

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

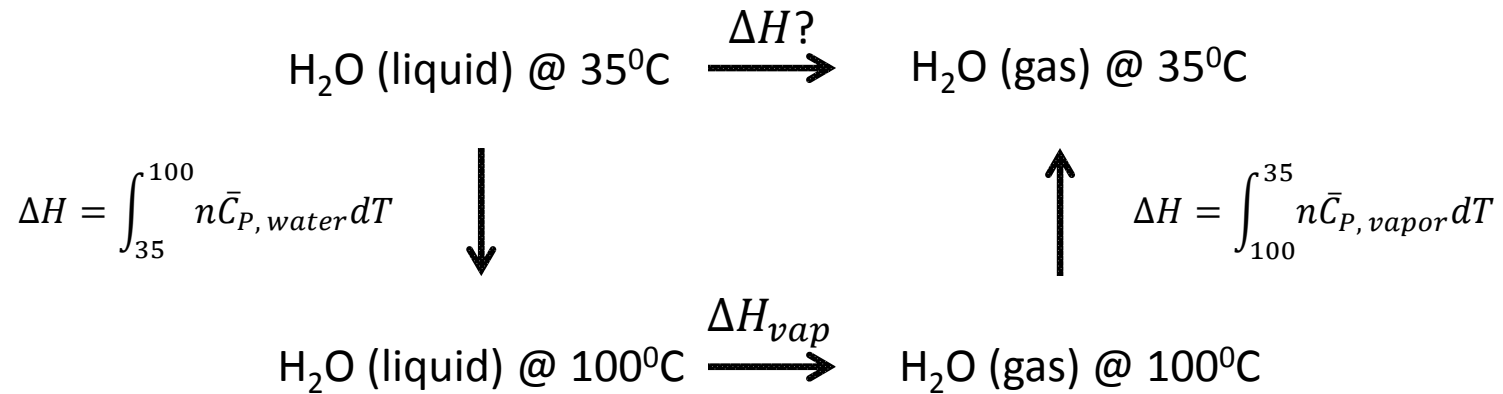
- The same applies to ΔE :

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

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

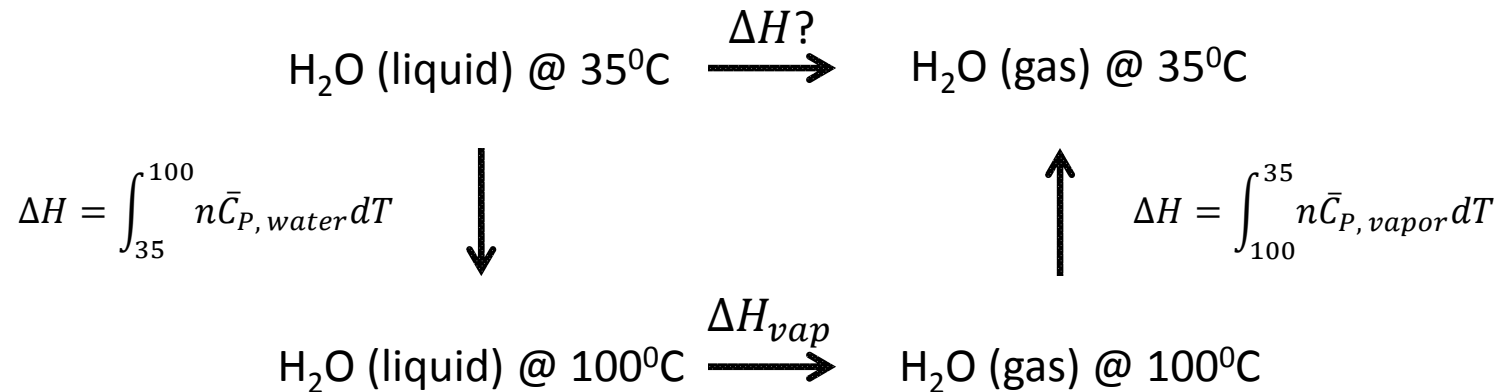
Others: True when V is constant

Example: Getting Fancy



- How to calculate the change in enthalpy?

Example: Getting Fancy



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

Chemistry, Here We Come...

- We've shown that (because H is a state function):

$$\begin{aligned}\Delta H &= H_{final} - H_{initial} \\ &= \sum H_{products} - \sum H_{reactants}\end{aligned}$$

- 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?*)

Chemistry, Here We Come...

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Chemistry 1 Reminder:

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

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Chemistry, Here We Come...

- We've shown that (because H is a state function):

$$\begin{aligned}\Delta H &= H_{final} - H_{initial} \\ &= \sum H_{products} - \sum H_{reactants}\end{aligned}$$

- Implication #2 (Hess's Law):
Consider $A \rightarrow B$ 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?*)

Chemistry, Here We Come...

- We've shown that (because H is a state function):

$$\begin{aligned}\Delta H &= H_{final} - H_{initial} \\ &= \sum H_{products} - \sum H_{reactants}\end{aligned}$$

- Implication #3:
The temperature dependence of a reaction enthalpy is can be calculated from individual heat capacities of products and reactants.

If Only We Knew H...

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

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

- The reference state is often chosen relative to a pure compound, and can be measured calorimetrically
- *Enthalpies of formation* work exactly the same way as regular enthalpies, and you can look them up