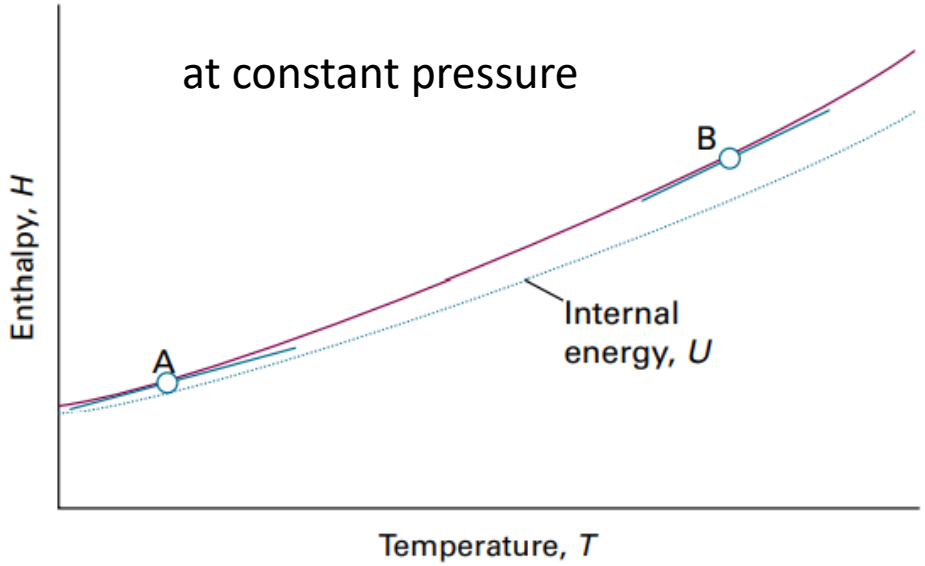
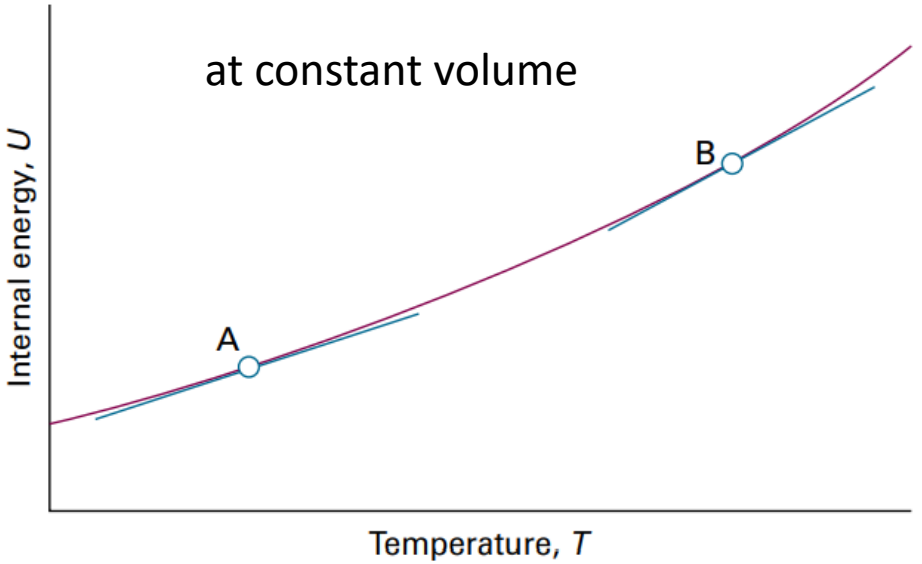
C_p and C_v





$$C_p = \left(\frac{\partial H}{\partial T}\right)_p > C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

perfect gas: $C_p - C_V = nR$

R = 8.314 J mol^{-1} K^{-1}
= 0.082 05 L atm mol^{-1} K^{-1}

Variation of heat capacity (molar)

$$C_{p,\mathrm{m}} = a + bT + \frac{c}{T^2}$$

a, b, and c are empirical parameters

	a	$b/(10^{-3}\ \mathrm{K}^{-1})$	$c/(10^{5}\ \mathrm{K}^{2})$
C(s, graphite)	16.86	4.77	−8.54
$CO_2(g)$	44.22	8.79	−8.62
$H_2O(l)$	75.29	0	0
$N_2(g)$	28.58	3.77	−0.50

Question What is the change in molar enthalpy of N_2 when it is heated from 25 °C to 100 °C? Use the heat capacity information in Table

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$$= 2.20\ \text{kJ mol}^{-1}$$

Focus 2: The First Law

Internal Energy

Enthalpy

Thermochemistry

State functions

Adiabatic changes

Enthalpy change

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exothermic (exenthalpic) process: $\Delta H < 0$
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Standard (molar) enthalpy of vaporization

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta_{vap}H^{\ominus}(373\,K) = +40.66\,kJ\,mol^{-1}$$

Enthalpy change

All are molar quantities

Transition	Exemplary Chemical Reaction	Symbol
Transition (Phase α → Phase β)	$\mathrm{Diamond} \rightarrow \mathrm{Graphite}$	$\Delta_{\mathrm{trs}}H$
Fusion (s → l)	$\mathrm{H_2}O(s) \rightarrow \mathrm{H_2}O(l)$	$\Delta_{\mathrm{fus}}H$
Vaporization (l → g)	$\mathrm{H_2}O(l) \rightarrow \mathrm{H_2}O(g)$	$\Delta_{\mathrm{vap}}H$
Sublimation (s → g)	$\mathrm{CO_2}(s) \rightarrow \mathrm{CO_2}(g)$	$\Delta_{\mathrm{sub}}H$
Mixing (Pure → Mixture)	$\mathrm{NaCl} + \mathrm{H_2}O \rightarrow \mathrm{NaCl(aq)}$	$\Delta_{\mathrm{mix}}H$
Solution (Solute → Solution)	$\mathrm{KCl(s)} \rightarrow \mathrm{K^+}(aq) + \mathrm{Cl^-}(aq)$	$\Delta_{\mathrm{sol}}H$
Hydration ($X^{\pm}(g) \rightarrow X^{\pm}(aq)$)	$\mathrm{Cu^{2+}}(g) + 6H_2O \rightarrow \mathrm{Cu^{2+}} \cdot 6H_2O(aq)$	$\Delta_{\mathrm{hyd}}H$
Atomization (Species → Atoms)	$\mathrm{H_2}(g) \rightarrow 2H(g)$	$\Delta_{\mathrm{at}}H$
Ionization ($X(g) \rightarrow X^+(g) + e^-$)	$\mathrm{Na}(g) \rightarrow \mathrm{Na^+}(g) + e^-$	$\Delta_{\mathrm{ion}}H$
Electron Gain ($X(g) + e^- \rightarrow X^-(g)$)	$\mathrm{Cl}(g) + e^- \rightarrow \mathrm{Cl^-}(g)$	$\Delta_{\mathrm{eg}}H$
Reaction (Reactants → Products)	$\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightarrow \mathrm{H_2}O(g)$	ΔH
Combustion	$\mathrm{CH_4}(g) + 2\mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) + 2\mathrm{H_2}O(g)$	$\Delta_{\mathrm{c}}H$
Formation (Elements → Compound)	$\mathrm{C}(s) + 2\mathrm{H_2}(g) \rightarrow \mathrm{CH_4}(g)$	$\Delta_f H$
Activation (Reactants → Activated Complex)	$\mathrm{H_2}(g) + \mathrm{I_2}(g) \rightarrow [H_2I_2]^{\ddagger}$	$\Delta^{\ddagger}H$

Enthalpy is a state function

- A state function means that its value depends only on the initial and final states of the system, not on the path taken.

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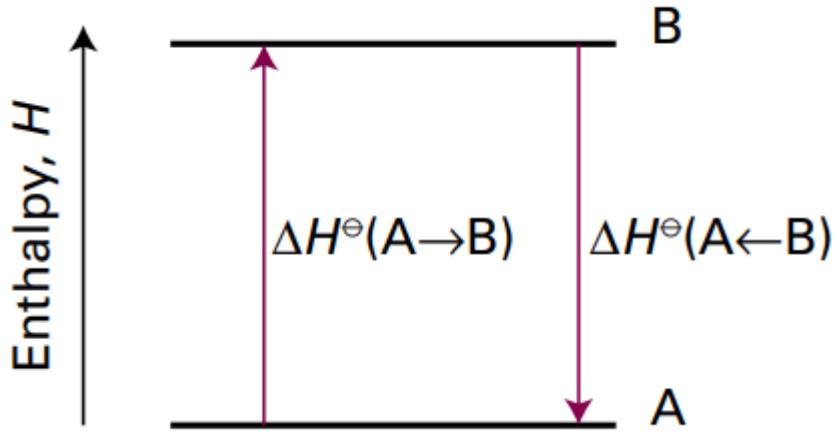
- A direct consequence of enthalpy being a state function is that the enthalpy change of a forward reaction is equal in magnitude but opposite in sign to that of the reverse reaction.

$$\Delta H^{\ominus}(\mathrm{A} \rightarrow \mathrm{B}) = -\Delta H^{\ominus}(\mathrm{A} \leftarrow \mathrm{B})$$



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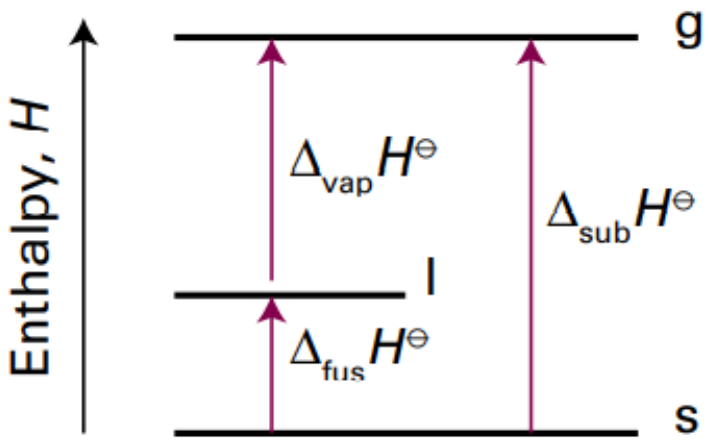

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standard reaction enthalpy, $\Delta_r H^\ominus$

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$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus$$

Hess's Law

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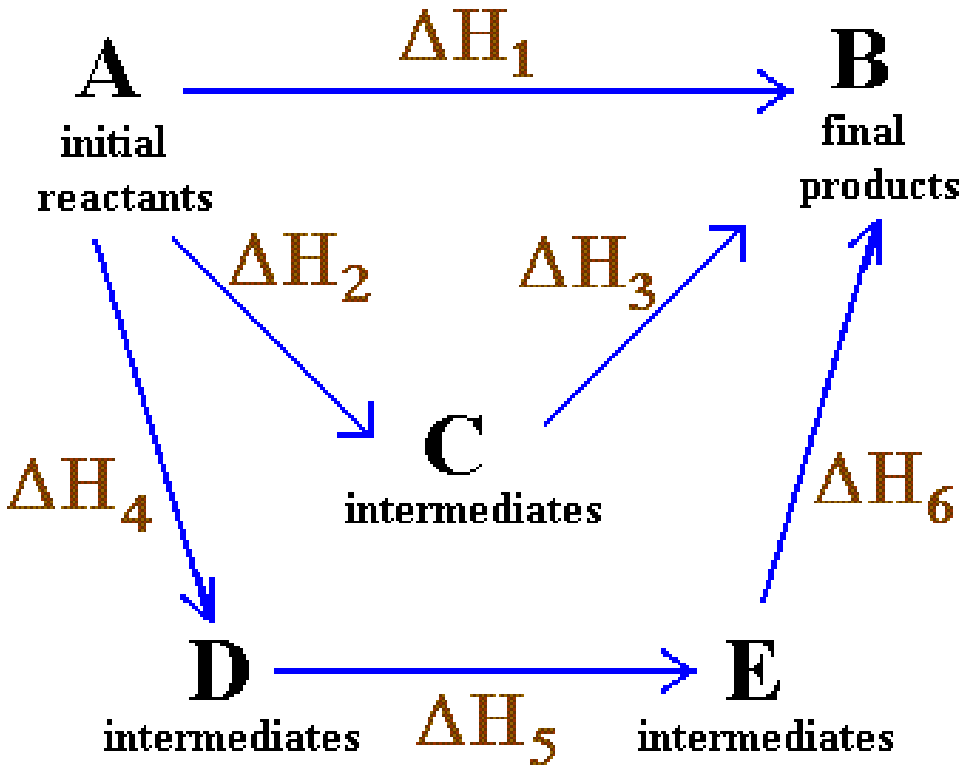

Standard enthalpy of formation

$$6\,C(s,graphite) + 3\,H_2(g) \rightarrow C_6H_6(l) \qquad +49.0\,kJ\,mol^{-1}.$$

The **standard enthalpy of formation**, $\Delta_f H^{\ominus}$, of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states:

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Enthalpy of formation of an element in reference states = 0 kJ/mol

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The reference state is specifically used for elements, not compounds.

Element	Reference State (Most Stable Form at 298 K, 1 bar)
Hydrogen (H)	$H_2(g)$
Oxygen (O)	$O_2(g)$
Bromine (Br)	$Br_2(l)$
Carbon (C)	Graphite $C(s)$
Sulfur (S)	Rhombic Sulfur $S_8(s)$
Phosphorus (P)	White Phosphorus $P_4(s)$
Iron (Fe)	$Fe(s)$
Mercury (Hg)	$Hg(l)$

Standard enthalpy of formation

	$\Delta_f H^{\ominus}/(\text{kJ mol}^{-1})$
$H_2O(l)$	−285.83
$H_2O(g)$	−241.82
$NH_3(g)$	−46.11
$N_2H_4(l)$	+50.63
$NO_2(g)$	+33.18
$N_2O_4(g)$	+9.16
NaCl(s)	−411.15
KCl(s)	−436.75

	$\Delta_f H^{\ominus}/(\text{kJ mol}^{-1})$
$CH_4(g)$	−74.81
$C_6H_6(l)$	+49.0
$C_6H_{12}(l)$	−156
$CH_3OH(l)$	−238.66
$CH_3CH_2OH(l)$	−277.69

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$$\Delta_f H^\ominus(H^+,aq) = 0$$

Stoichiometric numbers (vs Stoichiometric coefficients)

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$$\Delta_r H^{\ominus} = \sum_{\text{Products}} \nu \Delta_f H^{\ominus} - \sum_{\text{Reactants}} \nu \Delta_f H^{\ominus}$$

Standard reaction enthalpy
[practical implementation]

Stoichiometric numbers (vs Stoichiometric coefficients)

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Standard reaction enthalpy
[practical implementation]

$$\Delta_r H^{\ominus} = \sum_{J} \nu_J \Delta_f H^{\ominus}(J)$$

stoichiometric numbers

(positive for products and negative for reactants)

Example

$$2\,HN_3(l) + 2\,NO(g) \rightarrow H_2O_2(l) + 4\,N_2(g)$$

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$$= \{-187.78 + 4(0)\}\,kJ\,mol^{-1} - \{2(264.0) + 2(90.25)\}\,kJ\,mol^{-1}$$

$$= -896.3\,kJ\,mol^{-1}$$