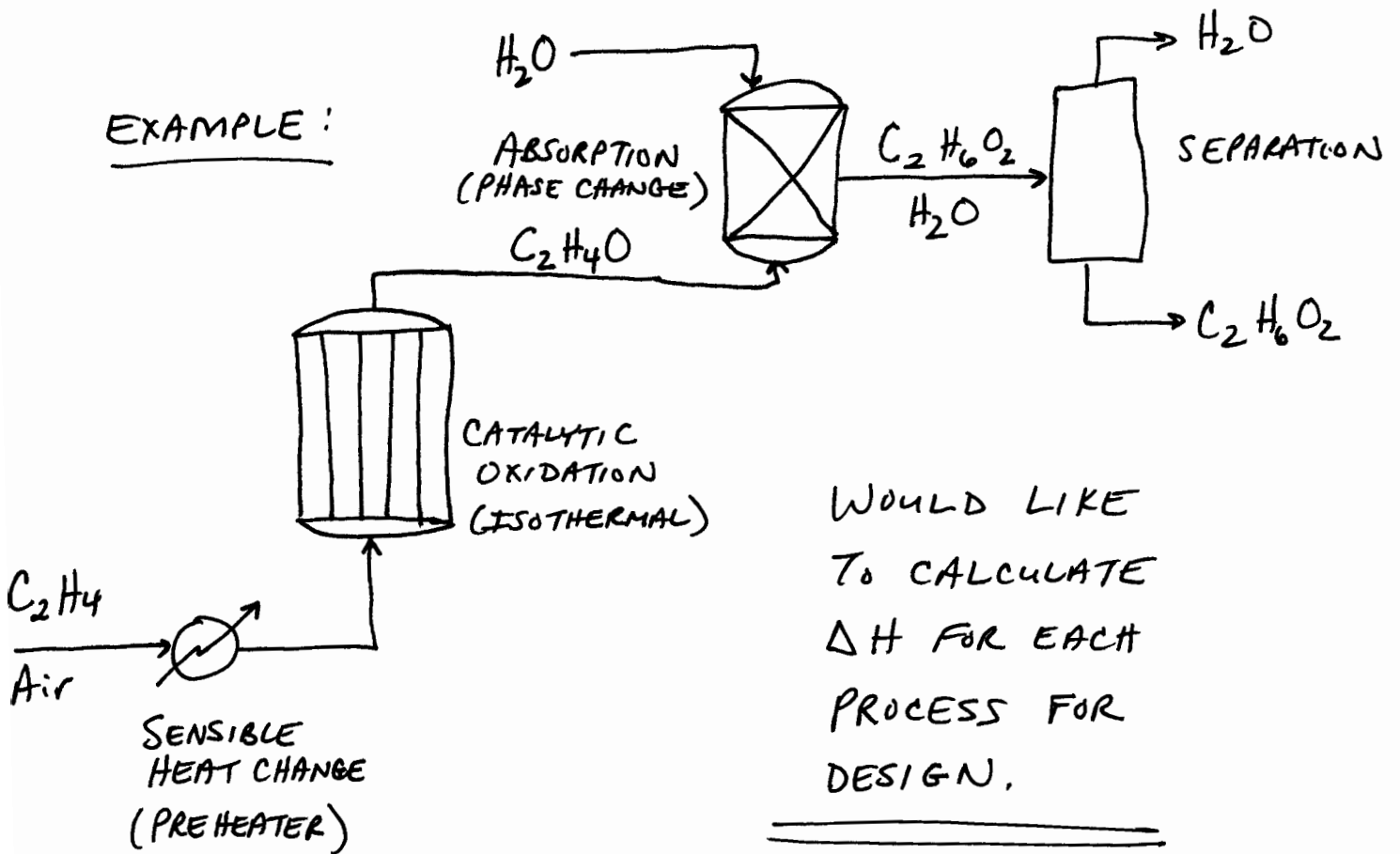


# CHAPTER 4 - HEAT EFFECTS

- SENSIBLE HEAT ( $\Delta T$ )
  - CHEMICAL REACTION
  - PHASE TRANSITION
  - FORMATION & SEPARATION
  - MIXING (CHAP. 12)
- } THIS CHAPTER

EXAMPLE :



WOULD LIKE  
TO CALCULATE  
 $\Delta H$  FOR EACH  
PROCESS FOR  
DESIGN.

---

Thermodynamics lets us do this.

---

# 4.1 SENSIBLE HEAT EFFECTS

- NO CHEMICAL REACTION
- NO PHASE CHANGE
- NO CHANGE IN COMPOSITION

⇒ STILL CAN GET ΔT

$$Q \propto \Delta T$$

LOOK AT IN A COUPLE DIFFERENT WAYS:

$$U = U(V, T)$$

$$H = H(P, T)$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT$$

@ Constant V

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

@ Constant P

$$dU = C_V dT$$

$$dH = C_P dT$$

$$\Rightarrow \Delta U = \int_{T_1}^{T_2} C_V dT = Q$$

$$\Rightarrow \Delta H = \int_{T_1}^{T_2} C_P dT = Q$$

CONSTANT VOLUME  
PROCESSES

---

Ideal Gas

CONSTANT PRESSURE  
PROCESSES

---

Ideal Gas

IN BOTH CASES, WE WILL APPLY TO STEADY FLOW IN HEAT EXCHANGERS.

WHY?  $\Delta E_k \approx 0, \Delta E_p \approx 0, W_s \approx 0$

So,  $C_p = f(T)$  (observed empirically)

Curve fit:

$\frac{C_p}{R} = \alpha + \beta T + \gamma T^2$  or  $\frac{C_p}{R} = a + bT + cT^{-2}$

We can combine these ...

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

Values of A, B, C, and D in Appendix C.

---

**EXAMPLE 4.1**

FOR METHANE

(4)

$$A = 1.702$$

$$\Rightarrow A = 1.702$$

$$10^3 B = 9.081$$

$$\Rightarrow B = 9.081 \times 10^{-3}$$

$$10^6 C = -2.164$$

$$\Rightarrow C = -2.164 \times 10^{-6}$$

$$10^{-5} D = 0$$

$$\Rightarrow D = 0$$

all for  $T$  in K.Evaluate  $C_p$  @ 298K, 308K, and 398K

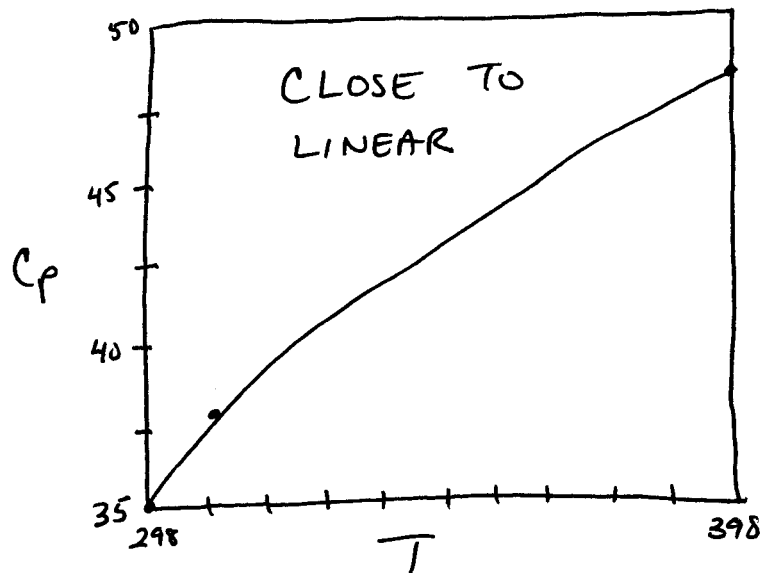
$$C_p(T) = \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \left[ 1.702 + 9.081 \times 10^{-3} T - 2.164 \times 10^{-6} T^2 \right]$$

Plug + Chug:

$$C_p(298\text{K}) = \frac{35.05 \text{ J}}{\text{mol} \cdot \text{K}}$$

$$C_p(308\text{K}) = \frac{37.87 \text{ J}}{\text{mol} \cdot \text{K}}$$

$$C_p(398\text{K}) = \frac{48.29 \text{ J}}{\text{mol} \cdot \text{K}}$$



$$\text{So, } \int dH = \int C_p dT = \langle C_p \rangle \int dT$$

$$\Delta H = \langle C_p \rangle (T_2 - T_1)$$

↑  
AVERAGE VALUE

(5)

WHAT IF GAS MIXTURE?

$$C_{p_{mix}}^{ig} = y_A C_{p_A}^{ig} + y_B C_{p_B}^{ig} + y_C C_{p_C}^{ig} + \dots$$

**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.

$$Q = \Delta H = R \int_{T_1}^{T_2} \frac{C_p}{R} dT$$

$$T_1 = 260 + 273,15 = 533,15 \text{ K}$$

$$T_2 = 600 + 273,15 = 873,15 \text{ K}$$

$$Q = R \int_{T_1}^{T_2} (A + BT + CT^2) dT$$

$$= R \left[ AT + \frac{BT^2}{2} + \frac{CT^3}{3} \right] \Big|_{T_1}^{T_2}$$

$$= \left( \frac{8,314 \text{ J}}{\text{mol} \cdot \text{K}} \right) \left[ 1,702 (873,15 - 533,15) + \frac{(9,081 \times 10^{-3})}{2} (873,15^2 - 533,15^2) - \frac{2,164 \times 10^{-6}}{3} (873,15^3 - 533,15^3) \right]$$

$$Q = 19,778 \frac{\text{J}}{\text{mol}}$$

# 4.2 LATENT HEAT OF PURE SUBSTANCES

→ PHASE CHANGE

LATENT HEAT OF FUSION }  
 LIQ → SOLID OR SOLID → LIQ

LATENT HEAT OF VAPORIZATION }  
 LIQ → VAPOR OR VAPOR → LIQ

$\Delta T = 0$  even though  $Q \neq 0$

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

LATENT HEAT      VOLUME CHANGE w/ PHASE CHANGE      SATURATION PRESSURE  
 Pure Species at temperature T.

CLAPEYRON EQUATION (DERIVED CHAP. 6)

## How TO GET $\Delta H$ ?

→ Volumetric + Vapor Pressure Data

or

→ Measure experimentally w/ Calorimeter

or

→ Estimate @ Boiling Point or from known value.

## EXAMPLE ESTIMATION TECHNIQUES:

- PURE LIQUID @ NORMAL BOILING POINT  
(AT ATMOSPHERIC PRESSURE)

TROUTON'S RULE: (from 1884)

$$\frac{\Delta H_n}{RT_n} \sim 10 \quad (\text{dimensionless})$$

Good Approximation?

Species	$\frac{\Delta H_n}{RT_n}$
Ar	8.0
N <sub>2</sub>	8.7
O <sub>2</sub>	9.1
C <sub>6</sub> H <sub>6</sub>	10.5
H <sub>2</sub> O	13.1

} All within  $\pm 20-30\%$  of Trouton's Rule.  
(Good to see if reasonable value)

- PURE LIQUID @ NORMAL BOILING POINT

RIEDEL (1954)

$$\frac{\Delta H_n}{RT_n} = \frac{1.092 (\ln P_c - 1.013)}{0.930 - T_{rn}} \quad \text{in bar}$$

Very good estimate ( $\pm 5\%$ )

- ESTIMATION BASED ON KNOWN VALUE

$$\frac{\Delta H_2}{\Delta H_1} = \left( \frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38} \quad (\text{Watson, 1943})$$

⇒ Not at  $T_n$ .

**EXAMPLE 4.4** GIVEN THAT THE LATENT HEAT OF VAPORIZATION OF WATER @ 100°C IS 2,257 J/g, ESTIMATE THE LATENT HEAT @ 300°C.

NEED  $T_c$ . (FROM APPENDIX B)  $T_c = 647.1 \text{ K}$

$$T_{r1} = \frac{100 + 273.15}{647.1} = 0.5766$$

$$T_{r2} = \frac{300 + 273.15}{647.1} = 0.8857$$

$$\Delta H_1 = 2,257 \text{ J/g}$$

Plug + Chug.

$$\Delta H_2 = (2,257 \frac{\text{J}}{\text{g}}) \left[ \frac{1 - 0.8857}{1 - 0.5766} \right]^{0.38}$$

$$\Delta H_2 = 1,372 \text{ J/g}$$

REASONABLE?

from Steam Tables: 1,405.5 J/g

⇒ NOT BAD.



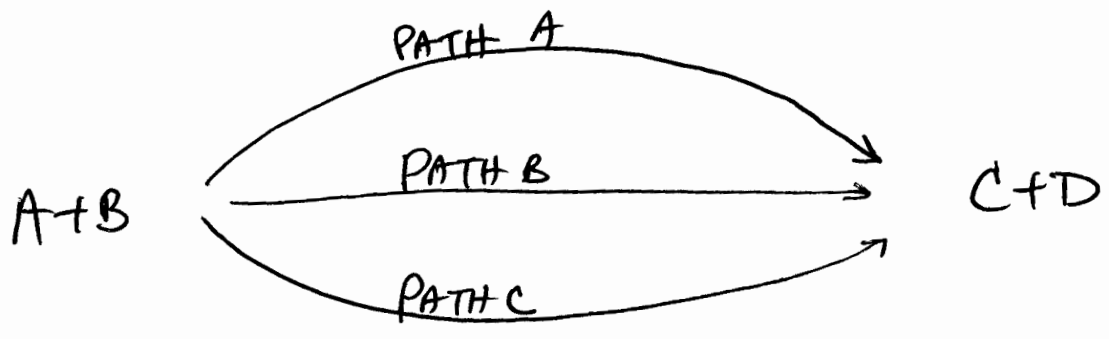
# 4.3 STANDARD HEAT OF REACTION

DIFFERENCES IN MOLECULAR STRUCTURE

REACTANTS → PRODUCTS

DURING REACTION, DIFFERENCES IN ENERGY IS RELEASED OR ABSORBED.

(EXOTHERMIC)      (ENDOTHERMIC)



LOTS OF WAYS TO DO THE REACTION, ... SO COME UP WITH A STANDARD WAY TO GET  $\Delta H_{\text{REACTION}}$ .

RECALL FLOW CALORIMETER.



$T_1 = T_2$       How?      Q transferred in Black Box.

$$\Rightarrow Q = \Delta H_{\text{REACTION}}$$

BECAUSE FLOW CALORIMETER,

$$\Delta E_k \cong 0$$

$$\Delta E_p \cong 0$$

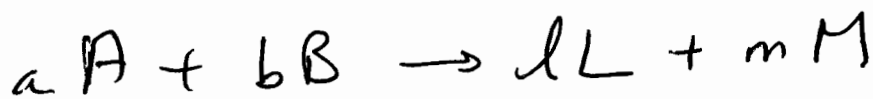
$$W_s \cong 0$$

$$\left. \begin{array}{l} \Delta E_k \cong 0 \\ \Delta E_p \cong 0 \\ W_s \cong 0 \end{array} \right\} Q = \Delta H$$

REASONABLE.

SO, WHAT ARE THE STANDARD STATES?

REACTION:



$\Rightarrow$  STOICHIOMETRIC QUANTITIES OF A+B

AT Temperature T react to form

STOICHIOMETRIC QUANTITIES of L+M

at Temperature T.

$\Rightarrow$  STANDARD PRESSURE = 1 bar

$\Rightarrow$  ASSUME PURE SPECIES

$\Rightarrow$  IDEAL GAS + REAL LIQ'S/SOL'DS.

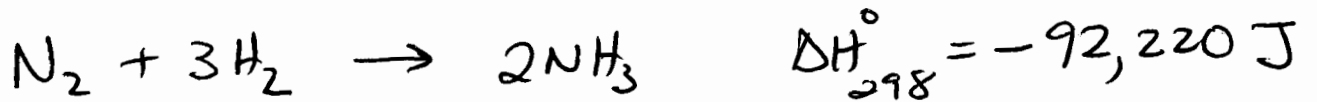
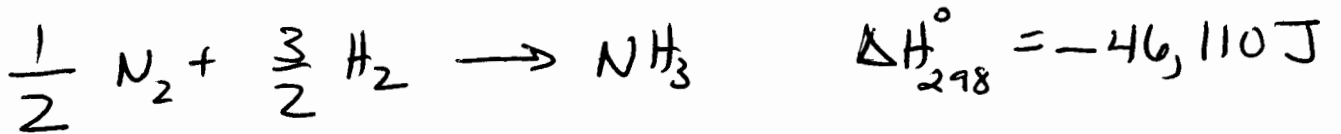
STANDARD PROPERTIES DENOTED WITH DEGREE SIGN (°)

⇒  $C_p^\circ \equiv$  Standard-state heat capacity

$$C_p^\circ = C_p^{ig} \text{ for Gases}$$

Because  $T$  floats, all standard properties are  $f(T)$  only.

NOTE: WATCH STOICHIOMETRIC COEFFICIENTS.



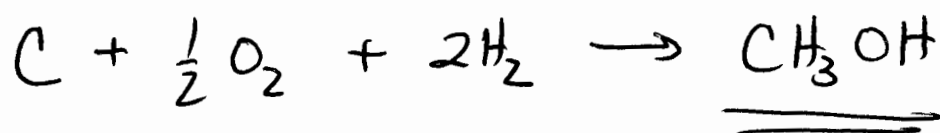
Next,  $\Delta H_{\text{formation}}^\circ$

## 4.4 STANDARD HEAT OF FORMATION

$$\Delta H_{\text{REACTION}}^{\circ} = f(\Delta H_f^{\circ})$$

⇒ BASED ON FORMATION FROM CONSTITUENT ELEMENTS.

Example: Methanol ( $\text{CH}_3\text{OH}$ )



↑ 1 mole of product formed,

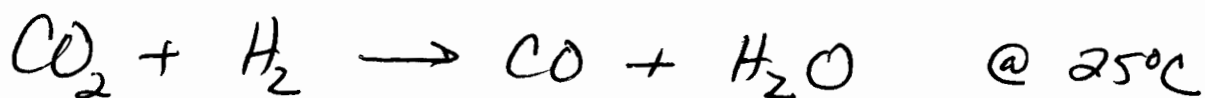
Usually do calculations based on single temperature.

(Common: Room temperature =  $25^{\circ}\text{C}$  or  $298.15\text{K}$ )

⇒  $\Delta H_{f,298}^{\circ} \equiv$  Standard Heat of Formation @  $298.15\text{K}$ .

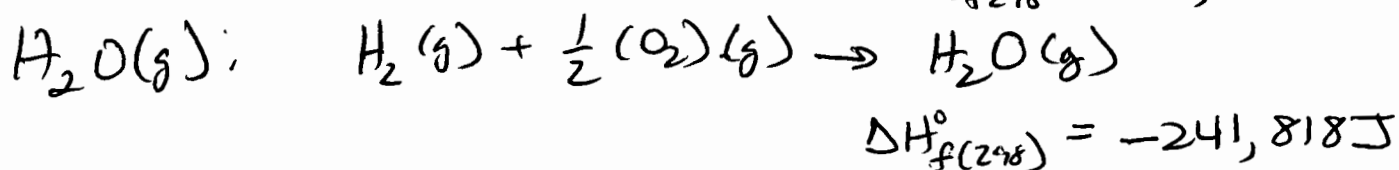
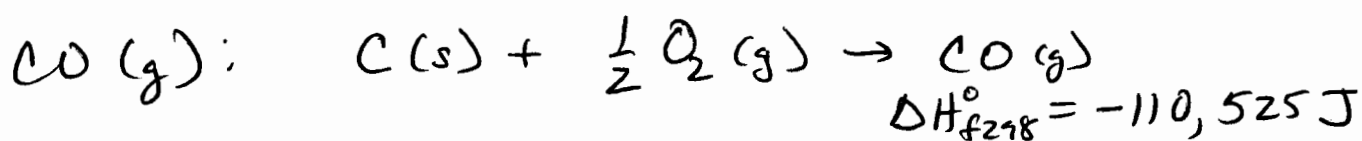
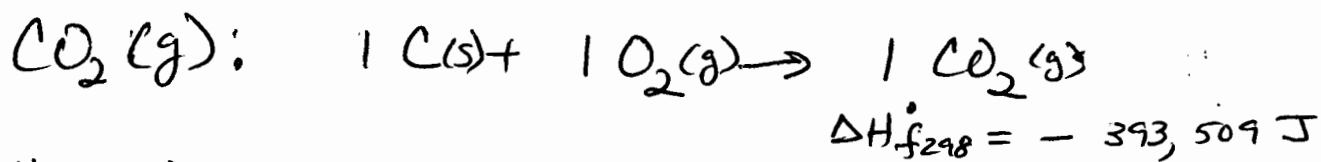
(Some values in Appendix C, Table C.4)

How to get  $\Delta H_{\text{Reaction}}^{\circ}$ ? Add up reactions based on constituent elements.

Example: Water-Gas Shift Reaction

(not really done @ 250°C, but this is first step)

So, what is  $\Delta H^\circ_{\text{Reaction}}$  @ 250°C?



Fictitious states?

$\text{H}_2\text{O}$  @ 250°C + 1 bar?

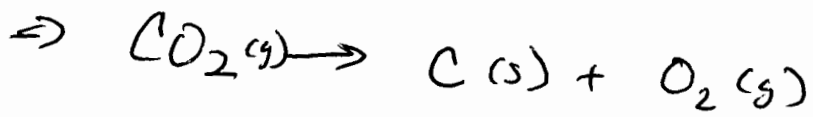
⇒ Should be liquid.

We often do things for convenience in thermodynamics...

(means to an end...)

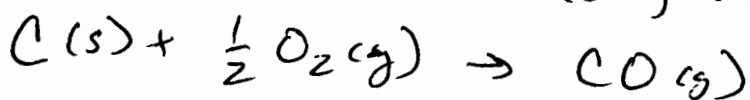
# How to add?

Reactants:  $\text{CO}_2 + \text{H}_2$  (left hand side)



$$\Rightarrow \Delta H_{f298}^\circ = +393,509 \text{ J}$$

Products:  $\text{CO} + \text{H}_2\text{O}$  (right hand side)



$$\Rightarrow \Delta H_{f298}^\circ = -110,525 \text{ J}$$



$$\Rightarrow \Delta H_{f298}^\circ = -241,818 \text{ J}$$

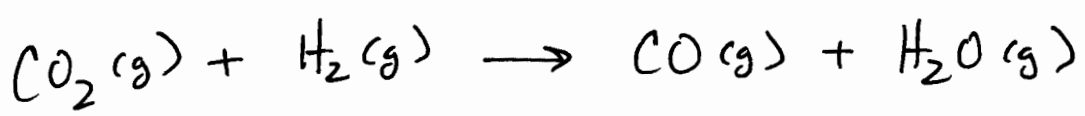
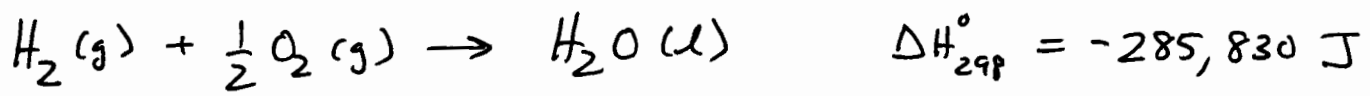
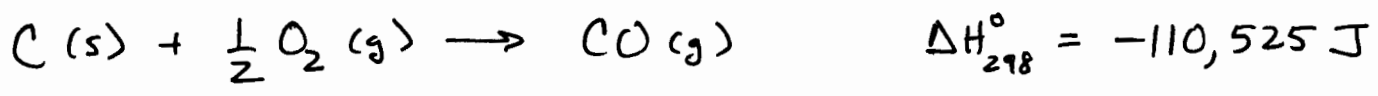
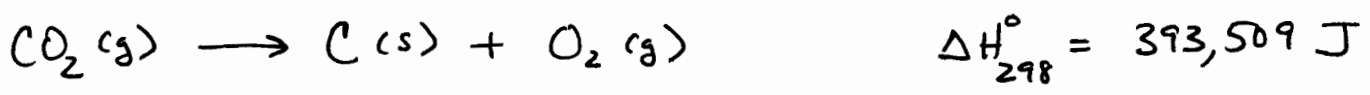
$$\sum \Delta H_{f298}^\circ = \underbrace{393,509 \text{ J}}_{\text{CO}_2} + \underbrace{0 \text{ J}}_{\text{H}_2}$$

$$- \underbrace{110,525 \text{ J}}_{\text{CO}} - \underbrace{241,818 \text{ J}}_{\text{H}_2\text{O}}$$

$$\Delta H_{\text{reaction}}^\circ = \sum \Delta H_{f298}^\circ = 41,166 \text{ J}$$

What if we don't have  $\Delta H_{f298}^\circ$  at correct phase?

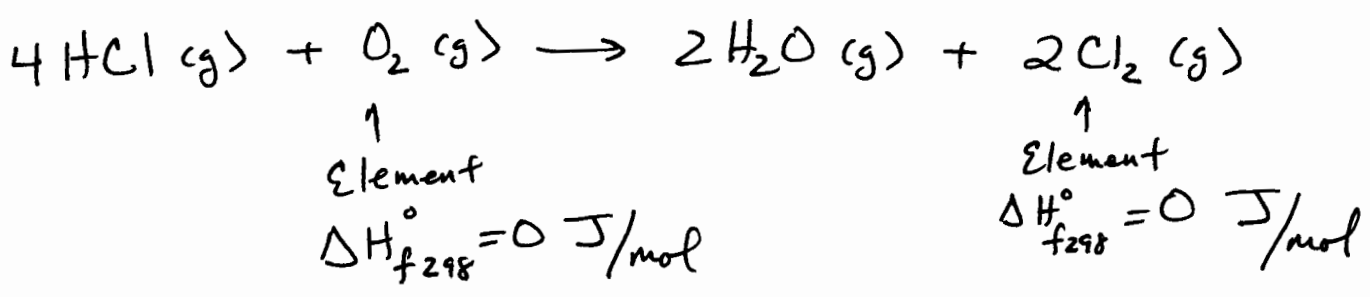
INCLUDE REACTION FOR PHASE TRANSFORMATION



$\Delta H_{298}^\circ = 41,166 \text{ J}$

JUST LIKE BEFORE.

**EXAMPLE 4.5** CALCULATE THE STANDARD HEAT AT 25°C FOR THE FOLLOWING REACTION:



$$\Delta H_{f298}^\circ (\text{HCl}(\text{g})) = -92,307 \text{ J/mol}$$

$$\Delta H_{f298}^\circ (\text{H}_2\text{O}(\text{g})) = -241,818 \text{ J/mol}$$

$$\sum H_{f298}^{\circ} = (-4 \text{ mol})(-92,307 \frac{\text{J}}{\text{mol}}) + (2 \text{ mol})(-241,818 \frac{\text{J}}{\text{mol}})$$

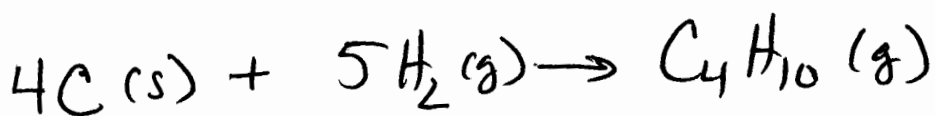
(16)

$$\Delta H_{298}^{\circ} = -114,408 \text{ J}$$

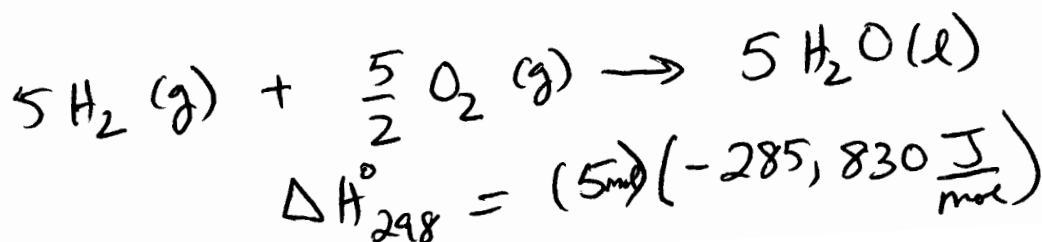
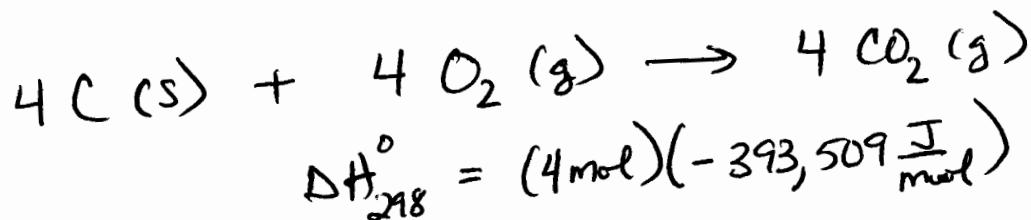
← Standard Heat of Reaction @ 298K

#### 4.5 STANDARD HEAT OF COMBUSTION

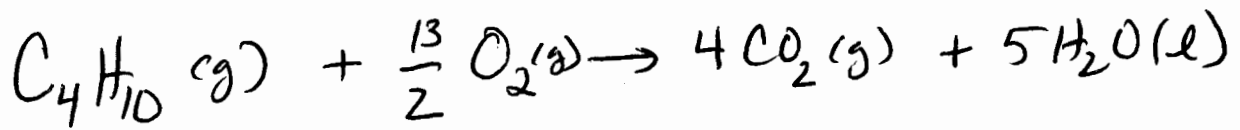
⇒ A WAY TO GET  $\Delta H_f^{\circ}$  EXPERIMENTALLY  
(BY BURNING STUFF) ... pyromania!



⇒ CANT GET DIRECTLY. HOWEVER, WE CAN COMBUST EACH REACTANT + PRODUCT...







$$\Delta H_{298}^\circ = -2,877,396 \text{ J}$$


---

$$\Delta H_{298}^\circ = \sum \Delta H_{f,298}^\circ = (4\text{mol})(-393,509 \frac{\text{J}}{\text{mol}}) + (5\text{mol})(-285,830 \frac{\text{J}}{\text{mol}}) + 2,877,396 \text{ J}$$

$$\Delta H_{298}^\circ = -125,790 \text{ J}$$

← Matches value in Table C.4.

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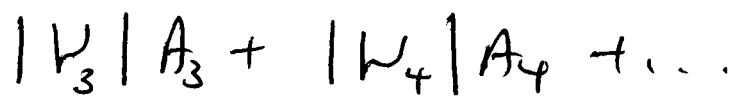
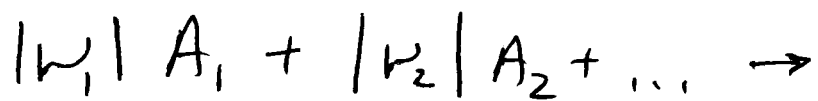
#### 4.6 TEMPERATURE DEPENDENCE OF $\Delta H^\circ$

MOST REACTIONS NOT AT 298K.

CAN WE USE  $\Delta H_{298}^\circ$  TO GET ACTUAL HEATS OF REACTION?

YES! NEED A PROCEDURE...

## GENERAL FORM CHEMICAL REACTION



$|v_i| \equiv$  stoichiometric coefficient

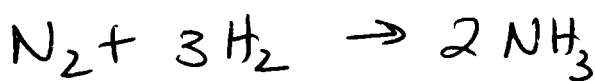
$A_i \equiv$  Chemical formula

Sign convention for  $v_i$ :

(+) PRODUCTS

(-) REACTANTS

Example:



$$A_1 = N_2$$

$$v_1 = -1$$

$$A_2 = H_2$$

$$v_2 = -3$$

$$A_3 = NH_3$$

$$v_3 = 2$$

$$\Rightarrow \Delta H^\circ \equiv \sum_i v_i H_i^\circ$$

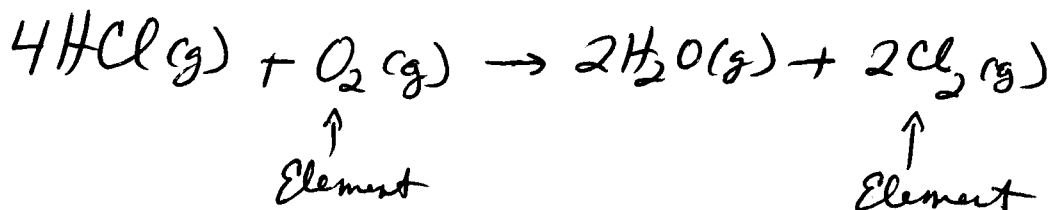
Enthalpy of species "i"  
at standard state

(19)

where  $H_i^\circ = \Delta H_{f,i}^\circ$

$$\Rightarrow \Delta H^\circ = \sum_i \nu_i \Delta H_{f,i}^\circ$$

Example:



$$\Delta H^\circ = -4 \Delta H_{f,\text{HCl}}^\circ - 0 + 2 \Delta H_{f,\text{H}_2\text{O}}^\circ + 2(0)$$

from Table C.4

$$\Delta H_{f,\text{HCl}}^\circ = -92,307 \text{ J/mol}$$

$$\Delta H_{f,\text{H}_2\text{O}}^\circ = -241,818 \text{ J/mol}$$

$$\Delta H^\circ = -114,408 \text{ J} \leftarrow @ 298\text{K}$$

Since already at 1 bar (constant)

$$dH_i^\circ = C_{p,i}^\circ dT$$

$$\nu_i dH_i^\circ = \nu_i C_{p,i}^\circ dT$$

Sum overall products + reactants

$$\sum_i \nu_i dH_i^\circ = \sum_i \nu_i C_{p,i}^\circ dT$$

NOTES:  $v_i$ 's are constant (pull inside differential)

$$\sum_i d v_i H_i^\circ = d \sum_i v_i H_i^\circ$$

$$\Rightarrow \underbrace{d \sum_i v_i H_i^\circ}_{\Delta H^\circ} = \underbrace{\sum_i v_i c_{p,i}^\circ}_{\Delta C_p^\circ} dT$$

$$d(\Delta H^\circ) = \Delta C_p^\circ dT$$

Integrate: @  $T_0$ ,  $\Delta H^\circ = \Delta H_0^\circ$   
@  $T$ ,  $\Delta H^\circ = \Delta H^\circ$

$$\int d\Delta H^\circ = \int_{T_0}^T \Delta C_p^\circ dT$$
$$\Delta H^\circ - \Delta H_0^\circ = R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT$$

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT$$

Two Options:

(1) Substitute for  $\frac{\Delta C_p^\circ}{R} = f(T)$   
+ Integrate.

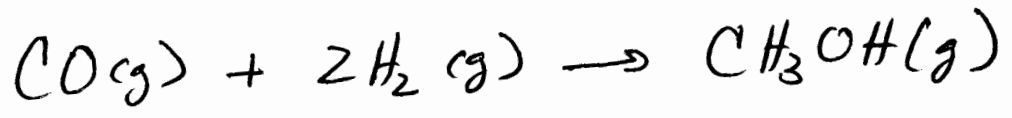
or

(2) Assume average  $\langle \Delta C_p^\circ \rangle$

$\Rightarrow \Delta H^\circ = \Delta H_0^\circ + \langle \Delta C_p^\circ \rangle (T - T_0)$

**EXAMPLE 4.6**

Calculate the standard heat of the methanol synthesis reaction @ 800°C



$\Delta H_0^\circ = (-1)(-110,525) + (-2)(0) + (1)(-200,660)$

$\Delta H_0^\circ = -90,135 \text{ J}$

Next, need  $\Delta C_p^\circ$  :

Species	A	$10^3 B$	$10^6 C$	$10^{-5} D$
CO	3.376	0.557	-	-0.031
H <sub>2</sub>	3.249	0.422	-	0.083
CH <sub>3</sub> OH	2.211	12.216	-3.450	-

$$\Delta(A) = \sum_i \nu_i (A_i)$$

$$= (-1)(3.376) + (-2)(3.249) + (1)(2.211) = -7.663$$
$$\Rightarrow \Delta A = -7.663$$

$$\Delta(10^3 B) = \sum_i \nu_i (10^3 B)$$

$$= (-1)(0.557) + (-2)(0.422) + (1)(12.216) = 10.815$$
$$\Rightarrow \Delta B = 10.815 \times 10^{-3}$$

$$\Delta(10^6 C) = \sum_i \nu_i (10^6 C)$$

$$= (-1)(0) + (-2)(0) + (1)(-3.450) = -3.450$$
$$\Rightarrow \Delta C = -3.450 \times 10^{-6}$$

$$\Delta(10^{-5} D) = \sum_i \nu_i (10^{-5} D)$$

$$= (-1)(-0.031) + (-2)(0.083) + 0 = -0.135$$
$$\Rightarrow \Delta D = -0.135 \times 10^{-5}$$

$$\text{So, } R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT$$

$$= R \int_{T_0}^T \left[ -7.663 + 10.815 \times 10^{-3} T - 3.450 \times 10^{-6} T^2 - \frac{0.135 \times 10^{-5}}{T^2} \right] dT$$

$$= R \left[ -7.663 T \Big|_{T_0}^T + \frac{10.815 \times 10^{-3}}{2} T^2 \Big|_{T_0}^T \right]$$

$$-\frac{3.450 \times 10^{-6}}{3} T^3 \Big|_{T_0}^T - \frac{0.135 \times 10^5 (-1)}{T} \Big|_{T_0}^T \Big]$$

$$= R \left[ -7.663 (1073 - 298) \right. \\ \left. + \frac{10.815 \times 10^{-3}}{2} (1073^2 - 298^2) \right. \\ \left. - \frac{3.450 \times 10^{-6}}{3} (1073^3 - 298^3) \right. \\ \left. + 0.135 \times 10^5 \left( \frac{1}{1073} - \frac{1}{298} \right) \right]$$

$$= R [-5938.8 + 5745.6 - 1390.2 - 32.7]$$

$$= \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} [-1616.1 \text{ K}] (1 \text{ mol Methanol}) = -13,436.3 \text{ J}$$

$$\Delta H^\circ = \Delta H^\circ_0 + (-13,436.3 \text{ J})$$

$$\Delta H^\circ = -90,135 \text{ J} - 13,436.3 \text{ J}$$

$$\boxed{\Delta H^\circ = -103,571 \text{ J}}$$

# 4.7 HEAT EFFECTS OF INDUSTRIAL REACTIONS

- NOT STANDARD STATE CONDITIONS
- NOT STOICHIOMETRIC PROPORTIONS
- REACTIONS DON'T GO TO COMPLETION
- $T_f \neq T_i$
- INERT SPECIES MAY BE PRESENT
- MULTIPLE REACTIONS OCCURRING AT THE SAME TIME.

We still use the same principles...

On to examples 4.7, 4.8, and 4.9.

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**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.

COMBUSTION OF METHANE:



$$\Delta H_{298}^\circ = (-1)(-74,520) + (-2)(0) + (1)(-393,509) + (2)(-241,818)$$

$\Delta H_{298}^\circ = -802,625 \text{ J}$       HIGHLY EXOTHERMIC

WANT MAXIMUM TEMPERATURE, SO SET Q=0 J  
(NO HEAT LOSS TO SURROUNDINGS)

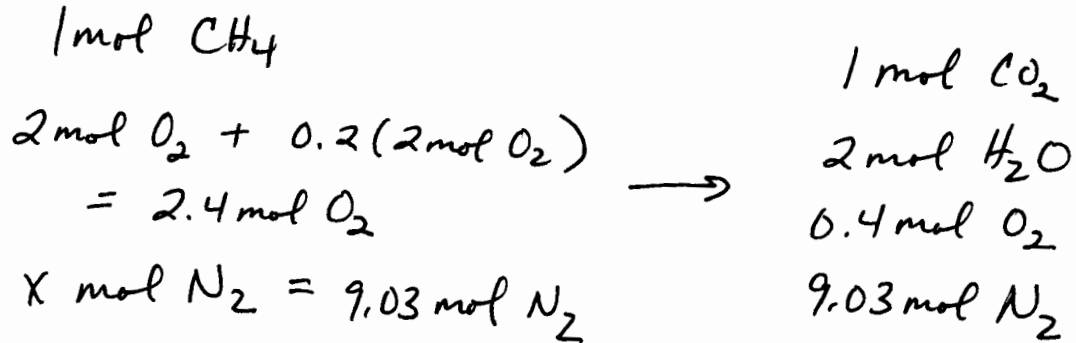
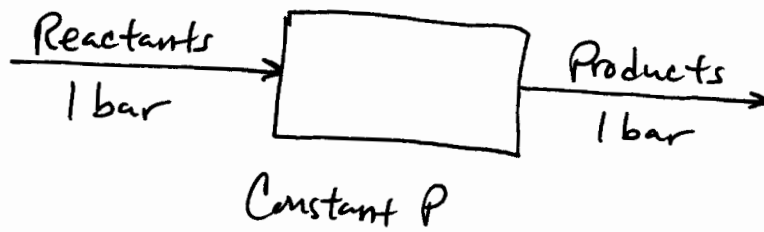
TWO STEPS:

(1) REACTION AT 25°C

(2)  $\Delta H_{298}^\circ \rightarrow$  HEATING PRODUCTS TO FINAL TEMPERATURE.

HOW MUCH OF EACH COMPONENT?

(+ AIR IS FED)



Air:  $\sim 21\% \text{ O}_2 + 79\% \text{ N}_2$

$$\Rightarrow 2.4 \text{ mol O}_2 \left| \frac{0.79 \text{ N}_2}{0.21 \text{ O}_2} = 9.03 \text{ mol N}_2 = X$$

ENERGY BALANCE:

$$\Delta(H + E_k + E_p) = Q + W_s$$

$$\Delta H + \cancel{\Delta E_k} + \cancel{\Delta E_p} = \cancel{Q} + \cancel{W_s}$$

$$\Rightarrow \boxed{\Delta H = 0 \text{ J}} \leftarrow \text{System.}$$

Our Path:

$$\Delta H = 0 \text{ J} = \Delta H_{298}^{\circ} + \Delta H_p^{\circ}$$

$$\Delta H_p^\circ \equiv \text{sensible heat change} = \langle C_p^\circ \rangle \Delta T$$

⇒ NEED  $\langle C_p^\circ \rangle$ :

$$C_p^\circ = \sum_i n_i \langle C_{p_i}^\circ \rangle$$

↑  
moles

NEED A, B, C, D FROM TABLE C.1:

Species	A	$10^3 B$	$10^6 C$	$10^{-5} D$
CO <sub>2</sub>	5.457	1.045	—	-1.157
H <sub>2</sub> O	3.470	1.450	—	0.121
O <sub>2</sub>	3.639	0.506	—	-0.227
N <sub>2</sub>	3.280	0.593	—	0.040

$$A = \sum_i n_i A_i = (1)(5.457) + (2)(3.470) + (0.4)(3.639) + (9.03)(3.280)$$

$A = 43.471$

$$B = (10^{-3}) \sum_i n_i B_i = (10^{-3}) \left[ (1)(1.045) + (2)(1.450) + (0.4)(0.506) + (9.03)(0.593) \right]$$

$B = 9.502 \times 10^{-3}$

$$C = (10^{-6}) \sum_i n_i C_i = (10^{-6}) \left[ (1)(0) + (2)(0) + (0.4)(0) + (9.03)(0) \right] \Rightarrow \boxed{C=0}$$

$$D = (10^5) \sum_i n_i D_i = (10^5) \left[ (1)(-1.157) + (2)(0.121) + (0.4)(-0.227) + (9.03)(0.040) \right]$$

$$\boxed{D = -0.6446 \times 10^5}$$

So,

$$\boxed{\frac{C_p^\circ}{R} = 43.471 + 9.502 \times 10^{-3} T - \frac{0.6446 \times 10^5}{T^2}}$$

$$\text{Now, } \Delta H_{298}^\circ + \Delta H_p^\circ = \Delta H = 0$$

$$\text{So, } \Delta H_p^\circ = -\Delta H_{298}^\circ = 802,625 \text{ J}$$

$$= R \int_{298}^T \frac{C_p^\circ}{R} dT$$

$$= R \int_{298}^T \left[ 43.471 + 9.502 \times 10^{-3} T - \frac{0.6446 \times 10^5}{T^2} \right] dT$$

$$= R \left[ 43.471 (T-298) + \frac{9.502 \times 10^{-3}}{2} (T^2 - 298^2) + 0.6446 \times 10^5 \left( \frac{1}{T} - \frac{1}{298} \right) \right] (1 \text{ mol})$$

So,

$$802,625 \text{ J} = \frac{8.314 \text{ J}}{\text{K}} [\text{RHS}]$$

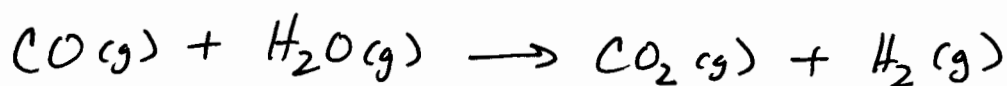
SOLVER:

$$T = 2,066 \text{ K}$$

**EXAMPLE 4.8** ONE METHOD FOR THE MANUFACTURE OF "SYNTHESIS GAS" (A MIXTURE OF CO AND H<sub>2</sub>) IS THE CATALYTIC REFORMING OF CH<sub>4</sub> WITH STEAM AT HIGH TEMPERATURE AND ATMOSPHERIC PRESSURE:



THE ONLY OTHER REACTION TO BE CONSIDERED IS THE WATER-GAS-SHIFT REACTION:

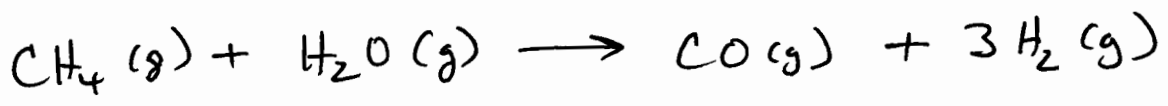


IF THE REACTANTS ARE SUPPLIED IN THE RATIO, 2 mol STEAM TO 1 mol CH<sub>4</sub>, AND IF HEAT IS

SUPPLIED TO THE REACTOR SO THAT THE PRODUCTS REACH A TEMPERATURE OF 1,300 K, THE CH<sub>4</sub> IS COMPLETELY CONVERTED AND THE PRODUCT STREAM CONTAINS 17.4 MOL% CO. ASSUMING THE REACTANTS TO BE PREHEATED TO 600 K, CALCULATE THE HEAT REQUIREMENT FOR THE REACTOR.

FIRST - Calculate  $\Delta H_{298}^{\circ}$  for each reaction.

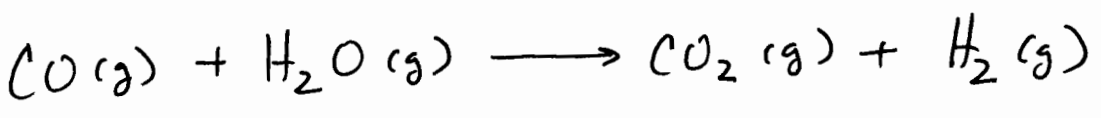
STEAM REFORMING:



$$\Delta H_{298}^{\circ} = (-1)(-74,520) + (-1)(-241,818) + (1)(-110,525) + (3)(0)$$

$$\Delta H_{298}^{\circ} = 205,813 \text{ J}$$

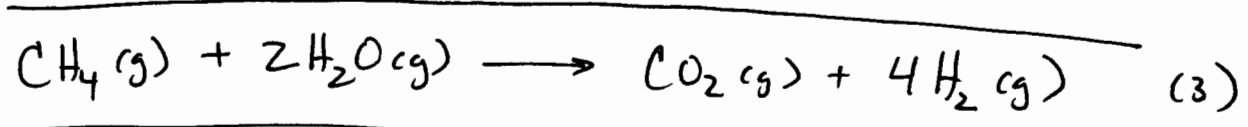
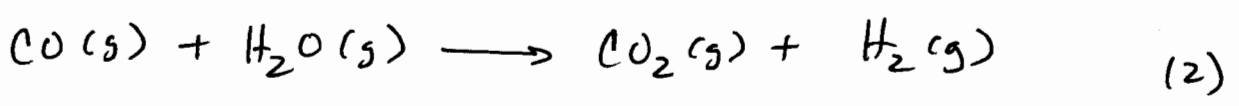
WATER-GAS-SHIFT:



$$\Delta H_{298}^{\circ} = (-1)(-110,525) + (-1)(-241,818) + (1)(-393,509) + (1)(0)$$

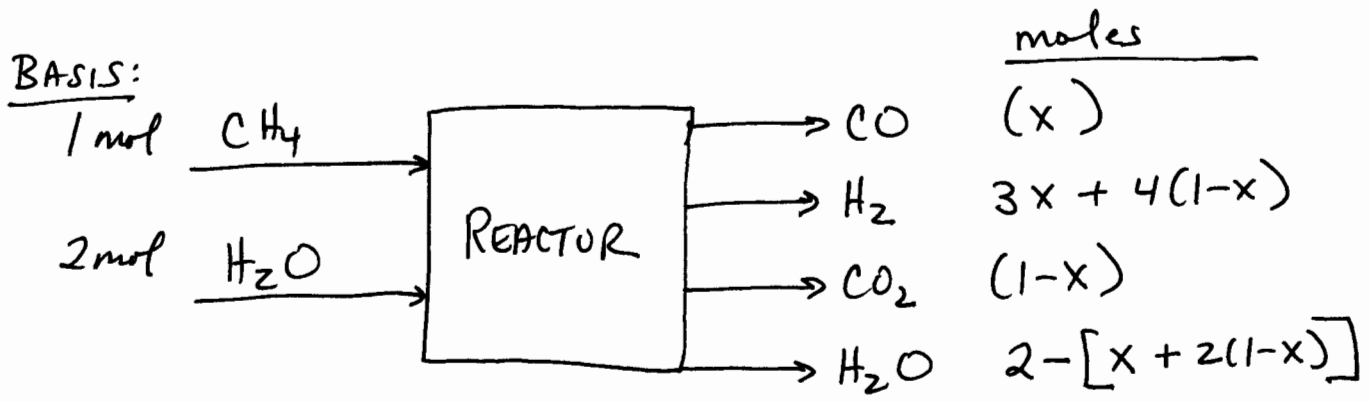
$$\Delta H_{298}^{\circ} = -41,166 \text{ J}$$

So, a third reaction (1 mol CH<sub>4</sub>)



$$\Delta H_{298}^{\circ} = 164,647 \text{ J}$$

Two REACTIONS. CHOOSE REACTIONS (1) + (3)  
BECAUSE WE KNOW HOW MUCH CO IS FORMED.



NO CH<sub>4</sub> IN REACTOR OUTPUT.  
(COMPLETE CONVERSION)

FINAL MOLES IN REACTOR OUTPUT:

$$= (x) + (3x + 4 - 4x) + (1 - x) + (2 - x - 2 + 2x)$$

$$= x(1 + 3 - 4 - 1 - 1 + 2) + (4 + 1 + 2 - 2)$$

$$= x(0) + (5)$$

$$= \boxed{5 \text{ moles product}}$$

PRODUCT STREAM COMPOSITION:

$$\text{CO: } y_{\text{CO}} = 0.174 \Rightarrow n_{\text{CO}} = 0.174(5)$$

$$x \rightarrow \boxed{n_{\text{CO}} = 0.87 \text{ moles}}$$

$$\text{H}_2: 4 - x = \boxed{3.13 \text{ moles} = n_{\text{H}_2}}$$

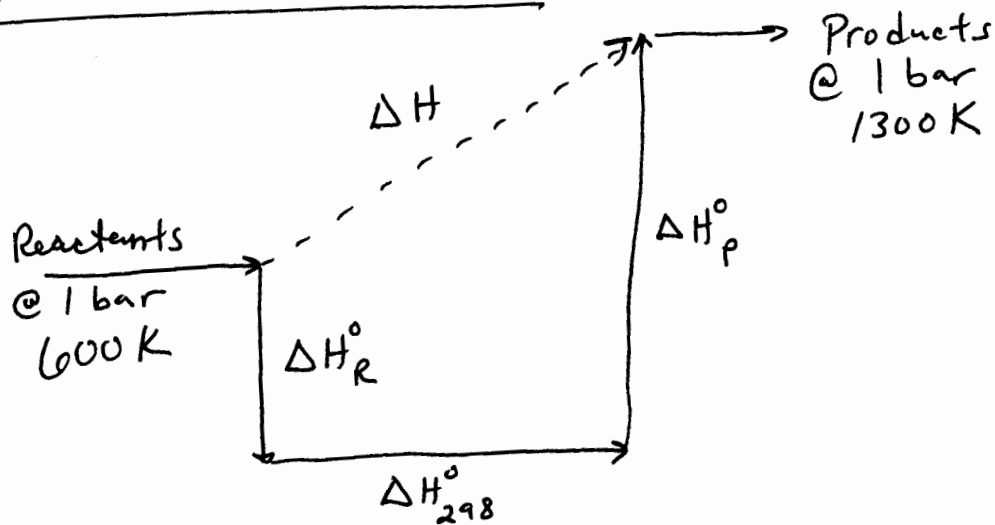
$$\text{CO}_2: 1 - x = \boxed{0.13 \text{ moles} = n_{\text{CO}_2}}$$

$$\text{H}_2\text{O: } x = \boxed{0.87 \text{ moles} = n_{\text{H}_2\text{O}}}$$

$$\sum_i n_i = 5 \text{ moles } \checkmark$$



NEXT, DEFINE PATHWAY:



ENERGY BALANCE:

$$\underline{\Delta H = \Delta H_R^\circ + \Delta H_{298}^\circ + \Delta H_P^\circ}$$

$$\Delta H_{298}^\circ = \underbrace{(0.13)(205,813 \text{ J})}_{(1)} + \underbrace{(0.87)(164,647 \text{ J})}_{(3)}$$

(NOTE: ERROR IN BOOK, P. 146)

$$\boxed{\Delta H_{298}^\circ = 169,999 \text{ J}}$$

NEXT, NEED  $\frac{C_p^\circ}{R}$  PARAMETERS FOR REACTANTS

AND PRODUCTS.

Species:	A	$10^3 B$	$10^6 C$	$10^{-5} D$
CH <sub>4</sub>	1.702	9.081	-2.164	-
H <sub>2</sub> O	3.470	1.450	-	0.121
CO	3.376	0.557	-	-0.031
H <sub>2</sub>	3.249	0.422	-	0.083
CO <sub>2</sub>	5.457	1.045	-	-1.157

REACTANTS:

1 mol CH<sub>4</sub>

2 mol H<sub>2</sub>O

$$A = 8.642$$

$$B = 11.981 \times 10^{-3}$$

$$C = -2.164 \times 10^{-6}$$

$$D = 0.121 \times 10^5$$

$$\Delta H_R^\circ = R \int_{600}^{298} \left[ 8.642 + 11.981 \times 10^{-3} T - 2.164 \times 10^{-6} T^2 + \frac{0.121 \times 10^5}{T^2} \right] dT$$

$$= 8.314 \left[ 8.642(298-600) + \frac{11.981 \times 10^{-3}}{2} (298^2 - 600^2) - \frac{2.164 \times 10^{-6}}{3} (298^3 - 600^3) - 0.121 \times 10^5 \left( \frac{1}{298} - \frac{1}{600} \right) \right]$$

$$\Delta H_R^\circ = -34,239 \text{ J}$$

PRODUCTS:

0.87 mol CO

3.13 mol H<sub>2</sub>0.13 mol CO<sub>2</sub>0.87 mol H<sub>2</sub>O

A = 16.835

B = 3.2028 × 10<sup>-3</sup>

C = 0

D = 0.1877 × 10<sup>5</sup>

$$\Delta H_p^\circ = R \int_{298}^{1300} \left[ 16.835 + 3.2028 \times 10^{-3} T + \frac{0.1877 \times 10^5}{T^2} \right] dT$$

$$= 8.314 \left[ 16.835 (1300 - 298) + \frac{3.2028 \times 10^{-3}}{2} (1300^2 - 298^2) - 0.1877 \times 10^5 \left( \frac{1}{1300} - \frac{1}{298} \right) \right]$$

$$\Delta H_p^\circ = 161,968 \text{ J}$$

Plug + Chug...

$$\Delta H = -34,239 \text{ J} + 169,999 \text{ J} + 161,968 \text{ J}$$

$$\text{So, } \Delta H = 297,728 \text{ J} = Q$$

for  $\Delta E_K, \Delta E_P, W_s$   
 $\approx 0.$

(Note: Error in Book)