Summary: ΔE, ΔH for Ideal Gasses

- Constant Pressure:

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

- Constant Volume:

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

- Constant Temperature:

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

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

$$(\mathrm{P}_1, \mathrm{V}_1, \mathrm{T}_1) \xrightarrow{\text{const. T}} (\mathrm{P}_2, \mathrm{V}^*, \mathrm{T}_1) \xrightarrow{\text{const. } P} (\mathrm{P}_2, \mathrm{V}_2, \mathrm{T}_2)$$

- Internal Energy ΔE:

Used the Ideal Gas Law

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

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

$$\begin{tikzcd}
\text{H}_2\text{O (liquid) @ }35^0\text{C} \arrow[r, "\Delta H?"] \arrow[d, swap, "\Delta H = \int_{35}^{100} n\bar{C}_{P,\,water}\,dT"] & \text{H}_2\text{O (gas) @ }35^0\text{C} \\
\text{H}_2\text{O (liquid) @ }100^0\text{C} \arrow[r, "\Delta H_{vap}"] & \text{H}_2\text{O (gas) @ }100^0\text{C} \arrow[u, swap, "\Delta H = \int_{100}^{35} n\bar{C}_{P,\,vapor}\,dT"]
\end{tikzcd}$$

- How to calculate the change in enthalpy?

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\end{tikzcd}$$

- 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 → B has an enthalpy of ΔH, then B → A has an enthalpy of –ΔH. *(Can you prove this?)*

Chemistry, Here We Come…

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Chemistry 1 Reminder:

- ΔH > 0: endothermic, system absorbs heat (Δq > 0)
- ΔH < 0: exothermic, system produces heat (Δq < 0)

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 → B with ΔH_{AB} and B → C with ΔH_{BC}. Then A → 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

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

- 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