

Summary: ΔE , ΔH for Ideal Gasses

- Constant Pressure:

$$q = N\bar{C}_P(T_2 - T_1) \quad w = -P(V_2 - V_1)$$

- Constant Volume:

$$q = N\bar{C}_V(T_2 - T_1) \quad w = 0$$

- Constant Temperature:

$$\Delta E = 0 \quad w = -NRT \ln \frac{V_2}{V_1} \quad q = -w$$

Conversion 1: Isothermal, Isochoric

$$(P_1, V_1, T_1) \xrightarrow{\text{const. } T} (P^*, V_2, T_1) \xrightarrow{\text{const. } V} (P_2, V_2, T_2)$$

- Internal Energy ΔE :

$$\begin{aligned}\Delta E_{tot} &= \Delta E_T + \Delta E_V \\ &= \Delta E_T + q_V + w_V \\ &= 0 + N\bar{C}_V(T_2 - T_1) + 0 \\ &= N\bar{C}_V(T_2 - T_1)\end{aligned}$$

Conversion 1: Isothermal, Isochoric

$$(P_1, V_1, T_1) \xrightarrow{\text{const. } T} (P^*, V_2, T_1) \xrightarrow{\text{const. } V} (P_2, V_2, T_2)$$

- Enthalpy ΔH :


$$\begin{aligned}\Delta H_{tot} &= \Delta E_{tot} + \Delta(PV) \\ &= N\bar{C}_V(T_2 - T_1) + NR(T_2 - T_1) \\ &= N(\bar{C}_V + R)(T_2 - T_1)\end{aligned}$$

Conversion 2: Isothermal, Isobaric

$$(P_1, V_1, T_1) \xrightarrow{\text{const. } T} (P_2, V^*, T_1) \xrightarrow{\text{const. } P} (P_2, V_2, T_2)$$

- Internal Energy ΔE :

$$\begin{aligned}\Delta E_{tot} &= \Delta E_T + \Delta E_P \\ &= \Delta E_T + q_P + w_P \\ &= 0 + N\bar{C}_P(T_2 - T_1) - NR(T_2 - T_1) \\ &= N(\bar{C}_P - R)(T_2 - T_1)\end{aligned}$$

Used the Ideal Gas Law


Wait a Second...

- First we showed that:

$$\Delta E_{tot} = N\bar{C}_V(T_2 - T_1)$$

- Then we proved that:

$$\Delta E_{tot} = N(\bar{C}_P - R)(T_2 - T_1)$$

- If E is a state function (it is), then it must be true that (for an ideal gas):

$$\bar{C}_V = \bar{C}_P - R$$

Wait a Second...

- Additionally, for **any** change of P, V, T in an ideal gas:

$$\Delta E = N\bar{C}_V\Delta T$$
$$\Delta H = N\bar{C}_P\Delta T$$

- This is true regardless of whether the change was done at constant volume or pressure!

What Have We Learned?

- We can calculate ΔE , ΔH for liquids/solids given the heat capacities
- For an ideal gas, we can calculate ΔE , ΔH for various paths *and given any change in temperature regardless of path!*
- For an ideal gas, $\bar{C}_V = \frac{3}{2}R$ and $\bar{C}_P = \bar{C}_V + R$

Two Key Points

(For systems with only PV Work)

- If we know \bar{C}_P , we can *always* calculate ΔH from T_1 and T_2 using:

$$\Delta H = \int_{T_1}^{T_2} n\bar{C}_P dT$$

Ideal gas: This is always true (P needn't be constant)

Others: True when P is constant

- The same applies to ΔE :

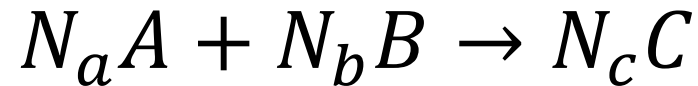
$$\Delta E = \int_{T_1}^{T_2} n\bar{C}_V dT$$

Ideal gas: This is always true (V needn't be constant)

Others: True when V is constant

Chemical Change

- Simple Chemical Reaction:



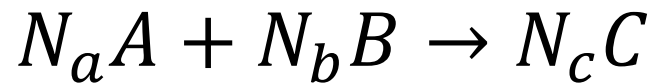
- Each component has an internal energy, \bar{E}_i :

$$\begin{aligned}\Delta E &= E_f - E_i \\ &= N_c \bar{E}_c - (N_a \bar{E}_a + N_b \bar{E}_b)\end{aligned}$$

- This is true because E is a state function

Chemical Change

- Simple Chemical Reaction:



- Works with enthalpy, too: $H = E + PV$:

$$H_f = N_c \bar{H}_c \quad H_i = (N_a \bar{H}_a + N_b \bar{H}_b)$$

$$\Delta H = H_f - H_i = H_{products} - H_{reactants}$$

- $\Delta \bar{E}$ and $\Delta \bar{H}$: Moles of what? (see p. 49)

State Function Implications

Implication #1:

If:

$A \rightarrow B$ has an enthalpy of ΔH

Then:

$B \rightarrow A$ has an enthalpy of $-\Delta H$.

(Can you prove this?)

State Function Implications

If:

A

Chemistry 1 Reminder:

- $\Delta H > 0$: endothermic, system absorbs heat ($\Delta q > 0$)

Then:

B

- $\Delta H < 0$: exothermic, system produces heat ($\Delta q < 0$)

(Can you prove this?)

State Function Implications

Implication #2 (Hess's Law)

If:

$A \rightarrow B$ with ΔH_{AB} , and

$B \rightarrow C$ with ΔH_{BC}

Then:

$A \rightarrow C$ has an enthalpy of $\Delta H_{AB} + \Delta H_{BC}$

(Can you prove this?)

State Function Implications

Implication #3

If:

A has \bar{H}_A at T_1

Heat capacity of A (\bar{C}_{PA}) is constant vs. T

Then (if P constant):

$$\bar{H}_A(T_2) = \bar{H}_A(T_1) + \bar{C}_P^A(T_2 - T_1)$$

(Can you prove this?)

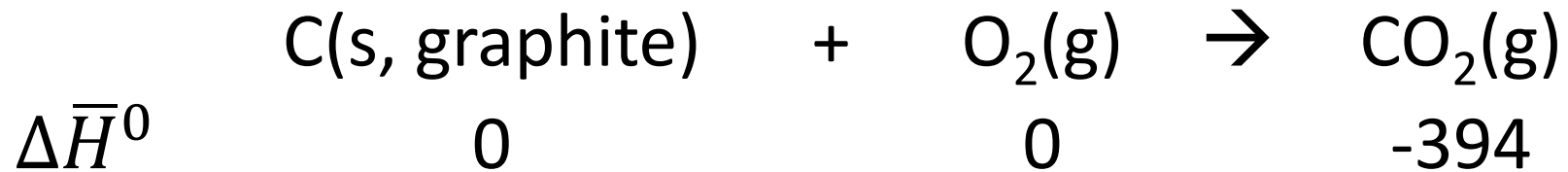
If Only We Knew H...

- We can't know H explicitly, but we can measure H relative to a *reference* state

$$\Delta\bar{H}_A^0 = \bar{H}_A - \bar{H}_{reference}$$

- Choose a standard *reference state*: pure elements in their maximally stable form at STP have $\Delta\bar{H}^0 = 0$
- If the reference is used consistently, $\Delta\bar{H}^0$ can be used for all calculations of $\Delta\bar{H}$ and all measurements of heat

Example: Enthalpy of Formation



- Because the reference of C, O₂ are defined at 0, the *heat* measured the reaction above (-394 kJ mol⁻¹) is $\Delta\bar{H}_{\text{CO}_2}^0$
- *Enthalpies (heats) of formation* can be found in appendices (Tables A.5-A-7)

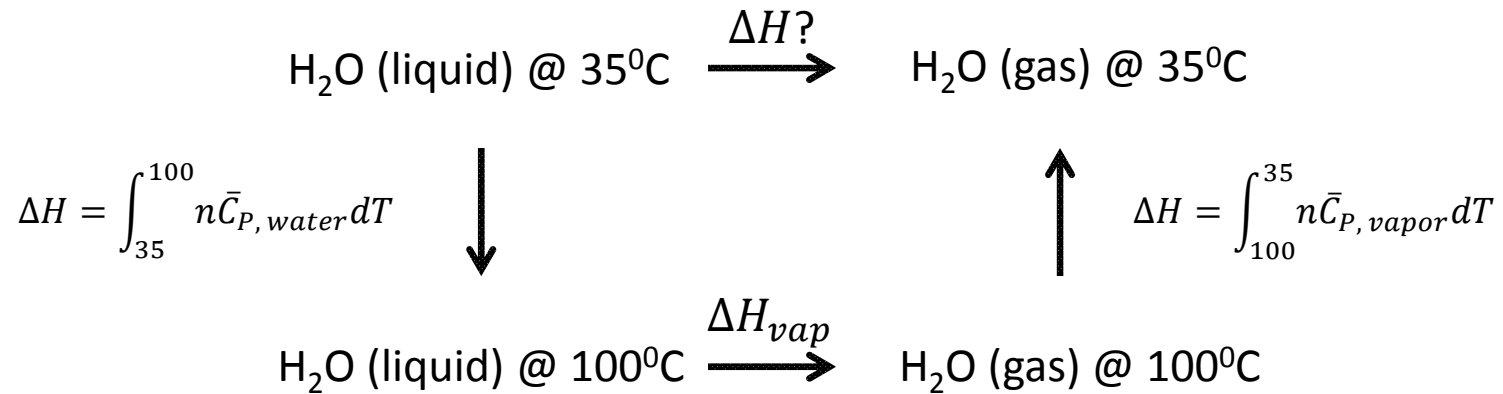
Phase Changes

- $\Delta\bar{H}$ of a phase change can be measured directly at constant P (why?)



- Change in internal energy can be calculated from $\Delta E = \Delta H - P\Delta V$
- Many properties of water available in Table 2.2

Putting it all Together

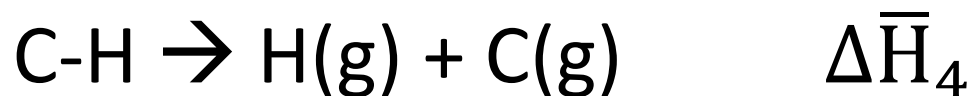
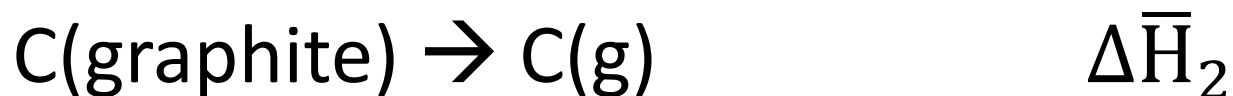
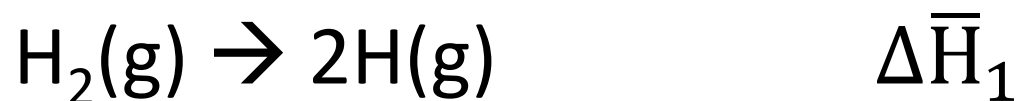


- How to calculate the change in enthalpy?
 - Use path independence!
 - What if I only know $\Delta H_{cond.}$?

Estimating $\Delta\bar{H}^0$ from Bond Energies

(Table 2.3)

- Simple reaction for creating ethylene:



- Then $\Delta\bar{H}^0$ of C_2H_4 would be (approximately):

$$\Delta\bar{H}_{\text{C}_2\text{H}_4}^0 = 2\Delta\bar{H}_1 + 2\Delta\bar{H}_2 - \Delta\bar{H}_3 - 4\Delta\bar{H}_4$$