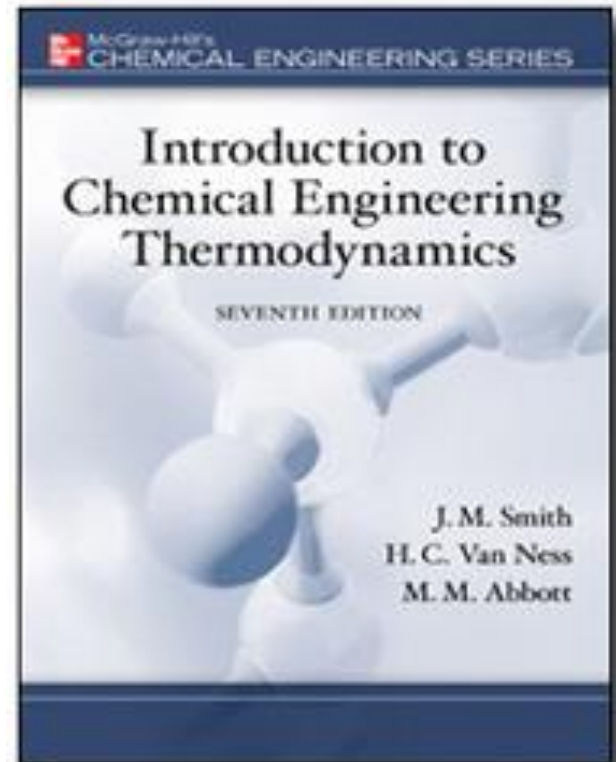


Chapter 4. Heat Effects



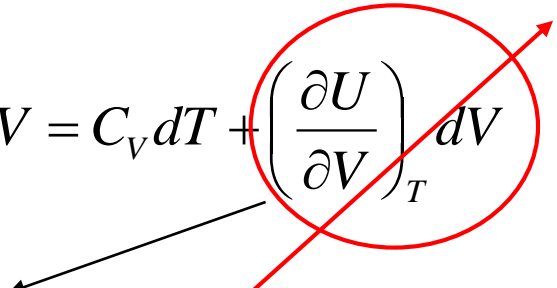
Introduction

□ Heat Transfer – Common operation in chemical industry

- Sensible Heat effect
- Latent Heat
- Heat of Reaction
- Heat of Mixing, Heat of Solution → *Covered later
(Thermodynamics II)*

4.1 Sensible Heat Effects

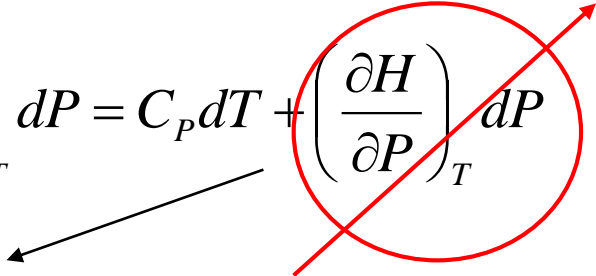
- Heat transfer to system with no phase transition, no reaction, no change in composition → ***T*** changes

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$
A red circle is drawn around the term $\left(\frac{\partial U}{\partial V} \right)_T dV$ in the equation. A red arrow points from the top right of the circle towards the top right, indicating it is to be removed. A black arrow points from the bottom left of the circle towards the text box below.

- Constant volume process
- Ideal gases
- Approximately zero for low-pressure gases

$$dU = C_V dT \qquad \Delta U = \int_{T_1}^{T_2} C_V dT$$

4.1 Sensible Heat Effects

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$


- **Constant pressure process**
- **Ideal gases**
- **Approximately zero for low-pressure gases**

$$dH = C_P dT \quad \Delta H = \int_{T_1}^{T_2} C_P dT$$

4.1 Sensible Heat Effect

□ Expressions for constant pressure heat capacities

- Heat capacity for a substance is a function of T and P

- Calculation of Fluid properties

- Based on ideal gas : Ideal gas properties
- Departure from ideal gas : residual properties

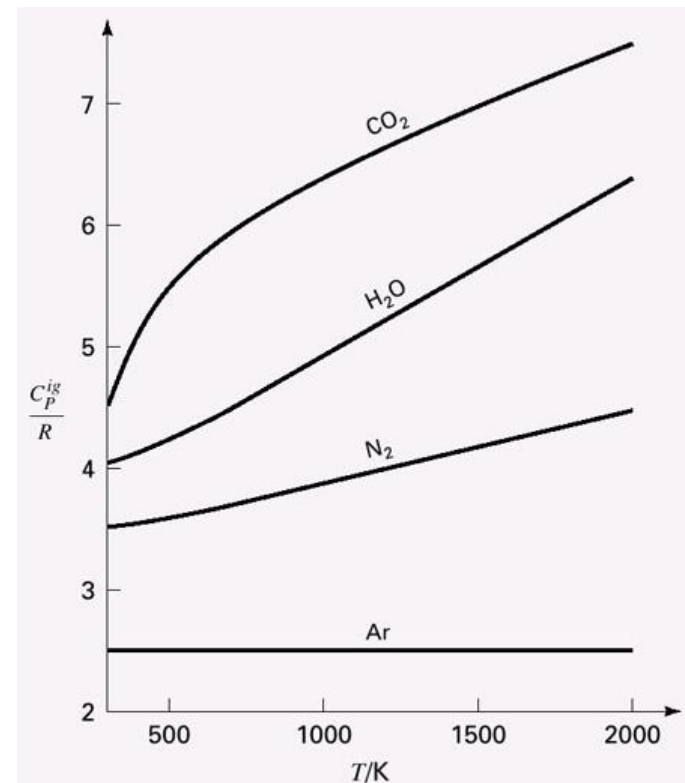
- Ideal Gas Heat Capacity

- Heat capacity at $P \rightarrow 0$
- Valid for low pressure gases

$$C_V = C_P - R$$

$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

Values A, B, C, and D for many chemical substances → Table C.1



Mean Heat Capacity

□ Calculation of enthalpy value

- evaluation of integrals are required

$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} (A + BT + CT^2 + DT^{-2}) dT \\ &= \left[AT + \frac{BT^2}{2} + \frac{CT^3}{3} - DT^{-1} \right]_{T_1}^{T_2}\end{aligned}$$

□ Mean Heat Capacity

$$\bar{C}_p(T_1 \rightarrow T_2) = \frac{H_2 - H_1}{T_2 - T_1} = \frac{\int_{T_1}^{T_2} C_p dT}{T_2 - T_1}$$

$$\Delta H = \bar{C}_p (T_2 - T_1)$$

—————> Always two temperature values are required !

Mean Heat Capacity

□ Tabulation

- Based on a reference temperature T_{ref}

표 8-3-1 연소기체의 평균 열용량 : SI 단위계*

\bar{C}_p (J/mol·°C)

Reference state : $P_{ref} = 1\text{atm}$, $T_{ref} = 25^\circ\text{C}$

$T(^{\circ}\text{C})$	Air	O ₂	N ₂	H ₂	CO	CO ₂	H ₂ O
0	28.94	29.24	29.03	28.84	29.00	36.63	33.55
25	29.05	29.39	29.06	28.84	29.06	37.15	33.63
100	29.21	29.80	29.16	28.86	29.23	38.63	33.92
200	29.45	30.32	29.32	28.90	29.47	40.45	34.34
300	29.71	30.80	29.52	28.95	29.72	42.10	34.80
400	29.97	31.24	29.74	29.03	29.99	43.59	35.29
500	30.25	31.65	29.98	29.12	30.27	44.93	35.81
600	30.53	32.02	30.24	29.23	30.56	46.14	36.36
700	30.81	32.39	30.51	29.35	30.85	47.23	36.92
800	31.10	32.71	30.79	29.48	31.14	48.20	37.49
900	31.38	33.02	31.07	29.63	31.42	49.07	38.08
1000	31.65	33.30	31.34	29.78	31.70	49.85	38.66
1100	31.92	33.55	31.62	29.94	31.97	50.54	39.24
1200	32.18	33.79	31.88	30.12	32.23	51.18	39.81
1300	32.42	34.02	32.13	30.29	32.47	51.75	40.37
1400	32.65	34.23	32.37	30.47	32.69	52.28	40.91
1500	32.85	34.42	32.58	30.66	32.89	52.77	41.42

Mean Heat Capacity

□ Calculation of Enthalpy

$$\Delta H = \bar{C}_p (T_2 - T_1)$$

$$\Delta H(T_1 \rightarrow T_2) = \Delta H(T_{ref} \rightarrow T_2) - \Delta H(T_{ref} \rightarrow T_1)$$

$$\Delta H = (\bar{C}_p)_{T_2} (T_2 - T_{ref}) - (\bar{C}_p)_{T_1} (T_1 - T_{ref})$$

Enthalpy Calculation

1. Heat Capacity $\Delta H = \int_{T_1}^{T_2} C_P dT = \int_{T_1}^{T_2} (A + BT + CT^2 + DT^{-2}) dT$

2. Table $\Delta H = \sum n_{\text{out}} \hat{H}_{\text{out}} - \sum n_{\text{in}} \hat{H}_{\text{in}}$ \hat{H} : Specific enthalpy (from table)

3. Mean heat capacity $\Delta H = \bar{C}_p (T_2 - T_1)$

□ **Heat capacity for mixtures**

$$C_{pm}(T) = \sum y_i C_{pi}(T) \quad y_i \rightarrow \text{mole fraction of } i$$

$$\Delta H = \int_{T_1}^{T_2} C_{pm}(T) dT$$

Evaluation of the Sensible-Heat Integral

Evaluation of the integral $\int C_P dT$ is accomplished by substitution for C_P as a function of T , followed by formal integration. For temperature limits of T_0 and T the result is conveniently expressed as:

$$\int_{T_0}^T \frac{C_P}{R} dT = AT_0(\tau - 1) + \frac{B}{2}T_0^2(\tau^2 - 1) + \frac{C}{3}T_0^3(\tau^3 - 1) + \frac{D}{T_0} \left(\frac{\tau - 1}{\tau} \right) \quad (4.7)$$

where

$$\tau \equiv \frac{T}{T_0}$$

Given T_0 and T , the calculation of Q or ΔH is straightforward. Less direct is the calculation of T , given T_0 and Q or ΔH . Here, an iteration scheme may be useful. Factoring $(\tau - 1)$ from each term on the right-hand side of Eq. (4.7) gives:

$$\int_{T_0}^T \frac{C_P}{R} dT = \left[AT_0 + \frac{B}{2}T_0^2(\tau + 1) + \frac{C}{3}T_0^3(\tau^2 + \tau + 1) + \frac{D}{\tau T_0} \right] (\tau - 1)$$

Because

$$\tau - 1 = \frac{T - T_0}{T_0}$$

this may be written:

$$\int_{T_0}^T \frac{C_P}{R} dT = \left[A + \frac{B}{2}T_0(\tau + 1) + \frac{C}{3}T_0^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2} \right] (T - T_0)$$

We identify the quantity in square brackets as $\langle C_P \rangle_H / R$, where $\langle C_P \rangle_H$ is defined as a *mean heat capacity*:

$$\frac{\langle C_P \rangle_H}{R} = A + \frac{B}{2}T_0(\tau + 1) + \frac{C}{3}T_0^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2} \quad (4.8)$$

Equation (4.2) may therefore be written:

$$\Delta H = \langle C_P \rangle_H (T - T_0) \quad (4.9)$$

The angular brackets enclosing C_P identify it as a mean value; subscript “H” denotes a mean value specific to enthalpy calculations, and distinguishes this mean heat capacity from a similar quantity introduced in the next chapter.

Solution of Eq. (4.9) for T gives:

$$T = \frac{\Delta H}{\langle C_P \rangle_H} + T_0 \quad (4.10)$$

A starting value for T (and hence for $\tau = T/T_0$) allows evaluation of $\langle C_P \rangle_H$ by Eq. (4.8). Substitution of this value into Eq. (4.10) provides a new value of T from which to reevaluate $\langle C_P \rangle_H$. Iteration continues to convergence on a final value of T .

Use of Defined Functions

The integral $\int (C_P/R) dT$ often appears in thermodynamic calculations. As a matter of convenience, we therefore define the right side of Eq. (4.7) as the function, $\text{ICPH}(T_0, T; A, B, C, D)$, and write a computer routine for its evaluation. Equation (4.7) then becomes:

$$\int_{T_0}^T \frac{C_P}{R} dT \equiv \text{ICPH}(T_0, T; A, B, C, D)$$

The function name is **ICPH**, and the quantities in parentheses are the variables T_0 and T , followed by parameters A , B , C , and D . When these quantities are assigned numerical values, the notation represents a value for the integral. Thus, for the evaluation of Q in Ex. 4.2:

$$Q = 8.314 \times \text{ICPH}(533.15, 873.15; 1.702, 9.081\text{E-}3, -2.164\text{E-}6, 0.0) = 19,778 \text{ J}$$

Representative computer programs for evaluation of the integral are given in App. D. For added flexibility the programs also evaluate the dimensionless quantity $\langle C_P \rangle_H / R$ as given by Eq. (4.8). The right-hand side of this equation is another function, **MCPH**($T_0, T; A, B, C, D$). With this definition, Eq. (4.8) becomes:

$$\frac{\langle C_P \rangle_H}{R} = \text{MCPH}(T_0, T; A, B, C, D)$$

A specific numerical value of this function is:

$$\text{MCPH}(533.15, 873.15; 1.702, 9.081\text{E-}3, -2.164\text{E-}6, 0.0) = 6.9965$$

representing $\langle C_P \rangle_H / R$ for methane in the calculation of Ex. 4.2. By Eq. (4.9),

$$\Delta H = (8.314)(6.9965)(873.15 - 533.15) = 19,778 \text{ J}$$

Example 4.2

Calculate the heat required to raise the temperature of 1 mol of methane from 260 to 600°C in a steady-flow process at a pressure sufficiently low that methane may be considered an ideal gas.

Solution 4.2

Equation (4.3) in combination with Eq. (4.7) provides the required result. Parameters for C_P^{ig}/R come from Table C.1; temperatures are:

$$T_0 = 533.15 \text{ K} \qquad T = 873.15 \text{ K} \qquad \tau = \frac{873.15}{533.15} = 1.6377$$

Whence,
$$Q = \Delta H = R \int_{533.15}^{873.15} \frac{C_P^{ig}}{R} dT$$

$$Q = (8.314) \left[1.702 T_0 (\tau - 1) + \frac{9.081 \times 10^{-3}}{2} T_0^2 (\tau^2 - 1) - \frac{2.164 \times 10^{-6}}{3} T_0^3 (\tau^3 - 1) \right] = 19,778 \text{ J}$$

Example 4.2

- Calculate the heat required to raise the temperature of 1 mol of methane from 260 °C to 600 °C in a steady-flow process at a pressure sufficiently low that methane may be considered as an ideal gas.

Energy balance for steady-state flow

$$\Delta \left[\left(H + \frac{1}{2}u^2 + zg \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s \longrightarrow \Delta H = Q$$

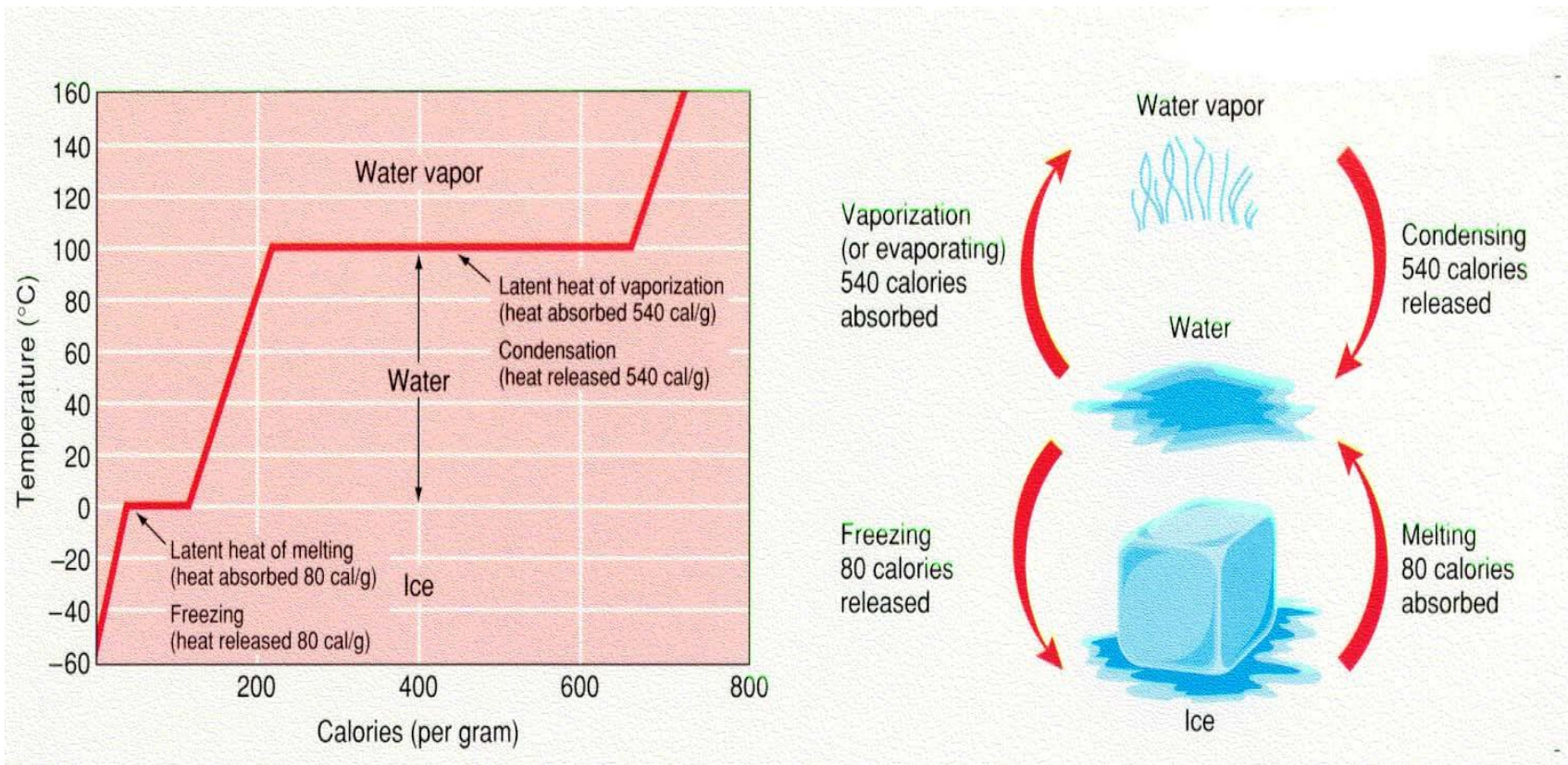
From Table C.1

$$\bar{C}_{p,CH_4} = R(1.702 + 9.081 \times 10^{-3}T - 2.164 \times 10^{-6}T^2)$$

$$Q = \Delta H = \int_{533.15}^{873.15} 8.314(1.702 + 9.081 \times 10^{-3}T - 2.164 \times 10^{-6}T^2) dT = 19,778 J$$

4.2 Latent Heat of Pure Substances

□ Heat Effects of Phase Change



Latent Heat

☐ Phase changes are usually accompanied by large changes in *U* and *H*

- fusion
- vaporization
- sublimation

☐ Latent Heat

- the enthalpy changes associated with phase transition of a unit amount of a substance applied heat goes to phase changes
- at constant *T* and *P*
- no temperature change

- Latent heat of vaporization

$$\Delta\hat{H}_v$$

- Latent heat of fusion

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

- Latent heat of sublimation

$$\Delta\hat{H}_s$$

Estimation and Correlation of Latent Heat

□ Clapeyron Equation

$$\Delta H = T\Delta V \frac{dP^{sat}}{dT}$$

slope of vapor pressure curve, volume change → heat of vaporization

- Derivation will be given in Chapter 6

Estimation and Correlation of Latent Heat

□ Standard Heat of Vaporization

- Trouton's Rule : Rough estimates (30 % accuracy for hydrocarbons)

$$\begin{aligned}\Delta\hat{H}_v \text{ (kJ/mol)} &\approx 0.088T_b \text{ (K)} \quad \text{(Non-polar liquids)} \\ &\approx 0.109T_b \text{ (K)} \quad \text{(water, alcohols)}\end{aligned}$$

- Chen's equation (2 % accuracy for hydrocarbons)

$$\Delta\hat{H}_v \text{ (kJ/mol)} = \frac{T_b (0.0331(T_b / T_c) - 0.0327 + 0.0297 \log_{10} P_c)}{1.07 - (T_b / T_c)}$$

□ Standard Heat of Fusion

$$\begin{aligned}\Delta\hat{H}_m \text{ (kJ/mol)} &\approx 0.0092T_m \text{ (K)} \quad \text{(metallic elements)} \\ &\approx 0.025T_m \text{ (K)} \quad \text{(inorganic compounds)} \\ &\approx 0.050T_m \text{ (K)} \quad \text{(organic compounds)}\end{aligned}$$

Heat of Vaporization at other temperature

□ Watson Correlation

$$\Delta H_v(T_2) = \Delta H_v(T_1) \left(\frac{T_c - T_2}{T_c - T_1} \right)^{0.38}$$

$$\Delta H_v(T_2) = \Delta H_v(T_1) \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38}$$

4.3 Standard Heat of Reaction

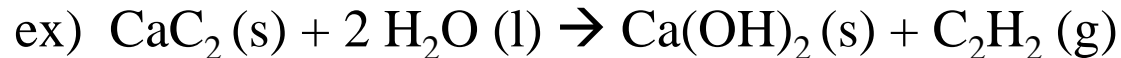
- ☐ Heat effects accompanying when reaction occur**
- ☐ Reaction may be carried out in many different ways**
 - Tabulation of all possible reactions is impossible**
 - Convenient way**
 - “Standard way” $\rightarrow Q = \Delta H$, and ΔH is the state function
 - The required data to be a minimum
 - Use Hess’s Law

Heat of Reaction

□ Heat of Reaction (Enthalpy of Reaction)

$$\Delta \hat{H}_r(T, P) = H_{\text{products}} - H_{\text{reactants}}$$

- Reactants : stoichiometric quantities
- Complete Reaction
- Reactants are fed at T, P
- Products are emerging at T, P



$$\Delta \hat{H}_r(25^\circ\text{C}, 1 \text{ atm}) = -125.4 \text{ kJ / mol}$$

Standard Condition

- ❑ A standard state is a particular state of a species at temperature T and at specified conditions of pressure, composition and physical condition as, e.g., gas, liquid or solid.

- Standard state pressure : 1 atm (101,325 Pa)
- Standard state temperature : 25 °C (298.15 K)
- Gas : The pure substance in ideal gas state at 1 bar
- Liquid and solid : The real pure liquid or solid at 1 bar

Heat of Reaction : Per mole of what ?

□ Example



$$\Delta \hat{H}_r = \frac{-50\text{kJ}}{2 \text{ mol A reacted}} = \frac{-50\text{kJ}}{1 \text{ mol B reacted}} = \frac{-50\text{kJ}}{3 \text{ mol C produced}}$$

$$\Delta H = \frac{\Delta H_r}{\nu_A} n_A$$

n_A : moles of A consumed or produced
 ν_A : the stoichiometric coefficient of A

□ Extent of Reaction, ξ

- Amount of reactants with stoichiometric coefficient of “1” that have been reacted.

$$\Delta H = \frac{\Delta H_r}{\nu_A} n_A = \Delta H_r \times \xi$$

Properties of Heat of Reaction

□ “Standard” heat of reaction ΔH_r° or $\Delta H_r(25^\circ\text{C})$

● at reference T and P (25 °C, 1 atm)

□ Exothermic : $\Delta H_r < 0$

Endothermic : $\Delta H_r > 0$

□ Value depends on stoichiometric eqn.



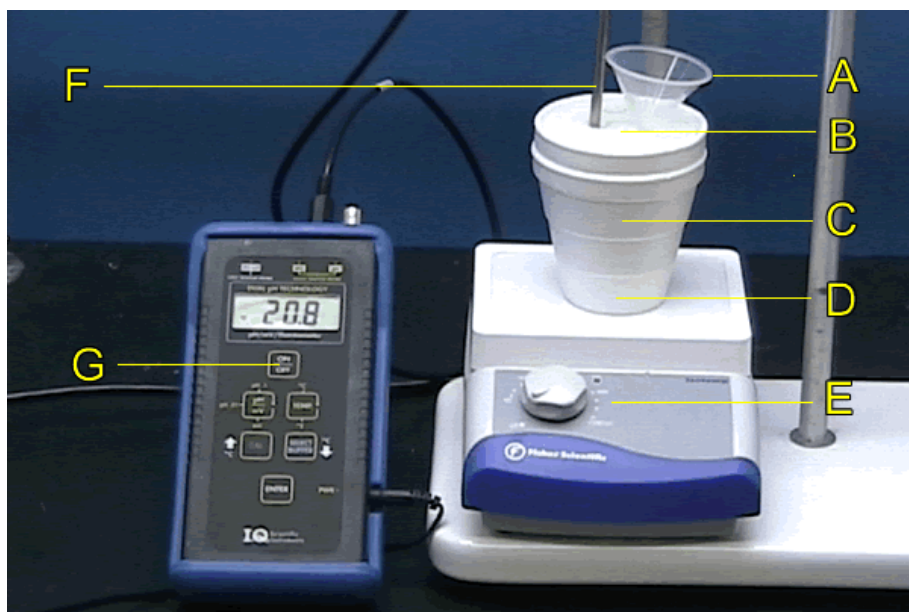
□ Value depends on the state (gas, liquid, solid)



Measurement of Heats of Reaction

☐ Measurements of heats of reaction : Calorimeter

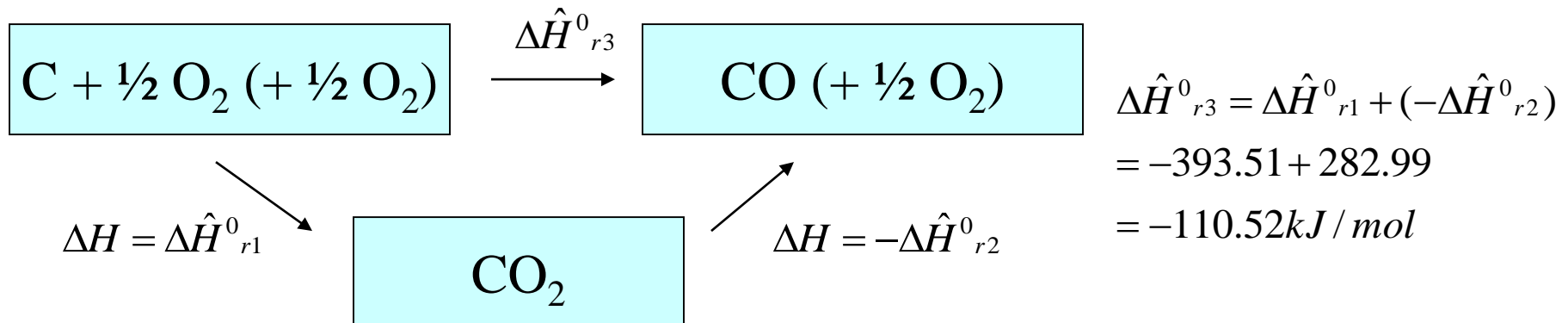
- Temperature rise or fall of the fluid can be measured and heat of reactions are determined.



- A: Small funnel
- B: Styrofoam lid
- C: Two styrofoam cups glued together
- D: Magnetic stir bar (inside the cups)
- E: Magnetic stir plate
- F: Temperature probe
- G: Thermometer

Difficulties for measuring heat of reaction

- ❑ Some reactions cannot be accomplished.
- ❑ Ex) $2\text{C} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}$ (incomplete combustion)
 - It is impossible to determine the heat of the incomplete combustion only.
 - The reaction cannot proceed at such low temperature.
- ❑ Alternative method
 - $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ $\Delta H_r = -393.51 \text{ kJ/mol}$ (Easily measured)
 - $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$ $\Delta H_r = -282.99 \text{ kJ/mol}$ (Easily measured)



Hess's Law

If the stoichiometric equation for a reaction can be obtained by algebraic operations (+, −, ×, /) on the other stoichiometric equations (2,3,...), then the heat of reaction can be obtained by performing the same operations on the heats of reactions (2,3,...).

□ *H* is state property

→ the enthalpy change for a reaction, ΔH_r , is the same whether it occurs by one step or by a series of steps.

→ Only depends on the initial and final state.

4.4 Heats of Formation

□ Formation reaction :

- Reaction which the compound is formed from its atomic constituents.
- Normally **occur in nature** (O₂ instead of O)

□ Heat of formation $\Delta\hat{H}_f$

- ΔH associated with the formation of 1 mole of the compound.
- Reference state: 25 °C and 1 atm

□ Examples

- Ammonium Nitrate :



- Benzene :



**Table C.4: Standard Enthalpies and Gibbs Energies of Formation
at 298.15 K[†]**

Joules per mole of the substance formed

Chemical species		State (Note 2)	ΔH_{f298}° (Note 1)	ΔG_{f298}° (Note 1)
Paraffins:				
Methane	CH ₄	(g)	−74,520	−50,460
Ethane	C ₂ H ₆	(g)	−83,820	−31,855
Propane	C ₃ H ₈	(g)	−104,680	−24,290
<i>n</i> -Butane	C ₄ H ₁₀	(g)	−125,790	−16,570
<i>n</i> -Pentane	C ₅ H ₁₂	(g)	−146,760	−8,650
<i>n</i> -Hexane	C ₆ H ₁₄	(g)	−166,920	150
<i>n</i> -Heptane	C ₇ H ₁₆	(g)	−187,780	8,260
<i>n</i> -Octane	C ₈ H ₁₈	(g)	−208,750	16,260
1-Alkenes:				
Ethylene	C ₂ H ₄	(g)	52,510	68,460
Propylene	C ₃ H ₆	(g)	19,710	62,205
1-Butene	C ₄ H ₈	(g)	−540	70,340
1-Pentene	C ₅ H ₁₀	(g)	−21,280	78,410
1-Hexene	C ₆ H ₁₂	(g)	−41,950	86,830
1-Heptene	C ₇ H ₁₄	(g)	−62,760	
Miscellaneous organics:				
Acetaldehyde	C ₂ H ₄ O	(g)	−166,190	−128,860
Acetic acid	C ₂ H ₄ O ₂	(l)	−484,500	−389,900
Acetylene	C ₂ H ₂	(g)	227,480	209,970
Benzene	C ₆ H ₆	(g)	82,930	129,665
Benzene	C ₆ H ₆	(l)	49,080	124,520

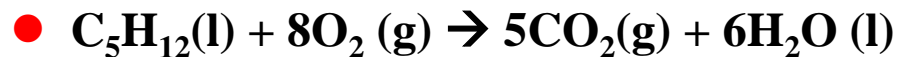
Determination of Heats of Reaction using Heats of Formation

- Heats of reactions can be determined from heats of formation using

Hess's Law

$$\Delta \hat{H}^0_r = \sum_{\text{products}} \nu_i (\Delta \hat{H}^0_f)_i - \sum_{\text{reactants}} \nu_i (\Delta \hat{H}^0_f)_i$$

- Example



$$\Delta \hat{H}^0_r(\text{C}_5\text{H}_{12}) = 5(\Delta \hat{H}^0_f)_{\text{CO}_2(\text{g})} + 6(\Delta \hat{H}^0_f)_{\text{H}_2\text{O}(\text{l})} - (\Delta \hat{H}^0_f)_{\text{C}_5\text{H}_{12}(\text{l})}$$

4.5 Standard Heats of Combustion

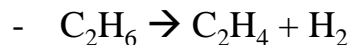
□ Standard Heat of Combustion

- Heat of reaction of the substance with oxygen to yield specified products
- Condition : 25 °C, 1 atm
- Products : CO₂ (g), H₂O (l), SO₂ (g), NO₂ (g)

□ Using Hess's Law heat of reaction can be calculated from heats of combustion

$$\Delta \hat{H}^o_r = \sum_{\text{reactants}} \nu_i (\Delta \hat{H}^o_c)_i - \sum_{\text{products}} \nu_i (\Delta \hat{H}^o_c)_i$$

● Example



$$\Delta \hat{H}^o_r = (\Delta \hat{H}^o_c)_{\text{C}_2\text{H}_6} - (\Delta \hat{H}^o_c)_{\text{C}_2\text{H}_4} - (\Delta \hat{H}^o_c)_{\text{H}_2}$$

4.6 Temperature Dependence of ΔH°

□ General Procedure

● Choice of reference conditions

1. Heat of Reaction method

- Usually for single reaction, ΔH_r is known
- Reactants and products : T_0 where ΔH_r is known
- Non-reactive species (e.g., N_2) : any convenient T

$$\Delta H = \frac{n_{AR} \Delta \hat{H}_r^\circ}{\nu_A} + \sum_{\text{product}} n_i H_i - \sum_{\text{reactant}} n_i H_i$$

n_A : moles of A consumed or produced

ν_A : the stoichiometric coefficient of A

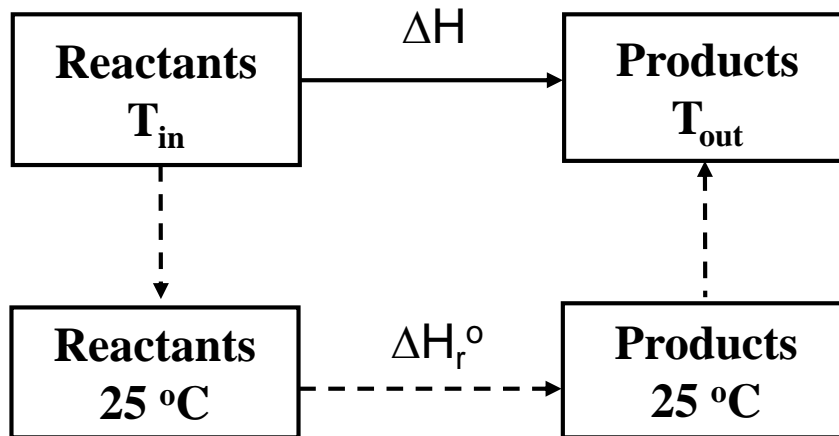
2. Heat of Formation method

- Usually for multiple reactions, ΔH_r is unknown
- Reactants and Products : elements at 25 °C
 - » Use sum of heats of formation
- Non-reactive species (e.g., N_2) : any convenient T

$$\Delta H = \sum_{\text{product}} n_i H_i - \sum_{\text{reactant}} n_i H_i$$

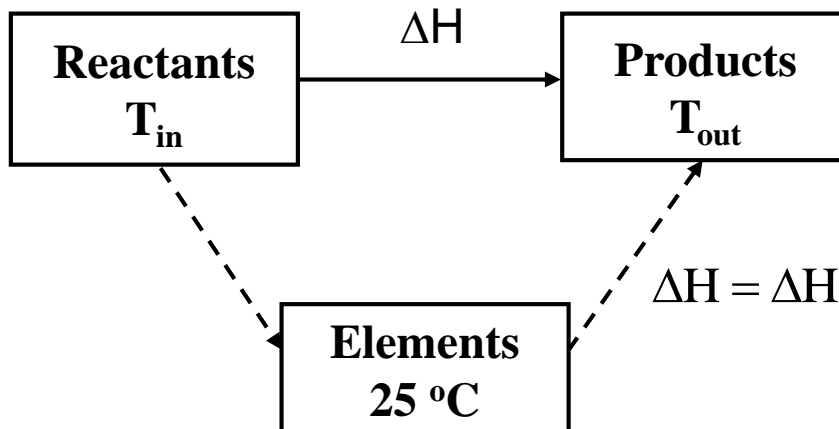
Method 1 vs. method 2

Heat of reaction method



$$\Delta H = \frac{n_{AR} \Delta \hat{H}_r^o}{\nu_A} + \sum_{\text{product}} n_i H_i - \sum_{\text{reactant}} n_i H_i$$

Heat of formation method



$$\Delta H = \sum_{\text{product}} n_i H_i - \sum_{\text{reactant}} n_i H_i$$

$$\Delta H = \Delta H_f^o + \int C_p dT$$

ΔH Calculations

☐ In the textbook of Thermodynamics

- Table C.1 – C3 : Heat capacity of gases, solids, and liquids (constants – A, B, C, D)
- Table C4 : Heat of formation
- Table F.1 – F.4 : Steam table

☐ In the textbook of Introduction to Chemical & Biological Engineering

- Table B.1 : Latent heat, heat of formation, heat of combustion
- Table B.2 : Heat capacity (constants – A, B, C, D)
- Table B.5 – B.7 : Steam table
- Table B.8 & B.9 : Specific enthalpy for simple gases (Air, O₂, N₂, H₂, CO, CO₂, H₂O)
- Table B.10 : Heat capacity for Kopp's rule

☐ It is convenient to **prepare the enthalpy table.**

substance	n_{reactant}	H_{reactant}	n_{product}	H_{product}
NH ₃	n1	H1		
O ₂	n2	H2	n3	H3
NO			n4	H4
H ₂ O			n5	H5

Example 4.7

- ❑ **What is the maximum temperature that can be reached by the combustion of methane with 20 % excess air? Both the methane and the air enter the burner at 25 °C.**

- ❑ **Processes with unknown outlet conditions : adiabatic reactors**
 - **Adiabatic reactor**
 - No heat exchange with surrounding → maximum temperature

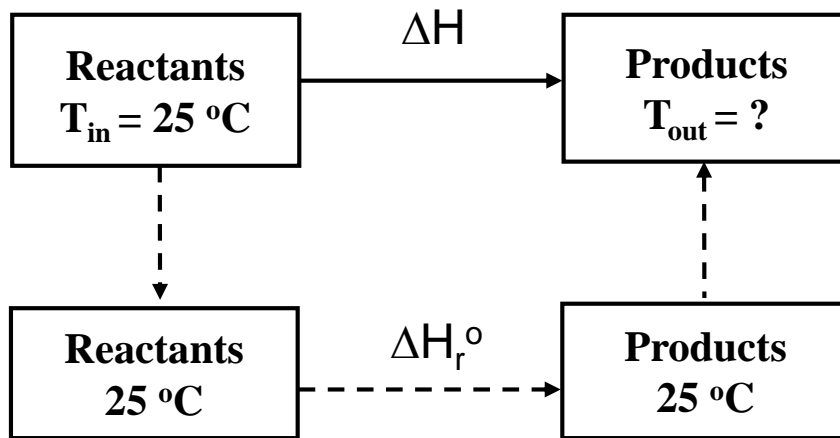
 - **$Q = \Delta H = 0$, then solve for unknown T**

Example 4.7 - solution

The standard heat of reaction is



Since $\Delta H_r(25^\circ\text{C})$ is known, use the heat of reaction method



Reactants

1 mol CH₄
2.4 mol O₂
9.03 mol N₂

Products

1 mol CO₂
2 mol H₂O
0.4 mol O₂
9.03 mol N₂

$$\Delta H = \frac{n_{AR} \Delta \hat{H}_r^\circ}{V_A} + \sum_{\text{product}} n_i H_i - \sum_{\text{reactant}} n_i H_i$$

20 % excess air?

Example 4.7 - solution

Using the mean heat capacity,

$$\Delta H = \bar{C}_p (T_2 - T_1)$$

$$\bar{C}_{p,O_2} = 34.42 J / mol \cdot K$$

$$\bar{C}_{p,N_2} = 32.58 J / mol \cdot K$$

$$\bar{C}_{p,H_2O} = 41.42 J / mol \cdot K$$

$$\bar{C}_{p,CO_2} = 52.77 J / mol \cdot K$$

Enthalpy table

substance	n _{in}	H _{in}	n _{out}	H _{out}
CH ₄	1	0	-	-
O ₂	2.4	0	0.4	34.42(T-298.15)
N ₂	9.03	0	9.03	32.58(T-298.15)
H ₂ O	-	-	2	41.42(T-298.15)
CO ₂	-	-	1	52.77(T-298.15)

$$\Delta H = \frac{n_{AR} \Delta \hat{H}^o_r}{V_A} + \sum_{\text{product}} n_i H_i - \sum_{\text{reactant}} n_i H_i = 0$$

$$-934585.6 + 443.6T = 0 \quad T = 2106.8K$$

*** Repeat this problem yourself using the heat capacity (use the value A, B, C, and D from Table C.1)**

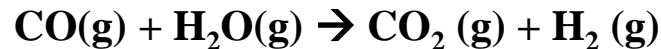
$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

Example 4.8

One method for the manufacture of “synthesis gas” (a mixture of CO and H₂) is the catalytic reforming of CH₄ with steam at high temperature and atmospheric pressure:



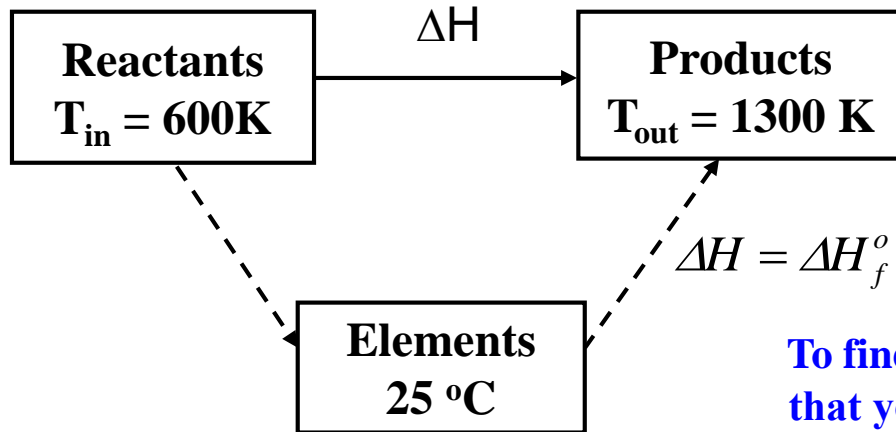
The only other reaction to be considered is the water-gas-shift reaction:



If the reactants are supplied in the ratio, 2 mol steam (H₂O) to 1 mol CH₄, and if heat is supplied to the reactor so that the products reach a temperature of 1300K, the CH₄ is completely converted and the product stream contains 17.4 mol % CO. Assuming the reactants to be preheated to 600K, calculate the heat requirement for the reactor.

Example 4.8 - solution

Since there are two reactions, it is convenient to use the heat of formation method.



$$\Delta H = \sum_{\text{product}} n_i H_i - \sum_{\text{reactant}} n_i H_i$$

$$\Delta H = \Delta H_f^o + \int C_p dT$$

To find the amount of product, use the extent of reaction that you have learned from “Intro. to Chem & Bio Eng”



CH_4 is completely converted $\rightarrow \xi_1 = 1 \text{ mol}$



Reactants
1 mol CH_4
2 mol H_2O

Products
 $\text{CH}_4 = 1 - \xi_1 = 0$
 $\text{H}_2\text{O} = 2 - \xi_1 - \xi_2 = 1 - \xi_2$
 $\text{CO} = \xi_1 - \xi_2 = 1 - \xi_2$
 $\text{CO}_2 = \xi_2$
 $\text{H}_2 = 3\xi_1 + \xi_2 = 3 + \xi_2$

Total = 5 mol

Example 4.8 - solution

Since the product stream contains 17.4 mol % CO,

$$(1 - \xi_2)/5 = 0.174$$

$$\xi_2 = 0.13 \text{ mol}$$

Products

$$\text{CH}_4 = 1 - \xi_1 = 0$$

$$\text{H}_2\text{O} = 2 - \xi_1 - \xi_2 = 1 - \xi_2 = 0.87 \text{ mol}$$

$$\text{CO} = \xi_1 - \xi_2 = 1 - \xi_2 = 0.87 \text{ mol}$$

$$\text{CO}_2 = \xi_2 = 0.13 \text{ mol}$$

$$\text{H}_2 = 3 \xi_1 + \xi_2 = 3 + \xi_2 = 3.13 \text{ mol}$$

substance	n_{in}	H_{in}	n_{out}	H_{out}
CH_4	1	H_1	0	0
H_2O	2	H_2	0.87	H_3
CO	-	-	0.87	H_4
CO_2	-	-	0.13	H_5
H_2	-	-	3.13	H_6

$$\Delta H = \Delta H_f^\circ + \int C_p dT$$

$$\bar{C}_{p,\text{CH}_4} = R(1.702 + 9.081 \times 10^{-3} T - 2.164 \times 10^{-6} T^2)$$

$$\bar{C}_{p,\text{H}_2\text{O}} = 38.66 \text{ J} / \text{mol} \cdot \text{K}$$

$$\bar{C}_{p,\text{CO}} = 31.70 \text{ J} / \text{mol} \cdot \text{K}$$

$$\bar{C}_{p,\text{CO}_2} = 49.85 \text{ J} / \text{mol} \cdot \text{K}$$

$$\bar{C}_{p,\text{H}_2} = 29.78 \text{ J} / \text{mol} \cdot \text{K}$$

Example 4.8 - Quiz

Perform the rest of calculation to obtain $Q = \Delta H$.

Heat of formation at 298 K is
(from Table C.4)

$$\Delta H_{f,CH_4}^o = -74,520 J / mol$$

$$\Delta H_{f,H_2O}^o = -285,830 J / mol$$

$$\Delta H_{f,CO}^o = -110,525 J / mol$$

$$\Delta H_{f,CO_2}^o = -393,509 J / mol$$

$$\Delta H_{f,H_2}^o = 0 \quad (\text{naturally occurring substance})$$

Example 4.8 - solution

Heat of formation at 298 K is

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$$\Delta H_{f,H_2O}^{\circ} = -285,830 J / mol$$

$$\Delta H_{f,CO}^{\circ} = -110,525 J / mol$$

$$\Delta H_{f,CO_2}^{\circ} = -393,509 J / mol$$

$$\Delta H_{f,H_2}^{\circ} = 0 \quad (\text{naturally occurring substance})$$

$$H_1 = \Delta H_{f,CH_4}^{\circ} + \int_{298}^{600} 8.314(1.702 + 9.081 \times 10^{-3}T - 2.164 \times 10^{-6}T^2) dT = -61,145 J / mol$$

$$H_2 = \Delta H_{f,H_2O}^{\circ} + 38.66(600 - 298) = -274,154 J / mol$$

$$H_3 = \Delta H_{f,H_2O}^{\circ} + 38.66(1300 - 298) = -247,092 J / mol$$

$$H_4 = \Delta H_{f,CO}^{\circ} + 31.70(1300 - 298) = -115,850 J / mol$$

$$H_5 = \Delta H_{f,CO_2}^{\circ} + 49.85(1300 - 298) = -343,559 J / mol$$

$$H_6 = \Delta H_{f,H_2}^{\circ} + 29.78(1300 - 298) = 47,588 J / mol$$

$$\begin{aligned} \Delta H = Q &= \sum_{\text{product}} n_i H_i - \sum_{\text{reactant}} n_i H_i \\ &= 397,980 J \end{aligned}$$

Homework

☐ Problems

- 4.2, 4.5, 4.21 [(a),(b),(c)], 4.32, 4.38, 4.41
- Due:

☐ Other Recommend Problems

- 4.35, 4.39, 4.46 [(a), (b), (c), (d)]