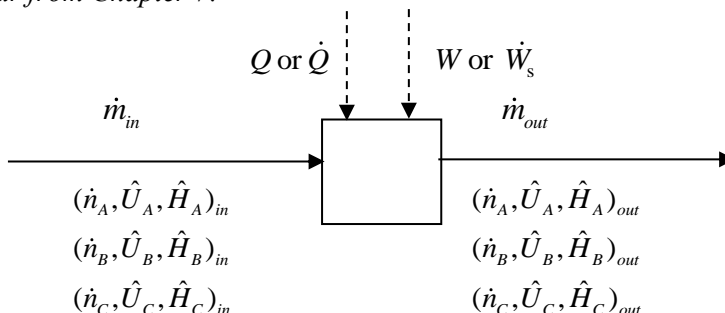


Section 6: F&R, Ch. 8 (Energy Balances – II)

ENERGY BALANCES ON NONREACTIVE PROCESSES

We solved problems in Chapter 4 and ignored the fact that heat was added and that temperatures might have changed. In Chapter 8 we will start to include the energy effects. Here's a brief review of what we've learned so far from Chapter 7:



m (kg) (closed) or \dot{m} (kg/s) (open)

n_i (mol) (closed) or \dot{n}_i (mol / s) (open)

\hat{U} (kJ / mol), \hat{H} (kJ / mol)

Each species in a feed or product stream is in a particular state (phase, T , P), and the same species may enter and leave in several different streams and states.

In Chapter 7, we saw that the first law of thermodynamics (energy balance equation) is

$$Q + W = \Delta U + \Delta E_k + \Delta E_p \quad [\text{Closed (batch) system}]$$

$$\dot{Q} + \dot{W}_s = \Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p \quad [\text{Open (continuous), steady - state system}]$$

where

$$\Delta U = \sum_{\substack{\text{species,} \\ \text{states}}} m_{\text{final}} \hat{U}_{\text{final}} - \sum_{\substack{\text{species,} \\ \text{states}}} m_{\text{initial}} \hat{U}_{\text{initial}}$$

$$\Delta \dot{H} = \sum_{\substack{\text{output} \\ \text{streams}}} \dot{m}_{\text{out}} \hat{H}_{\text{out}} - \sum_{\substack{\text{input} \\ \text{streams}}} \dot{m}_{\text{in}} \hat{H}_{\text{in}} \quad [\text{where } \hat{H} = \hat{U} + P\hat{V}]$$

$$\Delta \dot{E}_k = \sum_{\substack{\text{output} \\ \text{streams}}} \frac{1}{2} \dot{m}_{\text{out}} (u_{\text{out}})^2 - \sum_{\substack{\text{input} \\ \text{streams}}} \frac{1}{2} \dot{m}_{\text{in}} (u_{\text{in}})^2 \quad [\text{where } u(\text{m / s}) = \text{velocity}]$$

$$\Delta \dot{E}_p = \sum_{\substack{\text{output} \\ \text{streams}}} \dot{m}_{\text{out}} g z_{\text{out}} - \sum_{\substack{\text{input} \\ \text{streams}}} \dot{m}_{\text{in}} g z_{\text{in}} \quad [\text{where } z = \text{height}]$$

Each of these terms has units of (closed) or (open).

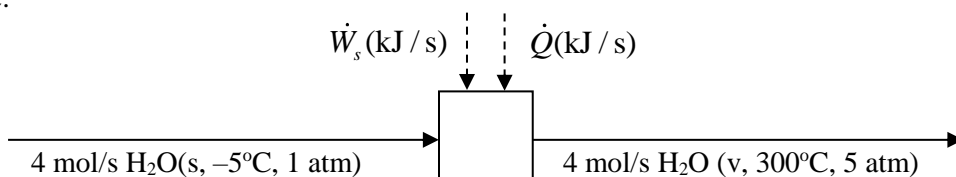
Section 6: F&R, Ch. 8 (Energy Balances – II)

Most problems in Ch. 8 have the following form:

- Given:
 - Feed and product states (phase, T , P), some flow rates (n 's) & compositions (y 's)
 - W (closed) or \dot{W}_s (open) = zero (no moving parts or electric currents)
- Calculate other flow rates (Ch. 4–6 methods)
- Determine ΔU (closed) or $\Delta \hat{H}$ (open), $\Delta \dot{E}_k$, $\Delta \dot{E}_p$ (usually neglect the latter two).
- Substitute into energy balance to determine Q or \dot{Q} .

If we have tables of specific internal energies and enthalpies (as we do for water in the steam tables), calculating ΔU , $\Delta \hat{H}$ is straightforward. Chapter 8 discusses how to do it if we don't have those tables.

Example:



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

$$\begin{aligned}
 &\Downarrow \Delta \dot{E}_p = 0 \text{ (Why? _____)} \\
 &\Downarrow \text{Neglect } \Delta \dot{E}_k \text{ (Why? _____)} \\
 &\Downarrow \\
 &\dot{Q} + \dot{W}_s \approx \Delta \dot{H} = \dot{n}_{out} \hat{H}_{out} - \dot{n}_{in} \hat{H}_{in} = 4 \left(\frac{\text{mol}}{\text{s}} \right) \hat{H}_2 \left(\frac{\text{kJ}}{\text{mol}} \right) - 4 \hat{H}_1 \\
 &\Downarrow \\
 &\dot{Q} + \dot{W}_s = 4 \Delta \hat{H}
 \end{aligned}$$

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

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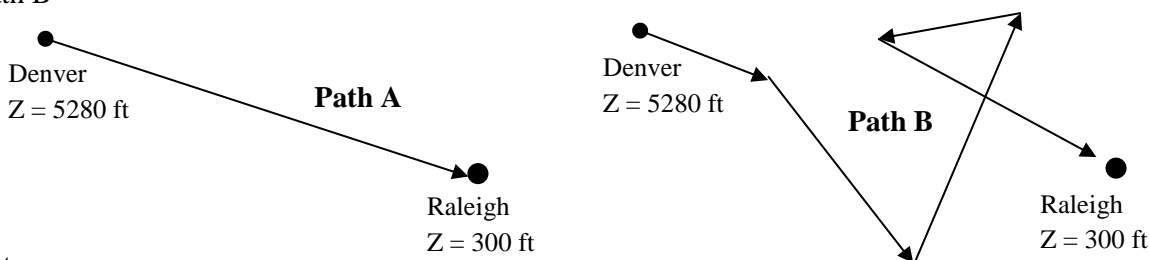
Constructing a hypothetical process path relies on the concept of **state variables** (Section 8.1).

- State of a system: Set of all intensive variables [variables that don't change with changing mass] that define the system (phase, T , P , height, velocity, ...)
- State variable or state property: If a system changes from State 1 to State 2 in a process and X is some property of the system (height, internal energy, ...)

$$\begin{array}{ccc} \text{State 1} & \longrightarrow & \text{State 2} \\ X_1 & & X_2 \end{array}$$

then X is a *state variable* if $\Delta X = X_2 - X_1$ depends only on the initial and final states, and not how the system got from State 1 to State 2.

Example: Travel from Denver, CO (elevation = 5280 ft) to Raleigh, NC (elevation = 300 ft). Path A vs. Path B



Let:

D = reading on odometer (miles traveled), $\Delta D = D_2 - D_1$

Z = reading on altimeter (ft), $\Delta Z = Z_2 - Z_1$

$(\Delta D)_{\text{Path A}} (=, \neq) (\Delta D)_{\text{Path B}}$, so D (is, is not) a state variable.

$(\Delta Z)_{\text{Path A}} (=, \neq) (\Delta Z)_{\text{Path B}}$ so Z (is, is not) a state variable.

Most important concept in Chapter 8: \hat{U} and \hat{H} are state variables.

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Exercise: For the water process shown in the example, construct a process path consisting of steps of some of the five types.



Exercise: Look at the two process paths in Section 8.1b. Identify Type (1–5) of each step on the hypothetical (bottom) path.

$$\Delta \hat{H}_1: \quad \Delta \hat{H}_2: \quad \Delta \hat{H}_3: \quad \Delta \hat{H}_4: \quad \Delta \hat{H}_5: \quad \Delta \hat{H}_6:$$

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

- (1) Cyclohexane vapor at 180°C and 5 atm is cooled and condensed to liquid cyclohexane at 25°C and 5 atm. We know the specific enthalpy change for the condensation of cyclohexane at 80.7°C and 1 atm.
- (2) Water at 30°C and 1 atm and solid NaOH at 25°C and 1 atm are mixed to form an aqueous NaOH solution at 50°C and 1 atm. We know the enthalpy change for the dissolution of NaOH in water at 25°C and 1 atm.

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- (3) O_2 at 170°C and 3 atm and CH_4 at 25°C at 3 atm are combined and react completely to form CO_2 and H_2O at 300°C and 3 atm. The enthalpy change for the reaction occurring at 25°C and 1 atm is known.

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Calculating $\Delta\hat{U}$ and $\Delta\hat{H}$ for Process Types 1 and 2

Process Type 1: Change P at constant T and phase. (Section 8.2)

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

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

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

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

Calculations for real gases are complex (topic in later thermodynamics class)

Process Type 2: Change T at constant P and phase. (Section 8.3)

Sensible heat: heat transferred to raise or lower the temperature depends strongly on T (molecules move faster at higher temperatures), and therefore so does $\hat{H}(=\hat{U} + P\hat{V})$.

Define $C_p(T) \left(\frac{\text{kJ}}{\text{mol} \times ^\circ\text{C}} \right) = \frac{d\hat{H}}{dT} = \left(\frac{\partial \hat{H}}{\partial T} \right)_P$ Constant pressure heat capacity

C_p is the rate of increase of specific enthalpy with temperature for a constant pressure process.

Graphically, it is the slope of the tangent to the plot of \hat{H} vs. T . To find the change in enthalpy from C_p :

$$\Delta\hat{H} =$$

If we combine this result with the previous expressions for Type 1 processes (change P at constant T), we get

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T) dT \quad \text{[exact for ideal gases with varying } P, \text{ any gas at constant } P] \quad (8.3-10a)$$

$$= \int_{T_1}^{T_2} C_p(T) dT + \hat{V}\Delta P \quad \text{[liquids and solids]} \quad (8.3-10b)$$

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

Acetone (liquid): C_p [kJ/(mol·°C)] =

Acetone (vapor): C_p [kJ/(mol·°C)] =

Substitute into $\Delta\hat{H} = \int_{T_o}^{T_f} C_p(T) dT$

We can also use APEX's Enthalpy function to calculate the enthalpy change as a result of a temperature change: = Enthalpy ("acetone", 150, 250, "C", "g") = 10.7237 kJ/mol

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- *Estimation of C_p for solids, liquids, mixtures:* **Kopp's Rule** (Section 8.3c and Table B.10 or the Kopp's function in APEX). Use when you can't find the data in Table B.2. See Example 8.3-4.

Kopp's Rule: C_p for a molecular compound is the sum of contributions (given in Table B.10) for each element of a compound.

$$\text{Example: } C_p [\text{Ca}(\text{OH})_2] = C_{pa} [\text{Ca}] + 2 C_{pa} [\text{O}] + 2 C_{pa} [\text{H}]$$

Note on Kopp's rule units: Note that the units for the atomic heat capacities in Table B.10 are listed as J/g-atom C. So what's a g-atom? A gram-mole (or mol) is the amount of a molecular species whose mass in grams equals the molecular weight of the species. Similarly, a gram-atom (g-atom) is the amount of an atomic species (C, H, S...) whose mass in grams equals the atomic weight of the species. The heat capacity terms in Table B.10 have units of J/g-atom C because they apply to atomic species instead of molecular species.

1 mole of water contains 2 g-atoms of H and 1 g-atom of O. So to estimate the heat capacity of liquid water, if you multiply the heat capacity term for H (18) by 2 g-atoms and add the term for O (25) multiplied by 1 g-atom, you get the heat capacity for a g-mole (mol) of H_2O and its C_p units would be J/mol C.

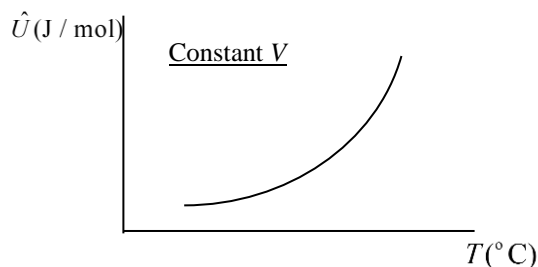
- *Heat capacity of a mixture*

$$(C_p)_{\text{mix}}(T) = \sum y_i C_{pi}(T)$$

- Note enthalpy values available for common gases (O_2 , N_2 , H_2 , air) in Tables B.8 and B.9

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How about the dependence of \hat{U} on T ? To find this, we do it the same way, starting by plotting \hat{U} vs. T for a process in which the temperature of a substance is raised holding the volume constant.



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

Proceeding exactly as before, we can show that, for a change in T at constant V :

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

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, *this equation applies well for processes with temperature changes but no phase changes.*

Recap: Eq. (8.3-6) is

- exact for ideal gases and an excellent approximation for liquids and solids, even if volume and pressure change.
- exact for constant volume processes. For real gases, C_v depends on the value of \hat{V} at which the process takes place.
- inapplicable for real gases in which significant volume changes occur.

So how do you determine C_v ?

- *Determination of C_v from C_p*

$$C_v = C_p - R \quad (\text{ideal gases}) \quad \text{where } R = 8.314 \times 10^{-3} \text{ kJ} / (\text{mol} \times \text{K}) \quad (8.3-11)$$

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

Substitute expression for C_v in integral expression for $\Delta \hat{U}$ (Eq. 8.3-6). (See Example 8.3-2)

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Example : Calculate $\Delta\hat{H}$ (kJ / mol) for $\text{H}_2\text{O}(\text{v}, 30^\circ\text{C}, 0.0424 \text{ bar}) \rightarrow \text{H}_2\text{O}(\text{v}, 350^\circ\text{C}, 1.5 \text{ bar})$

- (a) using the steam tables
- (b) using Eq. (8.3-10a)
- (c) using APEx's SteamSatT (B.5) and SteamSH (B.7) functions
- (d) Which calculated value is most accurate, and why?

Solution

- (a) From Tables B.5 and B.7,

$$\Delta\hat{H} = \frac{(\text{ } - \text{ }) \text{ kJ}}{\text{kg}} \bigg| \frac{0.01802 \text{ kg}}{\text{mol}} = 11.13 \text{ kJ / mol}$$

- (b.) From Table B.2, $C_p [\text{kJ}/(\text{mol}\cdot^\circ\text{C})] = 33.46 \times 10^{-3} + 0.6880 \times 10^{-5}T + 0.7604 \times 10^{-8}T^2 - 3.593 \times 10^{-12}T^3$

Pathway: $\text{H}_2\text{O}(\text{v}, 30^\circ\text{C}, 0.0424 \text{ bar}) \rightarrow \text{H}_2\text{O}(\text{v}, 350^\circ\text{C}, 0.0424 \text{ bar}) \rightarrow \text{H}_2\text{O}(\text{v}, 350^\circ\text{C}, 1.5 \text{ bar})$

Assume ideal-gas behavior. From Eq. (8.3-10a),

$$\Delta\hat{H} \approx \int_{30}^{350} [33.46 \times 10^{-3} + 0.6880 \times 10^{-5}T + 0.7604 \times 10^{-8}T^2 - 3.593 \times 10^{-12}T^3] dT$$

=

$$= 11.2 \text{ kJ / mol}$$

Q: Where did we use the assumption of ideal-gas behavior?

A: _____

- (c) Using APEx:

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- (d) Which estimate is more accurate, and why?

Process Type 3: Change phase at constant T, P (Section 8.4)

Latent Heat: enthalpy change associated with a phase transition (melting, vaporization, sublimation)

- (a) Solid to liquid : $A(s, T_m, 1 \text{ atm}) \rightarrow A(l, T_m, 1 \text{ atm})$, $\Delta\hat{H} = \Delta\hat{H}_m$ where :

T_m = normal melting point (Table B.1)

$\Delta\hat{H}_m$ = heat of fusion (melting) at T_m (Table B.1 or APEX function H_m)

$$\Delta\hat{U}_m \approx \Delta\hat{H}_m \quad (8.4-1)$$

What about liquid \rightarrow solid transition (freezing)? $\Delta\hat{H} = -\Delta\hat{H}_m$

- (b.) Liquid to vapor : $A(l, T_b, 1 \text{ atm}) \rightarrow A(v, T_b, 1 \text{ atm})$, $\Delta\hat{H} = \Delta\hat{H}_v$ where :

T_b = normal boiling point (Table B.1 or APEX function T_b)

$\Delta\hat{H}_v$ = heat of vaporization at T_b (Table B.1 or APEX function H_v)

$$\Delta\hat{U}_v \approx \Delta\hat{H}_v - \Delta P\hat{V} \approx \Delta\hat{H}_v - RT_b \quad (8.4-2)$$

What about vapor \rightarrow liquid transition (condensation)? $\Delta\hat{H} = \underline{\hspace{2cm}}$

- **Correlations for estimation of latent heats** $\Delta\hat{H}_v, \Delta\hat{H}_m$: Section 8.4b. Use Trouton's Rule and Watson's Correlation when you can't find the data in Table B.1. (See Example 8.4-3.)

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In most problems, we *neglect kinetic energy and potential energy*. Let's see why:

- (a) Calculate how much energy (kJ) is required to heat a bottle containing 300 mL of liquid water from room temperature (20 °C) to its normal boiling point (100 °C), while still remaining a liquid.

- (b) Calculate how much energy is required to heat a bottle containing 300 mL of liquid water at 100 °C, changing it from liquid to vapor.

- (c) Adding the two values calculated in parts (a) and (b), if that amount of energy was instead dedicated to accelerating the bottle of water, what would the final velocity be (miles per hour)?

- (d) Adding the two values calculated in parts (a) and (b), if that amount of energy was instead dedicated to lifting the bottle of water, what would the final height (meters)?

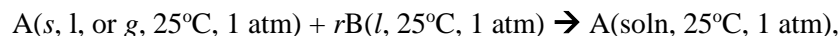
You can see in this example that compared to the *sensible heat* and the *latent heat* terms, kinetic and potential energy effects are much smaller and can usually be neglected.

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HEATS OF SOLUTION & MIXING (Sect. 8.5)

Ideal mixture: the heat of mixing or solution equals zero (gas mixtures, mixtures of similar liquids). When mixing acids and bases or dissolving certain gases or solids in a liquid solvent, the heat of mixing/solution may be far from zero.

Heat of Solution (dissolving a solid or gas in a liquid or mixing two liquids):



$$\Delta\hat{H} = \Delta\hat{H}_s(r) \frac{\text{kJ}}{\text{mol } A}$$

- A is the *solute* and B is the *solvent*. r = moles of solvent per mole of solute.

Q: What is the mole fraction of solute in terms of r ? **A:** $y_{\text{solute}} = \frac{r}{1+r}$

Values of $\Delta\hat{H}_s$ for aqueous solutions of HCl(g) (hydrochloric acid), NaOH (caustic soda), and H₂SO₄ (sulfuric acid) are given in Table B.11. Note that the unit of $\Delta\hat{H}_s$ is kJ/(mol of solute), so to calculate ΔH (kJ) or $\Delta\dot{H}$ (kJ/s) for formation of a solution at 25°C from a solute and solvent at 25°C, multiply $\Delta\hat{H}_s$ by # moles of *solute*, not total solution.

- Example: Calculate ΔH for a process in which 2.0 mole of NaOH is dissolved in 400 mol H₂O at 25°C.



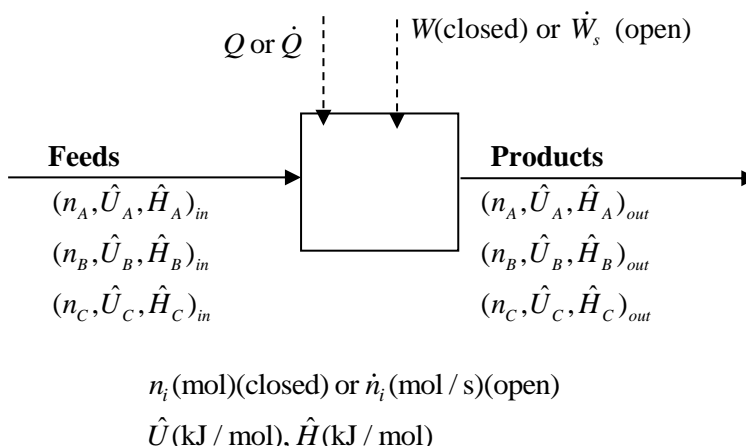
- What does $\Delta\hat{H}_s$ represent physically? It's the energy required to break solute-solute molecular bonds (strong for solids, moderate for liquids, negligible for gases) & solvent-solvent bonds minus energy released when solute-solvent bonds are formed (may be strong, moderate, or negligible)
- Values of $\Delta\hat{H}_s$ in Table B.11 are negative (the solution is at a lower energy level than the pure solute & solvent) \Rightarrow mixing & solution for the given solutes are *exothermic* \Rightarrow energy is released by the solution process. Unless you cool the mixer, the solution gets hot. Think about what happens when you mix acid with water.
- Another representation of the heat of mixing is the *enthalpy-concentration diagram*; two examples are given in Figure 8.5-1 (for aqueous sulfuric acid solutions) and Figure 8.5-2 (for solutions of ammonia in water). Example: Find the specific enthalpy of a 40 wt% solution of H₂SO₄ at 120 F relative to pure sulfuric acid at 77°F and pure water at 32°F (the reference conditions for Fig. 8.5-1).

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- Energy balances on processes involving mixing and solution are done in the same way used for other types of systems. References for enthalpy calculations are usually the pure solvent and solute at the conditions for which the heat of solution is known. If a reactant or product solution is at a different temperature, the process path for the enthalpy calculation is first to form the solution from the solute and solvent at 25°C and 1 atm (the usual reference conditions), and then heat the solution to its state in the process. See Example 8.5-1.

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Strategy for Solving the General Nonreactive System Energy Balance



Given information about

- (i) states (phase, T , P)
- (ii) amounts or flow rates (n) of feed and product components (A,B,C) (or equivalently, total amounts or flow rates and component fractions)
- (iii) Q
- (iv) W or \dot{W}_s

calculate the remaining variables.

Procedure:

- (v) *Draw and label the flowchart.* Include state information in the labeling, and label Q and W or \dot{W}_s unless you know they equal zero.
- *Perform a degree-of-freedom analysis.* Include one energy balance along with material balances and other relations when counting equations. If you don't get 0 degrees of freedom, try to figure out what's missing or if go to another subsystem if there are multiple units in the process.
- *Write all equations but the energy balance.*
 - If Q or W is unknown, you should be able to solve the equations for the unknown variables in them. If you plan to use Solver, you don't need to do anything at this point beyond writing the equations.
 - If Q and W or \dot{W}_s are given in the problem statement or known to be zero, write the energy balance equation and solve it simultaneously with the other equations.
- *Choose reference states for each species in the system for \hat{U} and \hat{H} calculations.*
 - For water, if you plan to use steam tables, choose $\text{H}_2\text{O}(\text{l}, \text{triple point})$.
 - For a gaseous species listed in Table B.8, choose the species at 25°C and 1 atm (the reference state used in the table). For Table B.9 (American engineering units), choose the species at 77°F and 1 atm.
 - Otherwise, choose the species in one of its feed or product states, so you can set at least one

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specific internal energy or enthalpy equal to zero.

- Prepare an inlet-outlet internal energy (closed) or enthalpy (open) table. The enthalpy table is shown below as an illustration.

References: A(state), B(state), C(state) (Fill in the reference states)

Species	\dot{n}_{in}	\hat{H}_{in}	\dot{n}_{out}	\hat{H}_{out}	
A	\dot{n}_a	\hat{H}_a	\dot{n}_d	\hat{H}_d	$\dot{n}(\text{mol} / \text{s})$
B	\dot{n}_b	\hat{H}_b	\dot{n}_e	\hat{H}_e	$\hat{H}(\text{kJ} / \text{mol})$
C	\dot{n}_c	\hat{H}_c	\dot{n}_f	\hat{H}_f	

- State = T, P, phase
- If a species exists in more than one inlet or outlet state in the process (e.g., in liquid and vapor phases), add extra rows to the table to make room for the flow rate and enthalpy in each state (phase), e.g. separate rows for B(l), B(v), T(l), T(v)
- Cross out cells that don't correspond to any inlet or outlet states, and replace the component flow rates in the table (\dot{n}_{A1} , \dot{n}_{B2} , etc.) with known values and variable names from the flow chart.
- Set $\hat{H} = 0$ for inlet and outlet species at their reference states, and label all unknown specific enthalpies.
- For a closed system, use amounts rather than flow rates and internal energies rather than enthalpies.
- Write and simplify the energy balance equation and substitute series expressions for $\Delta\hat{H}$ or ΔU , filling in values and labeled quantities from the enthalpy table.

$$Q = \Delta H = \left(\sum \dot{n} \hat{H} \right)_{out} - \left(\sum \dot{n} \hat{H} \right)_{in} = \dot{n}_d \hat{H}_d + \dot{n}_e \hat{H}_e + \dot{n}_f \hat{H}_f - \dot{n}_a \hat{H}_a - \dot{n}_b \hat{H}_b - \dot{n}_c \hat{H}_c$$

- Write expressions for all of the unknown specific enthalpies in the table. Calculate

$$\hat{H}_a \text{ as } \Delta\hat{H} \text{ for the process A(reference state)} \rightarrow \text{A(inlet state)}$$

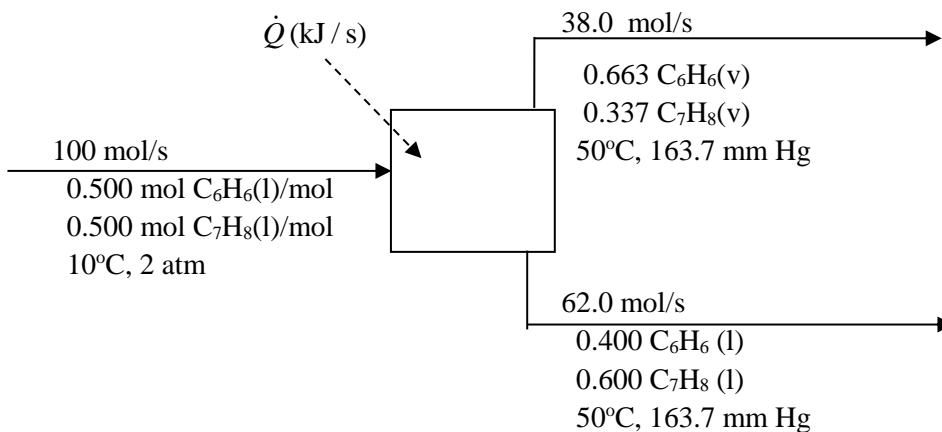
$$\hat{H}_d \text{ as } \Delta\hat{H} \text{ for the process A(reference state)} \rightarrow \text{A(outlet state)}$$

and similarly for B, C,.... (For closed systems, replace H with U .)

- Substitute the expressions for the enthalpies in the energy balance, which may now be solved simultaneously with the other system equations.

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Example: Inlet-outlet enthalpy (or internal energy) table (solve for Q)



References: $\text{C}_6\text{H}_6(\text{l}, 10^\circ\text{C}, 2 \text{ atm})$, $\text{C}_7\text{H}_8(\text{v}, 50^\circ\text{C}, 163.7 \text{ mm Hg})$

Species	n_{in}	\hat{H}_{in}	n_{out}	\hat{H}_{out}	
$\text{C}_6\text{H}_6(\text{l})$	50	\hat{H}_a	24.8	\hat{H}_c	$n(\text{mol/s})$
$\text{C}_6\text{H}_6(\text{v})$	—	—	25.2	\hat{H}_d	$\hat{H}(\text{kJ/mol})$
$\text{C}_7\text{H}_8(\text{l})$	50	\hat{H}_b	37.2	\hat{H}_e	
$\text{C}_7\text{H}_8(\text{v})$	—	—	12.8	\hat{H}_f	

\hat{H}_a path : at reference, = 0

\hat{H}_b path : $\text{T}(\text{v}, 50^\circ\text{C}, 163.7 \text{ mm Hg}) \rightarrow \text{T}(\text{v}, 50^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{T}(\text{v}, 110^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{T}(\text{l}, 110^\circ\text{C}, 1 \text{ atm})$
 $\rightarrow \text{T}(\text{l}, 10^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{T}(\text{l}, 10^\circ\text{C}, 2 \text{ atm})$

\hat{H}_c path : $\text{B}(\text{l}, 10^\circ\text{C}, 2 \text{ atm}) \rightarrow \text{B}(\text{l}, 50^\circ\text{C}, 2 \text{ atm}) \rightarrow \text{B}(\text{l}, 50^\circ\text{C}, 163.7 \text{ mm Hg})$

\hat{H}_d path : $\text{B}(\text{l}, 10^\circ\text{C}, 2 \text{ atm}) \rightarrow \text{B}(\text{l}, 80.1^\circ\text{C}, 2 \text{ atm}) \rightarrow \text{B}(\text{l}, 80.1^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{B}(\text{v}, 80.1^\circ\text{C}, 1 \text{ atm})$
 $\rightarrow \text{B}(\text{v}, 50^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{B}(\text{v}, 50^\circ\text{C}, 163.7 \text{ mm Hg})$

\hat{H}_e path : $\text{T}(\text{v}, 50^\circ\text{C}, 163.7 \text{ mm Hg}) \rightarrow \text{T}(\text{v}, 50^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{T}(\text{v}, 110^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{T}(\text{l}, 110^\circ\text{C}, 1 \text{ atm})$
 $\rightarrow \text{T}(\text{l}, 50^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{T}(\text{l}, 50^\circ\text{C}, 163.7 \text{ mm Hg})$

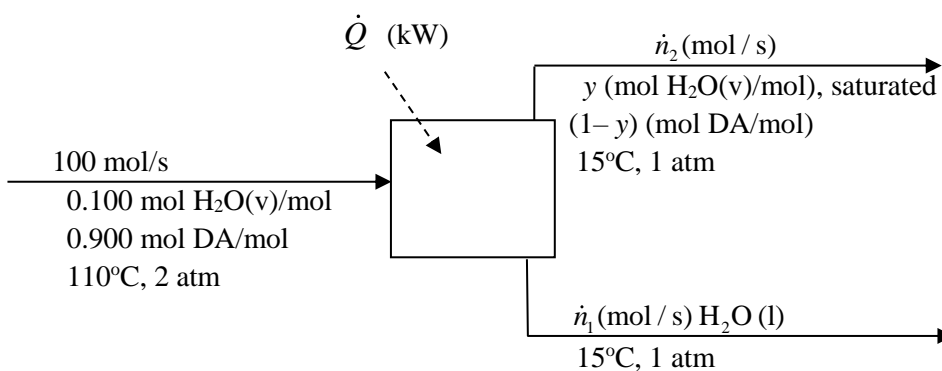
\hat{H}_f path : at reference, = 0

Section 6: F&R, Ch. 8 (Energy Balances – II)

Write expressions for all the specific enthalpies in the table and then the energy balance. State all your assumptions.

Section 6: F&R, Ch. 8 (Energy Balances – II)

Example: Continuous air conditioning process. Take basis of 100 mol/s feed. Calculate \dot{Q} .



Question: What sign should the value of \dot{Q} have?

Solution: Assume enthalpies are independent of pressure.

(a) **DOF Analysis:** _____ unknowns:

_____ equations:

(b) **Write all equations but energy balance.** Circle unknowns for which you would solve.

(c) **Choose references and prepare an inlet-outlet enthalpy table.**

References: H₂O(l, 15°C, 1 atm), DA(g, 25°C, 1 atm) (Why?)

Species	\dot{n}_{in}	\hat{H}_{in}	\dot{n}_{out}	\hat{H}_{out}	
H ₂ O(l)	—	—	\dot{n}_1	\hat{H}_c	\dot{n} (mol/s)
H ₂ O(v)	10	\hat{H}_a	$\dot{n}_2 y$	\hat{H}_d	\hat{H} (kJ/mol)
DA	90	\hat{H}_b	$\dot{n}_2 (1-y)$	\hat{H}_e	

(d) Write and simplify the energy balance equation, substituting values and labeled variables from the enthalpy table.

Section 6: F&R, Ch. 8 (Energy Balances – II)

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

- (e) Write expressions for each labeled specific enthalpy, using data in Tables B.2 and B.8. The first step is partially shown below as an illustration.

$$\hat{H}_a : \text{H}_2\text{O}(\text{l}, 15^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{l}, 100^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{v}, 100^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{v}, 110^\circ\text{C})$$

$$\Rightarrow \hat{H}_a =$$

Q: Why 100°C? **A:** _____

Continue with the remaining enthalpies in the table.

The values of the specific enthalpies may be substituted into the energy balance, which may then be solved together with the other system equations to determine \dot{Q} (kW).

Psychrometric Chart (Section 8.4d)

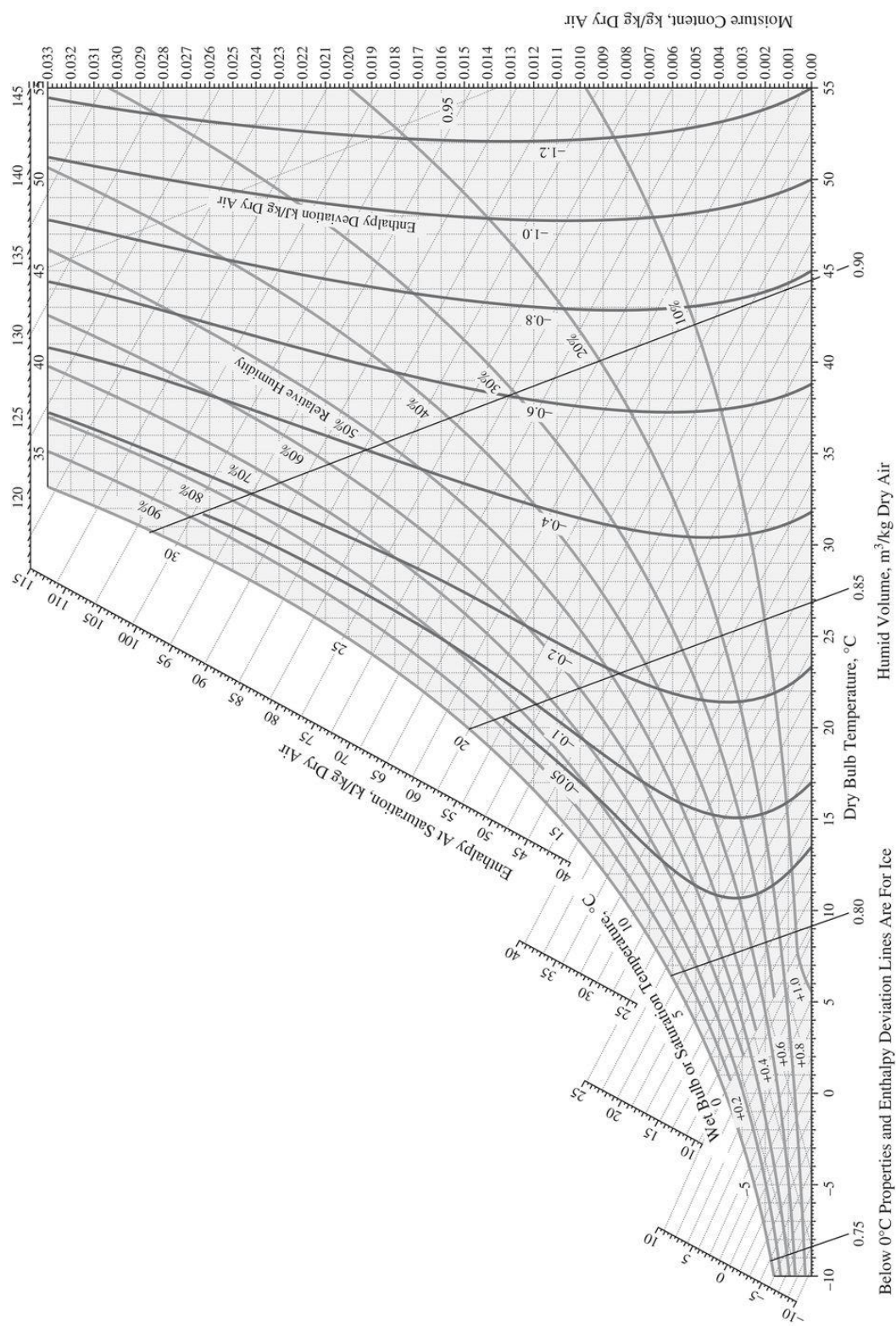


Figure 8.4-1
Psychrometric chart—SI units. Reference states: H₂O (liquid, 0°C, 1 atm), dry air (0°C, 1 atm). (Data obtained from Carrier Corporation.)

Section 6: F&R, Ch. 8 (Energy Balances – II)

Section 6: F&R, Ch. 8 (Energy Balances – II)

Why does it work? Gibbs phase rule for humid air gives

$$F = 2 + \text{components} - \text{phases} = 2 + 2 - 1 = 3$$

If we fix the system pressure at 1 atm, then we can specify any 2 intensive variables and determine all the other intensive system properties. These are the properties you can look up on the chart:

- a. **Dry bulb temperature:** Temperature as measured by a thermometer, thermocouple, etc.
- b. **Absolute humidity:** h_A ($\text{lb}_m \text{H}_2\text{O}/\text{lb}_m \text{DA}$) (also called moisture content). In terms of this quantity, the mass fraction of water is
$$y_i = \frac{h_a}{1 + h_a}$$
- c. **Relative humidity:**
$$h_r = 100 \frac{P_{H_2O}}{P_{H_2O}^*(T)}$$
- d. **Dew point temperature:** Temperature at which humid air becomes saturated if cooled at constant pressure. Follow any point horizontally to the left until you reach the saturation curve.
- e. **Humid volume:** \hat{V}_H ($\text{m}^3 / \text{kg DA}$) - volume accompanied by 1 $\text{lb}_m \text{DA}$ plus the water vapor that accompanies it
- f. **Wet bulb temperature:** T_{wb} – temperature reading on a thermometer with a water-saturated wick around the bulb immersed in a flowing stream of humid air. (*Why do you feel cold when you step out of the shower or pool?*)
- g. **Specific enthalpy of saturated air:** $\text{Btu}/\text{lb}_m \text{DA}$
- h. **Enthalpy deviation:** Used to determine the enthalpy of humid air that is not saturated. Subtract enthalpy deviation from specific enthalpy of saturated air, which you find by following the wet bulb temperature line to the saturation line.

Example: Use the psychrometric chart to estimate the following properties of humid air at 41°C and 10% relative humidity:

- Absolute humidity
- Wet-bulb temperature
- Humid volume
- Dew point
- Specific enthalpy

What is the amount of water in 150 m^3 of air at these conditions?

REVIEW OF KEY FORMULAS AND PROCEDURES IN CHAPTER 8

First law of thermodynamics (energy balance equation):

$$Q + W = \Delta U + \Delta E_k + \Delta E_p \quad [\text{Closed (batch) system}]$$

$$\dot{Q} + \dot{W}_s = \Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p \quad [\text{Open (continuous) steady - state system}]$$

where

$$\Delta U = \sum_{\substack{\text{species,} \\ \text{states}}} m_{\text{final}} \hat{U}_{\text{final}} - \sum_{\substack{\text{species,} \\ \text{states}}} m_{\text{initial}} \hat{U}_{\text{initial}}$$

$$\Delta \dot{H} = \sum_{\substack{\text{output} \\ \text{streams}}} \dot{m}_{\text{out}} \hat{H}_{\text{out}} - \sum_{\substack{\text{input} \\ \text{streams}}} \dot{m}_{\text{in}} \hat{H}_{\text{in}} \quad [\text{where } \hat{H} = \hat{U} + P\hat{V}]$$

$$\Delta \dot{E}_k = \sum_{\substack{\text{output} \\ \text{streams}}} \frac{1}{2} \dot{m}_{\text{out}} (u_{\text{out}})^2 - \sum_{\substack{\text{input} \\ \text{streams}}} \frac{1}{2} \dot{m}_{\text{in}} (u_{\text{in}})^2 \quad [\text{where } u(\text{m/s}) = \text{velocity}]$$

$$\Delta \dot{E}_p = \sum_{\substack{\text{output} \\ \text{streams}}} \dot{m}_{\text{out}} g z_{\text{out}} - \sum_{\substack{\text{input} \\ \text{streams}}} \dot{m}_{\text{in}} g z_{\text{in}} \quad [\text{where } z = \text{height}]$$

Determining kinetic and potential energy changes is straightforward (usually neglect both unless there's a big velocity change from inlet to outlet and no reactions, phase changes, or large temperature changes). Most problems in this course come down to determining values of ΔU or $\Delta \hat{H}$ for a given process & substituting it in the energy balance equation to determine heat. To do that, need to evaluate changes in \hat{U} or \hat{H} for each species in the process inlet and outlet streams.

Section 6: F&R, Ch. 8 (Energy Balances – II)

Process Type 1: Change P at constant T in a single phase (Section 8.2)

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

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

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

Process Type 2: Change T at constant P in a single phase (Section 8.3)

$$\Delta \hat{H} = \hat{H}_2 - \hat{H}_1 \quad [\text{if you have tabulated enthalpies, as you do for water \& species in Tables B.8 \& B.9}]$$

$$= \int_{T_1}^{T_2} C_p dT \quad [\text{exact for ideal gases with varying } P, \text{ any gas at constant } P.]$$

$$= \int_{T_1}^{T_2} C_p dT + \hat{V} \Delta P \quad [\text{liquids and solids}]$$

$$\Delta \hat{U} = \Delta \hat{H} - \Delta P \hat{V} \quad [\text{by definition}]$$

$$= \Delta \hat{H} - R \Delta T \quad (\text{ideal gases - be able to derive})$$

$$= \int_{T_1}^{T_2} C_v dT \quad [\text{exact for ideal gases or constant } \hat{V}, \text{ otherwise approximate}]$$

where

$$C_v = C_p - R \quad (\text{ideal gases})$$

$$\approx C_p \quad (\text{liquids and solids})$$

To evaluate $\int_{T_1}^{T_2} C_p dT$, integrate formula in Table B.2 term by term or (faster) use APEX property database.

Estimation of C_p for solids, liquids, mixtures—Section 8.3c.

Process Type 3: Change phase at constant T, P (Section 8.4)

$$A(s, T_m, 1 \text{ atm}) \rightarrow A(l, T_m, 1 \text{ atm}), \quad \Delta \hat{H} = \Delta \hat{H}_m$$

$$A(l, T_b, 1 \text{ atm}) \rightarrow A(v, T_b, 1 \text{ atm}), \quad \Delta \hat{H} = \Delta \hat{H}_v$$

where

- T_m = normal melting point, $\Delta \hat{H}_m$ = heat of fusion (melting) at T_m (Table B.1)

$$\Delta \hat{U}_m \approx \Delta \hat{H}_m$$

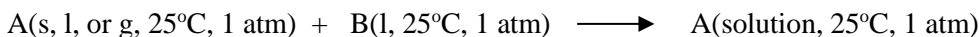
- T_b = normal boiling point, $\Delta \hat{H}_v$ = heat of vaporization at T_b (Table B.1)

$$\Delta \hat{U}_v \approx \Delta \hat{H}_v - RT_b$$

- Estimation of latent heats—Section 8.4b.

Section 6: F&R, Ch. 8 (Energy Balances – II)

Process Type 4: Mix two liquids or dissolve a solid or gas in a liquid at constant T, P (Section 8.5)



- $\Delta\hat{H} = \Delta\hat{H}_s(r) \frac{\text{kJ}}{\text{mol solute (A)}} \text{ heat of mixing or solution}$
- Found in Table B.11 or APEx functions HsHCL, HsNaOH, and HmH2SO4

Process Type 5: Reaction at constant T, P (Chapter 9)

Procedure for energy balance problems

1. Draw and label flow chart, do DOF analysis (if Q or W is given or is to be calculated, count it as a variable and count the energy balance as an equation).
2. Do the material balance calculations
3. Write the appropriate form of the energy balance equation and eliminate terms that are zero or negligible. Calculate nonzero kinetic and potential energy changes.
4. Choose reference states for each process species. If you're going to use tabulated enthalpies for a species, choose the same reference state used to generate the table (e.g. liquid at the triple point for water if you're going to use the steam tables, or gas at 25°C and 1 atm if you're going to use Table B.8).
5. Prepare an inlet-outlet enthalpy table (or internal energy table for closed systems), labeling all enthalpies that cannot be set to zero. (If the species is at its reference state in the process, its enthalpy is zero.)
6. Construct process paths from the reference state to each inlet and outlet state, calculate the associated enthalpy changes, and substitute them in the table.
7. Calculate $\Delta\hat{H}$ or ΔU and substitute it in the energy balance to determine heat or work.