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

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

- 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

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

- 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

Chemical Change

- Simple Chemical Reaction:

$$N_a A + N_b B \rightarrow N_c C$$

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

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

- This is true because E is a state function

Chemical Change

- Simple Chemical Reaction:

$$N_a A + N_b B \rightarrow N_c C$$

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

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

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

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

State Function Implications

Implication #1:

If:

A → B has an enthalpy of ΔH

Then:

B → A has an enthalpy of $-\Delta H$.

(Can you prove this?)

State Function Implications

If:

A

Then:

B

Chemistry 1 Reminder:

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

(Can you prove this?)

State Function Implications

Implication #2 (Hess's Law)

If:

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?)

State Function Implications

Implication #3

If:

A has $\bar{\bar{H}}_A$ at T_1

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

Then (if P constant):

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

(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

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

- Choose a standard *reference state*: pure elements in their maximally stable form at STP have $\Delta \overline{H}^0 = 0$

- If the reference is used consistently, $\Delta \overline{H}^0$ can be used for all calculations of $\Delta \overline{H}$ and all measurements of heat

Example: Enthalpy of Formation

	C(s, graphite)	+	O_2(g)	→	CO_2(g)
$\Delta\overline{H}^0$	0		0		-394

- Because the reference of C, O_2 are defined at 0, the *heat* measured the reaction above (-394 kJ mol^{-1}) is $\Delta\overline{H}^0_{CO_2}$

- *Enthalpies (heats) of formation* can be found in appendices (Tables A.5-A-7)

Phase Changes

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

H_2O (s) → H_2O (l) $\Delta\overline{H}_{\mathrm{melt}} = 6.01\ \mathrm{kJ\ mol^{-1}}$

- 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

H_2O (liquid) @ 35^0C $\xrightarrow{\Delta H?}$ H_2O (gas) @ 35^0C

$\Delta H = \int_{35}^{100} n\bar{C}_{P,\,water}dT$ ↓ ↑ $\Delta H = \int_{100}^{35} n\bar{C}_{P,\,vapor}dT$

H_2O (liquid) @ 100^0C $\xrightarrow{\Delta H_{vap}}$ H_2O (gas) @ 100^0C

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

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

(Table 2.3)

- Simple reaction for creating ethylene:

$H_2(g)$ → 2H(g)		$\Delta\overline{\mathrm{H}}_1$
C(graphite) → C(g)		$\Delta\overline{\mathrm{H}}_2$
C=C → 2C(g)		$\Delta\overline{\mathrm{H}}_3$
C-H → H(g) + C(g)		$\Delta\overline{\mathrm{H}}_4$

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

$$\Delta\overline{H}^0_{C_2H_4} = 2\Delta\overline{H}_1 + 2\Delta\overline{H}_2 - \Delta\overline{H}_3 - 4\Delta\overline{H}_4$$