/(\text{mol}\cdot{}^\circ\text{C})] = 0.02069 + 0.2199 \times 10^{-5}T + 0.5723 \times 10^{-8}T^2 - 2.871 \times 10^{-12}T^3$$

Calculate $\boldsymbol{\Delta \hat{U}}$

$$\Delta \hat{U} = \int_{90^\circ\text{C}}^{30^\circ\text{C}} C_v(T)\,dT$$

$$\Downarrow$$

$$\Delta \hat{U} = 0.02069T\Big]_{90^\circ\text{C}}^{30^\circ\text{C}} + 0.2199 \times 10^{-5}\,\frac{T^2}{2}\Big]_{90^\circ\text{C}}^{30^\circ\text{C}} + 0.5723 \times 10^{-8}\,\frac{T^3}{3}\Big]_{90^\circ\text{C}}^{30^\circ\text{C}} - 2.871 \times 10^{-12}\,\frac{T^4}{4}\Big]_{90^\circ\text{C}}^{30^\circ\text{C}}$$

$$= (-1.241 - 7.92 \times 10^{-3} - 1.34 \times 10^{-3} + 5 \times 10^{-5}) \text{ kJ/mol} = -1.250 \text{ kJ/mol}$$

Calculate n

At the initial condition (the only point at which we know P, V, and T)

$$n = PV/RT$$

$$= \frac{(3.00 \text{ bar})(5.00 \text{ L})}{[0.08314 \text{ L}\cdot\text{bar}/(\text{mol}\cdot\text{K})](363 \text{ K})} = 0.497 \text{ mol}$$

Calculate Q

$$Q = \Delta U = n\,\Delta \hat{U}$$

$$= (0.497 \text{ mol})(-1.250 \text{ kJ/mol}) = \boxed{-0.621 \text{ kJ}}$$

Example 8.3.3:

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.

$$\text{air(g, 430°C)} \longrightarrow \text{air(g, 100°C)}$$

$$\dot{Q} = \Delta\dot{H} = \dot{n}_{\text{air}}\hat{H}_{\text{air,out}} - \dot{n}_{\text{air}}\hat{H}_{\text{air,in}} = \dot{n}_{\text{air}}\,\Delta\hat{H}$$

Assume ideal gas behavior, so that pressure changes (if there are any) do not affect $\Delta\hat{H}$.

1. ***The hard way.*** Integrate the heat capacity formula in Table B.2.

$$\Delta\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right) = \int_{430°\text{C}}^{100°\text{C}} C_p(T)\,dT$$

$$= \int_{430°\text{C}}^{100°\text{C}} \left[0.02894 + 0.4147 \times 10^{-5}T + 0.3191 \times 10^{-8}T^2 - 1.965 \times 10^{-12}T^3\right] dT$$

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

$$= (-9.5502 - 0.3627 - 0.0835 + 0.0167)\ \text{kJ/mol} = -9.98\ \text{kJ/mol}$$

2. ***The easy way.*** Use tabulated enthalpies from Table B.8.

$\hat{H}$ for air at 100°C can be read directly from Table B.9 and $\hat{H}$ at 430°C can be estimated by linear interpolation from the values at 400°C (11.24 kJ/mol) and 500°C (14.37 kJ/mol).

$$\hat{H}(100°\text{C}) = 2.19\ \text{kJ/mol}$$

$$\hat{H}(430°\text{C}) = [11.24 + 0.30(14.37 - 11.24)]\ \text{kJ/mol} = 12.17\ \text{kJ/mol}$$

$$\Downarrow$$

$$\Delta\hat{H} = (2.19 - 12.17)\ \text{kJ/mol} = -9.98\ \text{kJ/mol}$$

Either way $\Delta\hat{H}$ is determined,

$$\dot{Q} = \Delta\dot{H} = \dot{n}\,\Delta\hat{H} = \frac{15.0\ \text{kmol}}{\text{min}}\left|\frac{10^3\ \text{mol}}{1\ \text{kmol}}\right|\frac{-9.98\ \text{kJ}}{\text{mol}}\left|\frac{1\ \text{min}}{60\ \text{s}}\right|\frac{1\ \text{kW}}{1\ \text{kJ/s}} = \boxed{-2500\ \text{kW}}$$

END Part 1