

# CH365 Chemical Engineering Thermodynamics

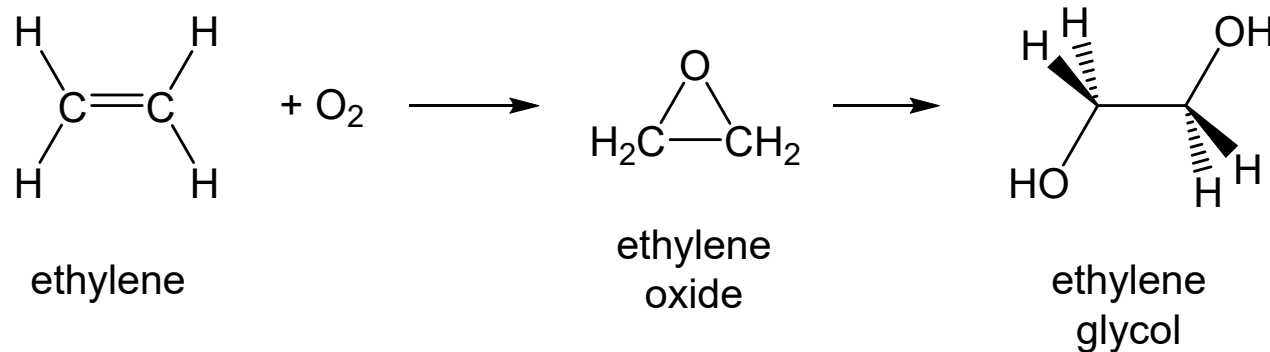
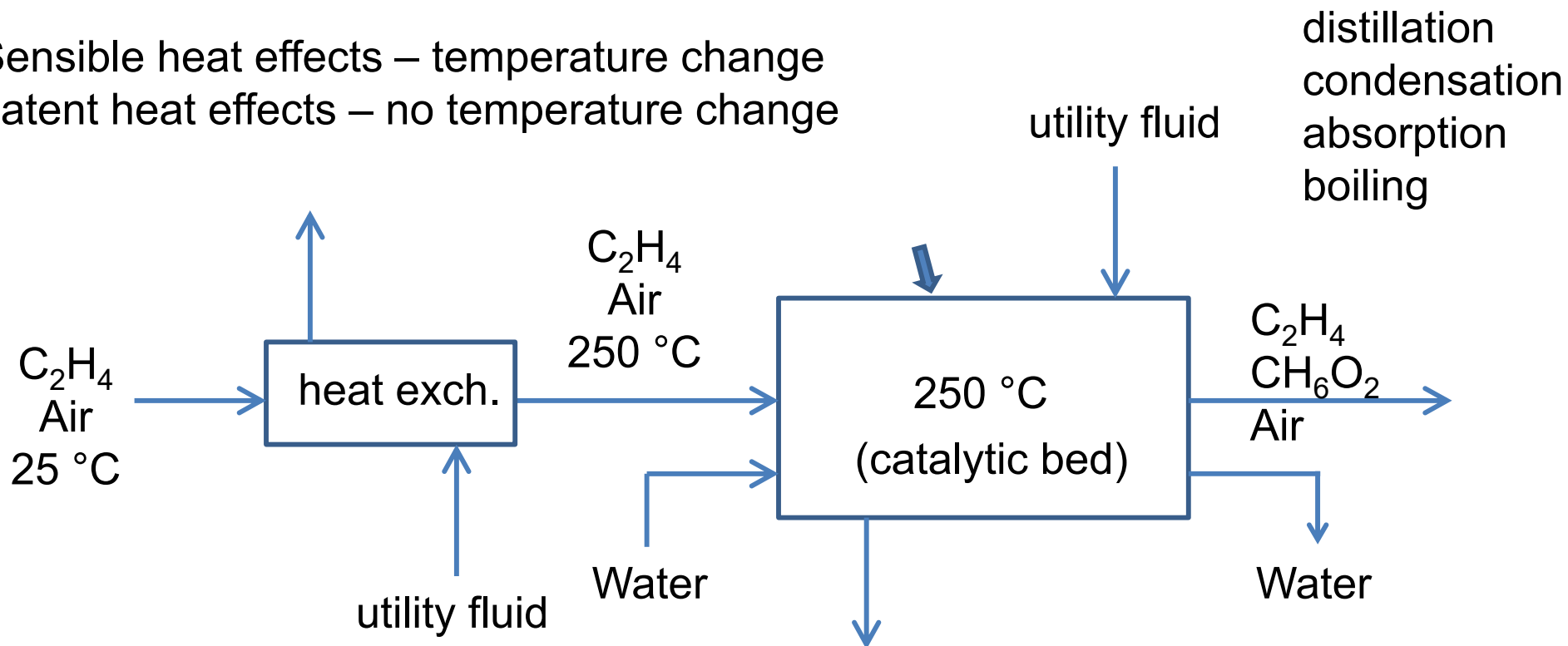
## Lesson 17

### Latent Heat and Heats of Reaction, Formation, and Combustion

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# Ethylene Glycol Process

- Sensible heat effects – temperature change  
 ➔ Latent heat effects – no temperature change



# Latent Heats of Pure Substances

One component evaporating or condensing – No temperature change but heat is transferred. Latent heat of fusion / vaporization.

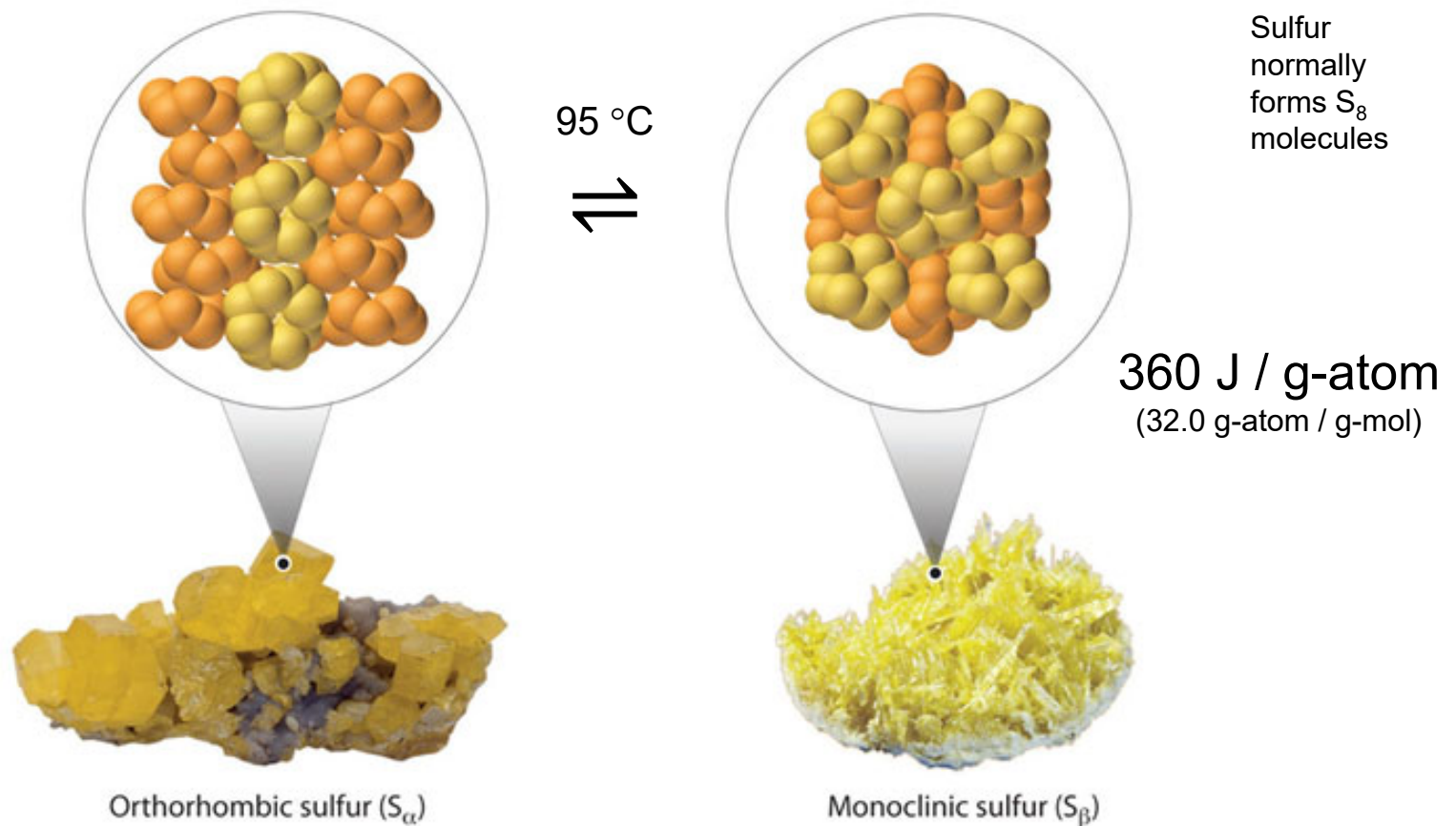


image from <http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0>

L10 Slide 3 Phase Rule:  $F = 2 - \pi + N = 2 - 2 + 1 = 1$

eq 3.1 p. 69

There must be an exact relationship in one intensive variable.

T

# Latent Heats of Pure Substances

One component evaporating or condensing.

## Clapeyron Equation

Calculating  $\Delta H$ :

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

Eq. 4.12, page 146

Molar volume difference  
Cubic EOS

$P^{\text{sat}}$  given by Antoine Equation

$$P^{\text{sat}} = 10^{A - \frac{B}{T+C}}$$

- exact relationship
- leads to Antoine Eq
- derived in Ch. 6

Rough estimate for  
calculating  $\Delta H$ :

## Trouton's Rule:

$$\frac{\Delta H}{RT_n} \sim 10$$

un-numbered equation, p. 142

Rule of Thumb  
Errors ~10%

Normal boiling point

# Latent Heats of Pure Substances

One component evaporating or condensing.

## Reidel's Equation

$$\frac{\Delta H}{RT_n} = \frac{1.092(\ln(P_c) - 1.013)}{0.93 - T_{r_n}}$$

Eq. 4.13, page 147

Empirical Correlation  
Errors < 5%

reduced boiling point

## Watson's Equation

$$\frac{\Delta H_2}{\Delta H_1} = \left( \frac{1 - T_{r_2}}{1 - T_{r_1}} \right)^{0.38}$$

Eq. 4.14, page 147

Error < 5%

reduced temperatures

# Standard Heat of Reaction

Heat effects in chemical reactions are manifestations of the differences in molecular structure.

There are a large number of chemical reactions, each of which can be carried out at an essentially infinite set of process conditions.

Tabulation of all possible heat effects for all possible reactions is impossible.

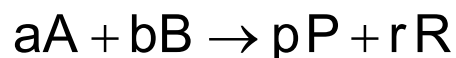
Heats are calculated from data for reactions conducted under standard conditions.

Heat associated with a chemical reaction depends on the temperatures of the reactants and products. A consistent standard treatment is that products and reactants at same temperature.

# Standard Heat of Reaction

Tabulation of all possible heat effects for all possible reactions is impossible. Heats are calculated from data for reactions conducted under standard conditions.

Products and reactants are at the same temperature

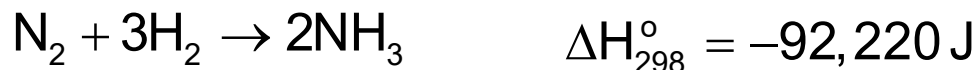


Standard Heat of Reaction is the enthalpy change when  $a$  moles of  $A$  and  $b$  moles of  $B$  in their standard states at temperature  $T$  react to form  $p$  moles of  $P$  and  $r$  moles of  $R$  in their standard states at temperature  $T$

Standard States:

Gases: ideal gas at 1 bar

Liquids and Solids: real pure liquid or solid at 1 bar



Degree symbol designates standard state

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

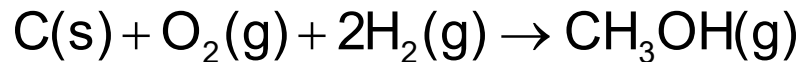
$\Delta H_{298}^{\circ}$  Standard value at 298.15 K

Standard state properties are functions of  $T$

# Standard Heat of Formation

Tabulation of all possible heats of reaction is not practical. The standard heat of reaction can be calculated if the heats of formation of the reactants and products are known.

In a *formation reaction*, a compound forms from its constituent elements.



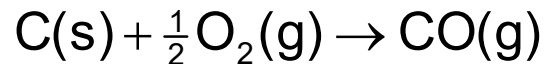
Heat of formation is based on one mole of product

Water-gas-shift reaction:

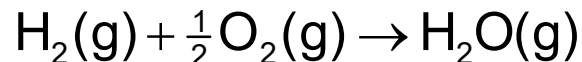
Table C.4, page 672



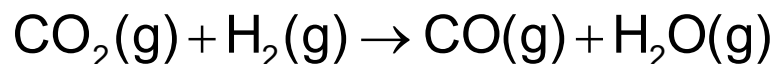
$$\Delta H_{298}^{\circ} = 393,509 \text{ J} \quad \text{negative in Table C.4 (listed as product)}$$



$$\Delta H_{298}^{\circ} = -110,525 \text{ J}$$



$$\Delta H_{298}^{\circ} = -241,818 \text{ J}$$



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



# Homework

# Problem 4.10

(a) For one of the compounds listed in Table B.2 of App. B, evaluate the latent heat of vaporization  $\Delta H_n$  by Eq. 4.13. How does this result compare with the value listed in Table B.2?

(b) Handbook values for latent heats of vaporization at 25 deg C of four compounds are given in the table below. Calculate  $\Delta H_n$  by Eq. 4.14 and compare the result with the value given in Table B.2. (Problem is continued on page 169.)

Latent heats of vaporization at 25 deg C in J/g			
n-Pentane	366.3	Benzene	433.3
n-Hexane	366.1	Cyclohexane	392.5

# Problem 4.12

Handbook values for the latent heat of vaporization in J/g are given in the table (below) for several pure liquids at 0 deg C.

$\Delta H^v$ in J/g at 0 deg	
Chloroform	270.9
Methanol	1189.5
Tetrachloromethane	217.8

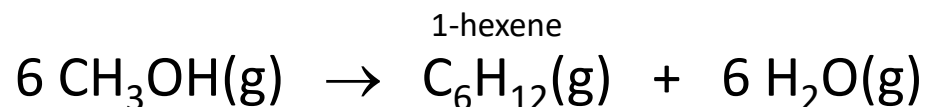
Calculate:

- (a) The value of the latent heat at  $T_n$  by Eq. 4.14, given the value at 0 deg C.
- (b) The value of the latent heat  $T_n$  by Eq. 4.13.

By what percentage do these results differ from the value listed in Table B.2 of App. B?

## Problem 4.20

Hydrocarbon fuels can be produced from methanol by reactions such as the following, which yields 1-hexene:



Compare the standard heat of combustion at 25 deg C of 6  $\text{CH}_3\text{OH}(\text{g})$  with the standard heat of combustion at 25 deg C of  $\text{C}_6\text{H}_{12}(\text{g})$  for reaction products  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$ .

# Lesson 17 – Bonus – 10 Points

Use the Gibbs reactor in CHEMCAD to reproduce your answers to Problem 4.20. That is, compare the standard heat of combustion from CHEMCAD to the results obtained from Mathematica or hand calculations for Problem 4.20.

Complete the following table:

	Mathematica	CHEMCAD
Methanol		
1-Hexene		