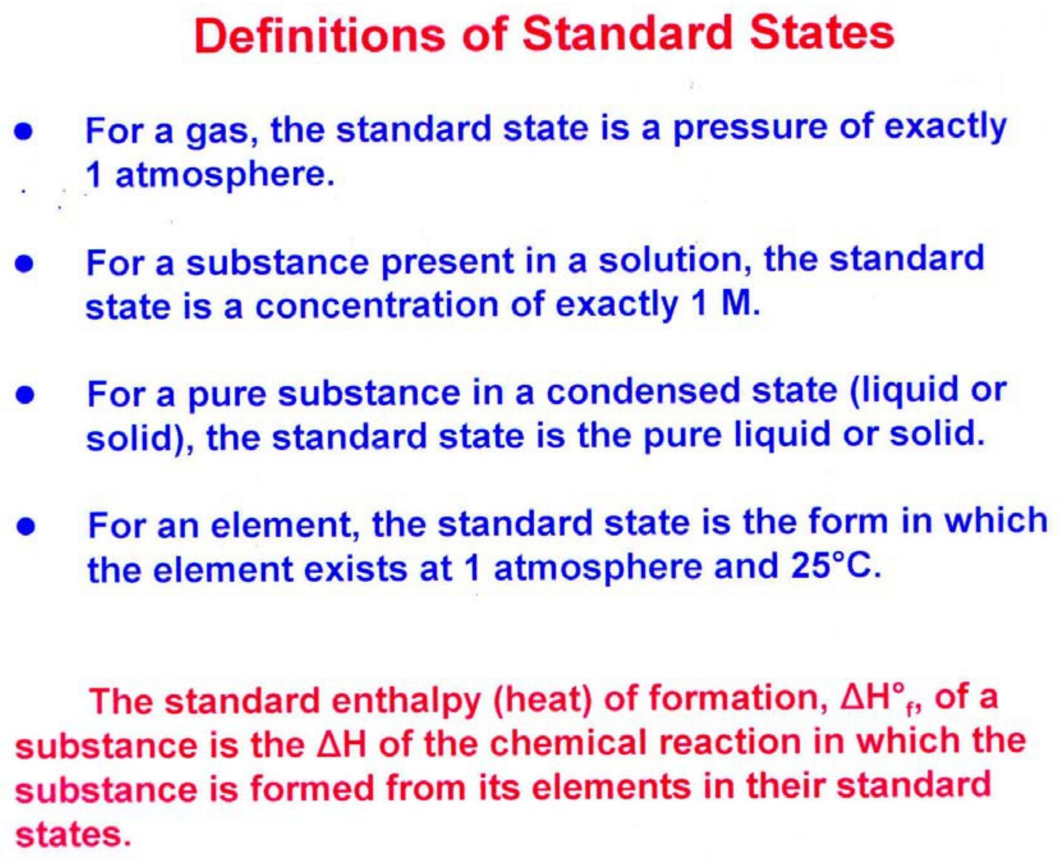
Topic 4D - Thermochemistry



Definitions of Standard States

- For a gas, the standard state is a pressure of exactly 1 atmosphere.
- For a substance present in a solution, the standard state is a concentration of exactly 1 M.
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
- For an element, the standard state is the form in which the element exists at 1 atmosphere and 25°C.

The standard enthalpy (heat) of formation, ΔH°_f, of a substance is the ΔH of the chemical reaction in which the substance is formed from its elements in their standard states.

Standard Enthalpies of Formation at 25°C

Compound	ΔH°_f (kJ/mol)
NH_3 *(g)*	−46
NO_2 *(g)*	34
H_2O *(l)*	−286
Al_2O_3 *(s)*	−1,676
Fe_2O_3 *(s)*	−826
CO_2 *(g)*	−394
CH_3OH *(l)*	−239
C_8H_{18} *(l)*	−269

$0.5\ N_2\ (g) + 1.5\ H_2\ (g) \rightarrow NH_3\ (g)$ $\Delta H^\circ = -46$ kJ/mol

$0.5\ N_2\ (g) + O_2\ (g) \rightarrow NO_2\ (g)$ $\Delta H^\circ = +34$ kJ/mol

$H_2\ (g) + 0.5\ O_2\ (g) \rightarrow H_2O\ (l)$ $\Delta H^\circ = -286$ kJ/mol

$2\ Al\ (s) + 1.5\ O_2\ (g) \rightarrow Al_2O_3\ (s)$ $\Delta H^\circ = -1{,}676$ kJ/mol

$2\ Fe\ (s) + 1.5\ O_2\ (g) \rightarrow Fe_2O_3\ (s)$ $\Delta H^\circ = -826$ kJ/mol

$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$ $\Delta H^\circ = -394$ kJ/mol

$C\ (s) + 2\ H_2\ (g) + 0.5\ O_2\ (g) \rightarrow CH_3OH\ (l)$ $\Delta H^\circ = -239$ kJ/mol

$8\ C\ (s) + 9\ H_2\ (g) \rightarrow C_8H_{18}\ (l)$ $\Delta H^\circ = -269$ kJ/mol

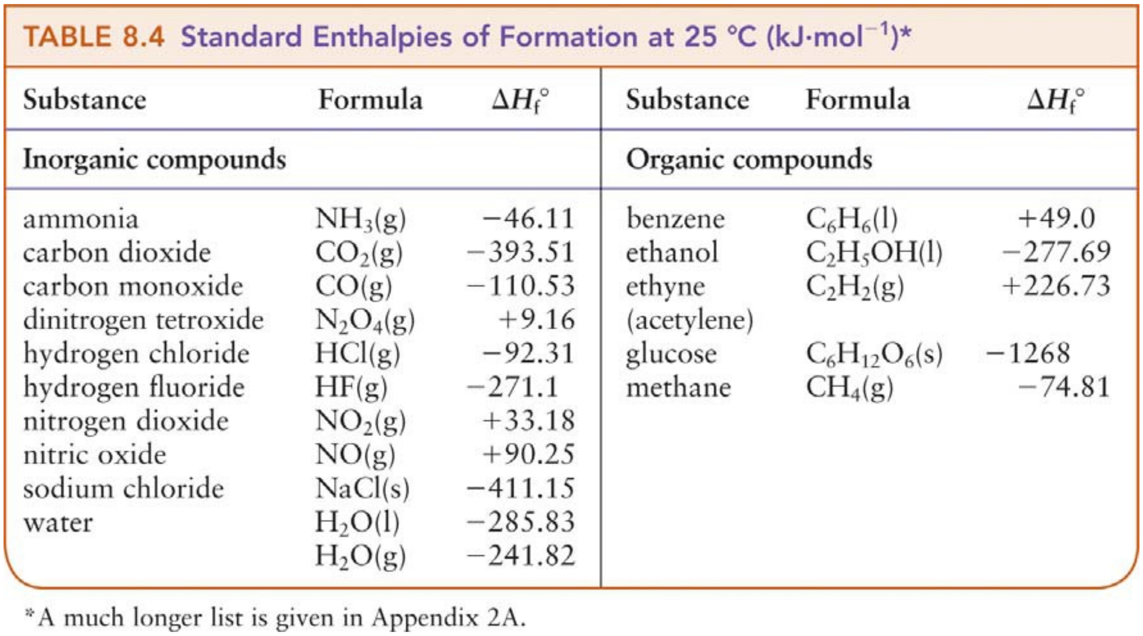
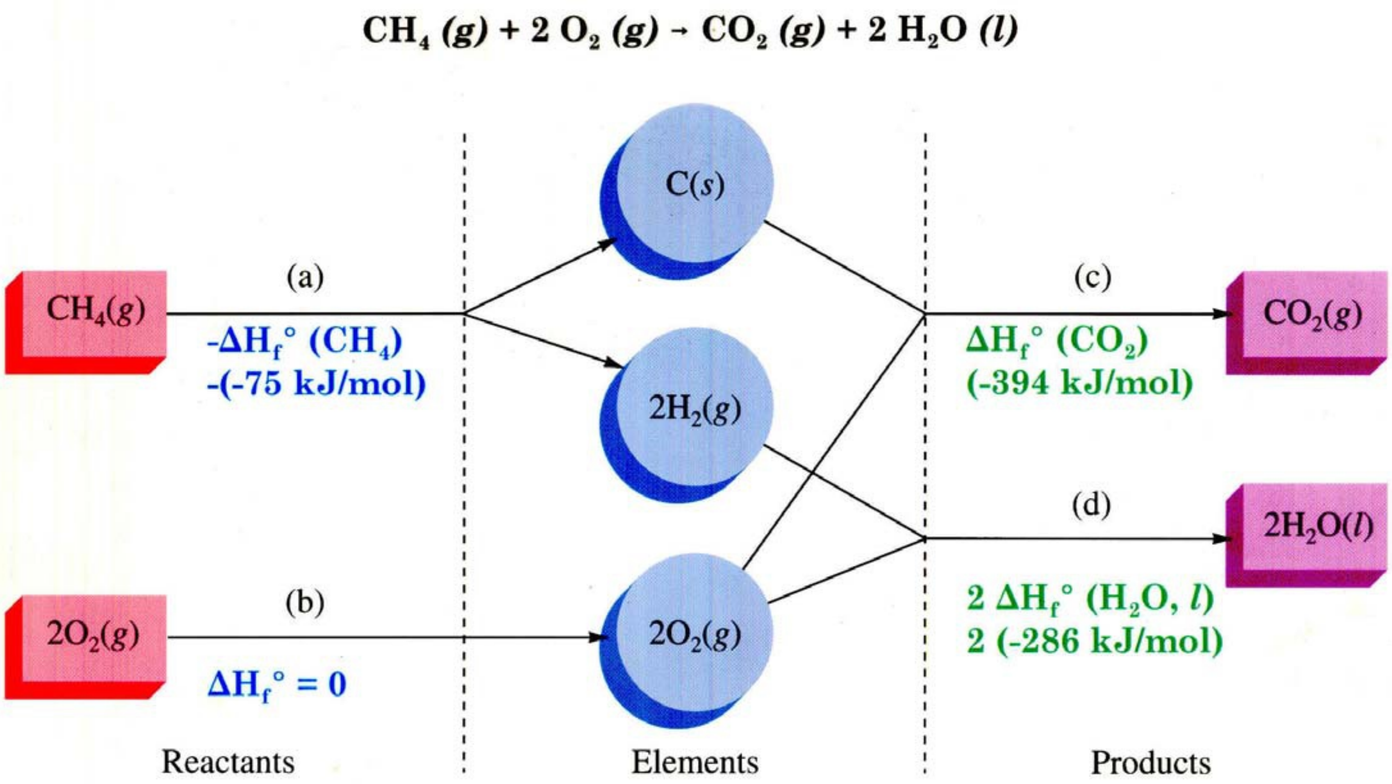


TABLE 8.4 Standard Enthalpies of Formation at 25 °C (kJ·mol^{-1})*

Substance	Formula	ΔH_f°	Substance	Formula	ΔH_f°
Inorganic compounds			**Organic compounds**		
ammonia	$NH_3(g)$	−46.11	benzene	$C_6H_6(l)$	+49.0
carbon dioxide	$CO_2(g)$	−393.51	ethanol	$C_2H_5OH(l)$	−277.69
carbon monoxide	$CO(g)$	−110.53	ethyne (acetylene)	$C_2H_2(g)$	+226.73
dinitrogen tetroxide	$N_2O_4(g)$	+9.16			
hydrogen chloride	$HCl(g)$	−92.31	glucose	$C_6H_{12}O_6(s)$	−1268
hydrogen fluoride	$HF(g)$	−271.1	methane	$CH_4(g)$	−74.81
nitrogen dioxide	$NO_2(g)$	+33.18			
nitric oxide	$NO(g)$	+90.25			
sodium chloride	$NaCl(s)$	−411.15			
water	$H_2O(l)$	−285.83			
	$H_2O(g)$	−241.82			

*A much longer list is given in Appendix 2A.



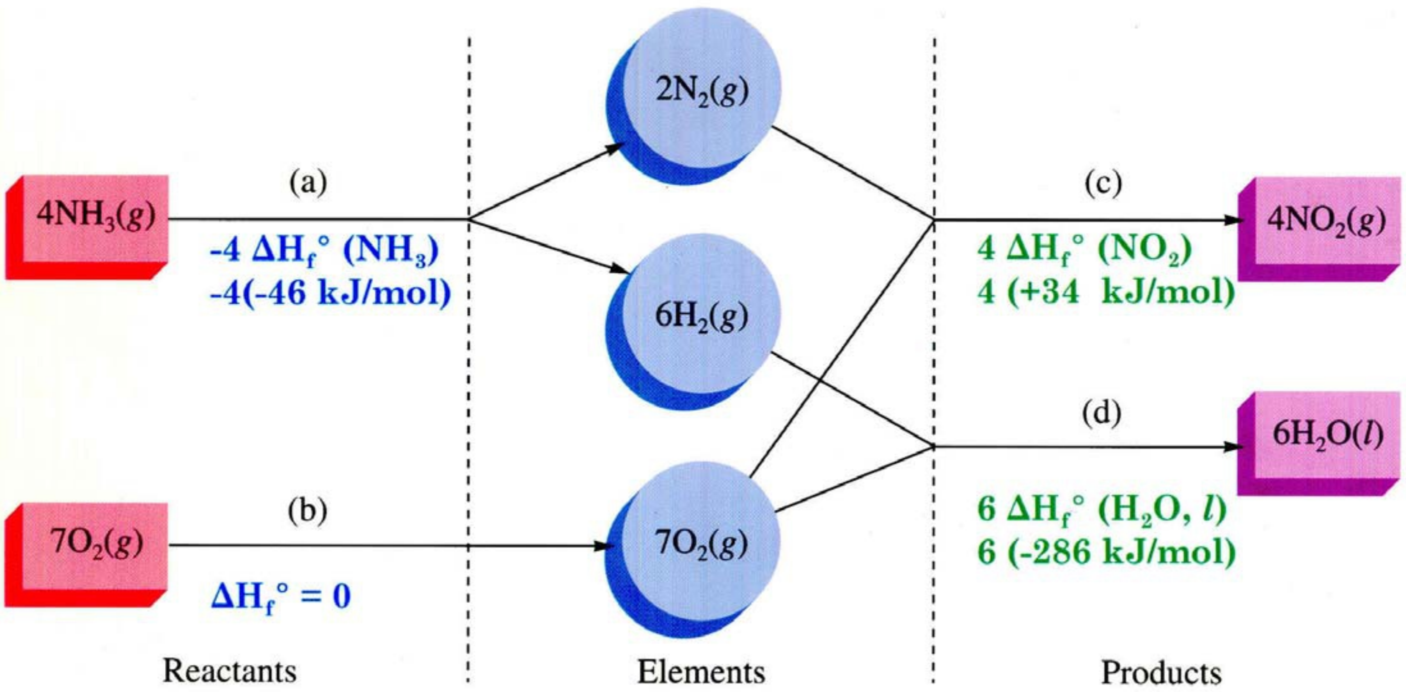
$$\Delta H^\circ = \Delta H_{(c)}{}^\circ + 2\ \Delta H_{(d)}{}^\circ - \Delta H_{(a)}{}^\circ - \Delta H_{(b)}{}^\circ$$

$$= -394 + 2(-286) - (-75) - 0 \qquad = -891\ \text{kJ/mol}\ CH_4$$

Figure 6.8

Pathway for combustion of methane

$$4\ NH_3\ (g) + 7\ O_2\ (g) \rightarrow 4\ NO_2\ (g) + 6\ H_2O\ (l)$$



$$\Delta H° = 4\ \Delta H_{(c)}° + 6\ \Delta H_{(d)}° - 4\ \Delta H_{(a)}° - 7\ \Delta H_{(b)}°$$
$$= 4(+34) + 6(-286) - 4(-46) - 7\ (0) \qquad = -\ 1396\ kJ/mol$$
$$= -\ 349\ kJ/mol\ NH_3$$

Figure 6.9
Pathway for combustion of ammonia

Keep in Mind the Following Key Concepts When Doing Enthalpy Calculations:

- When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.

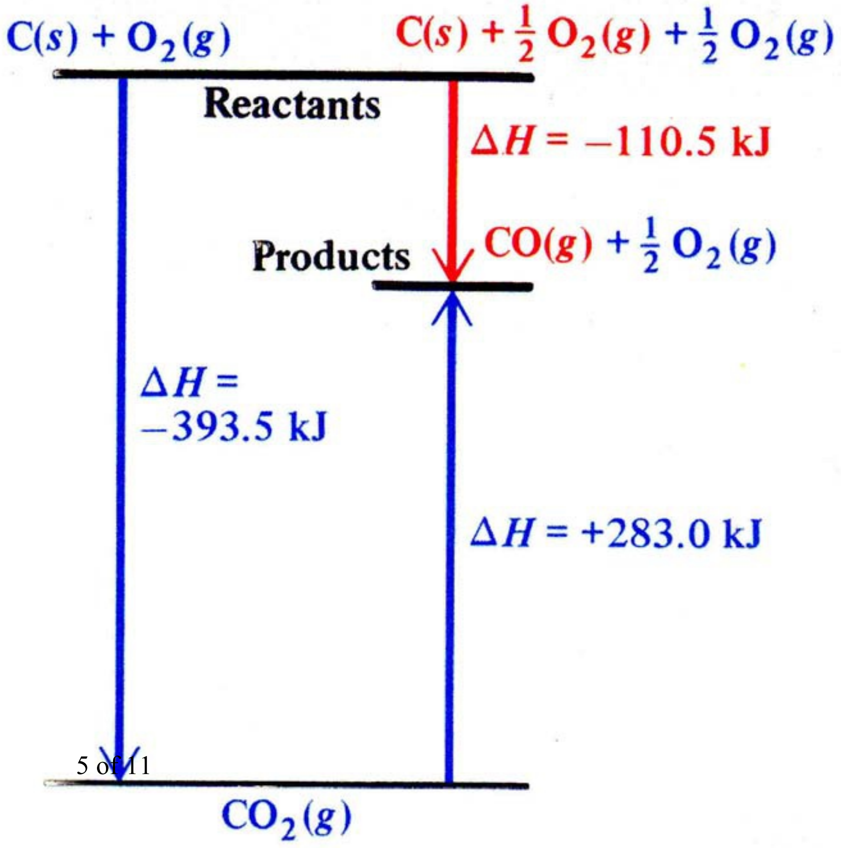
- When the balanced equation for a reaction is multiplied by an integer, the value of ΔH for that reaction must be multiplied by the same integer.

- The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^\circ_{\text{reaction}} = \sum n_p \Delta H^\circ_f(\text{products}) - \sum n_r \Delta H^\circ_f(\text{reactants})$$

- Elements in their standard states are not included in the $\Delta H_{\text{reaction}}$ calculations. That is, ΔH°_f for an element in its standard state is zero.

Key concepts for enthalpy calculations



Hess' Law Examples

Given:

$-[N_2\,(g) + O_2\,(g) \rightarrow 2\,NO\,(g)]$ $-[\Delta H^\circ = +180.5\ kJ]$
$N_2\,(g) + 2\,O_2\,(g) \rightarrow 2\,NO_2\,(g)$ $\Delta H^\circ = +66.4\ kJ$

Determine:

$2\,NO\,(g) + O_2\,(g) \rightarrow 2\,NO_2\,(g)$ $\Delta H^\circ = -114.1\ kJ$

Given:

$-2[S\,(s) + O_2\,(g) \rightarrow SO_2\,(g)]$ $-2[\Delta H^\circ = -296.8\ kJ]$
$2\,S\,(s) + 3\,O_2\,(g) \rightarrow 2\,SO_3\,(g)$ $\Delta H^\circ = -791.4\ kJ$

Determine:

$2\,SO_2\,(g) + O_2\,(g) \rightarrow 2\,SO_3\,(g)$ $\Delta H^\circ = -197.8\ kJ$

Given:

$-2[NH_3\,(g) + HCl\,(g) \rightarrow NH_4Cl\,(s)]$ $-2[\Delta H^\circ = -176.0\ kJ]$
$-[N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g)]$ $-[\Delta H^\circ = -92.2\ kJ]$
$N_2\,(g) + 4\,H_2\,(g) + Cl_2\,(g) \rightarrow 2\,NH_4Cl\,(s)$ $\Delta H^\circ = -628.8\ kJ$

Determine:

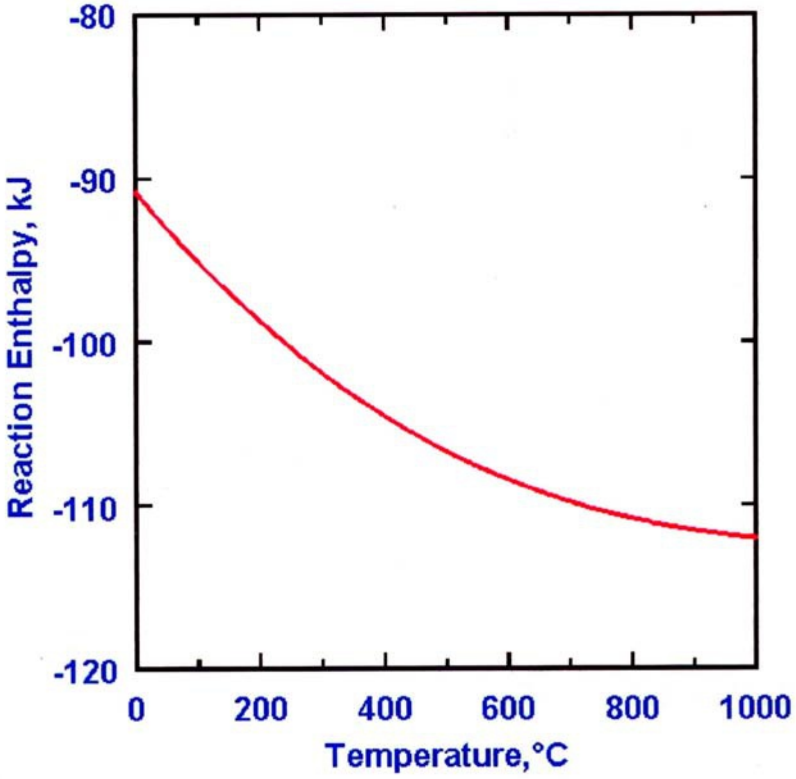
$H_2\,(g) + Cl_2\,(g) \rightarrow 2\,HCl\,(g)$ $\Delta H^\circ = -184.6\ kJ$

Effect of Temperature on ΔH

For the reaction:

$N_2\ (g) + 3\ H_2\ (g) \rightleftarrows 2\ NH_3\ (g)$ $\Delta H^\circ_{298} = -92.2$ kJ

$\Delta C_p = -[29.1 + 3\ (28.8)] + 2\ (35.1) = -45.3$ J/K



Since $\Delta H = nC_p\Delta T$, and because the total heat capacity of the products of the above reaction is less than that of the reactants, then ΔH becomes increasingly more negative with increasing temperature.

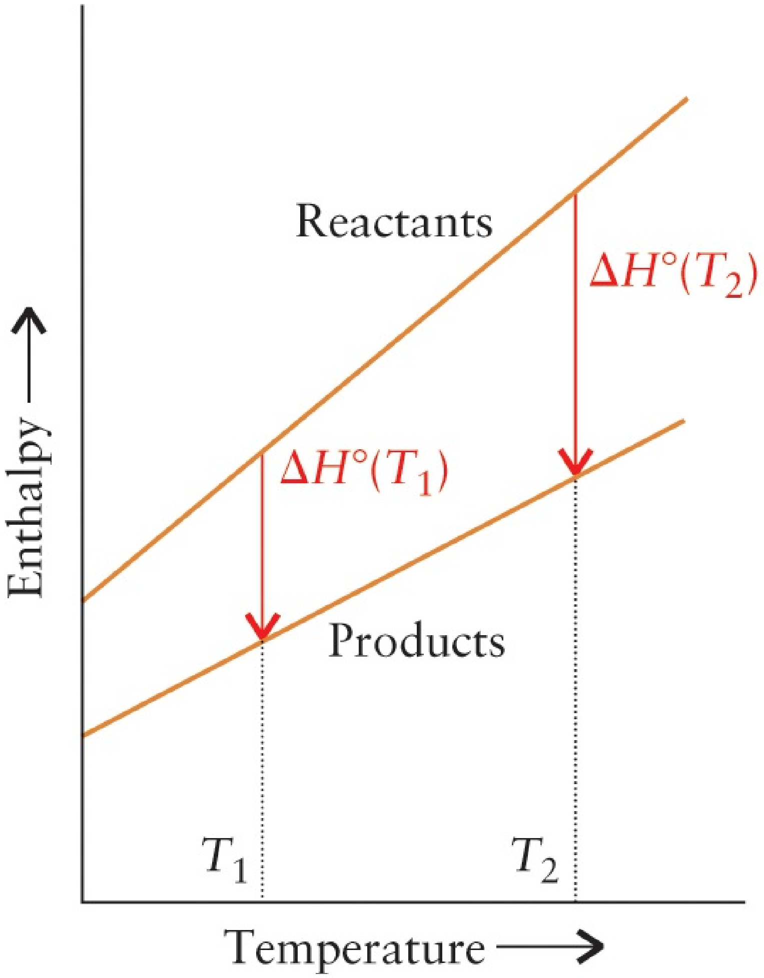
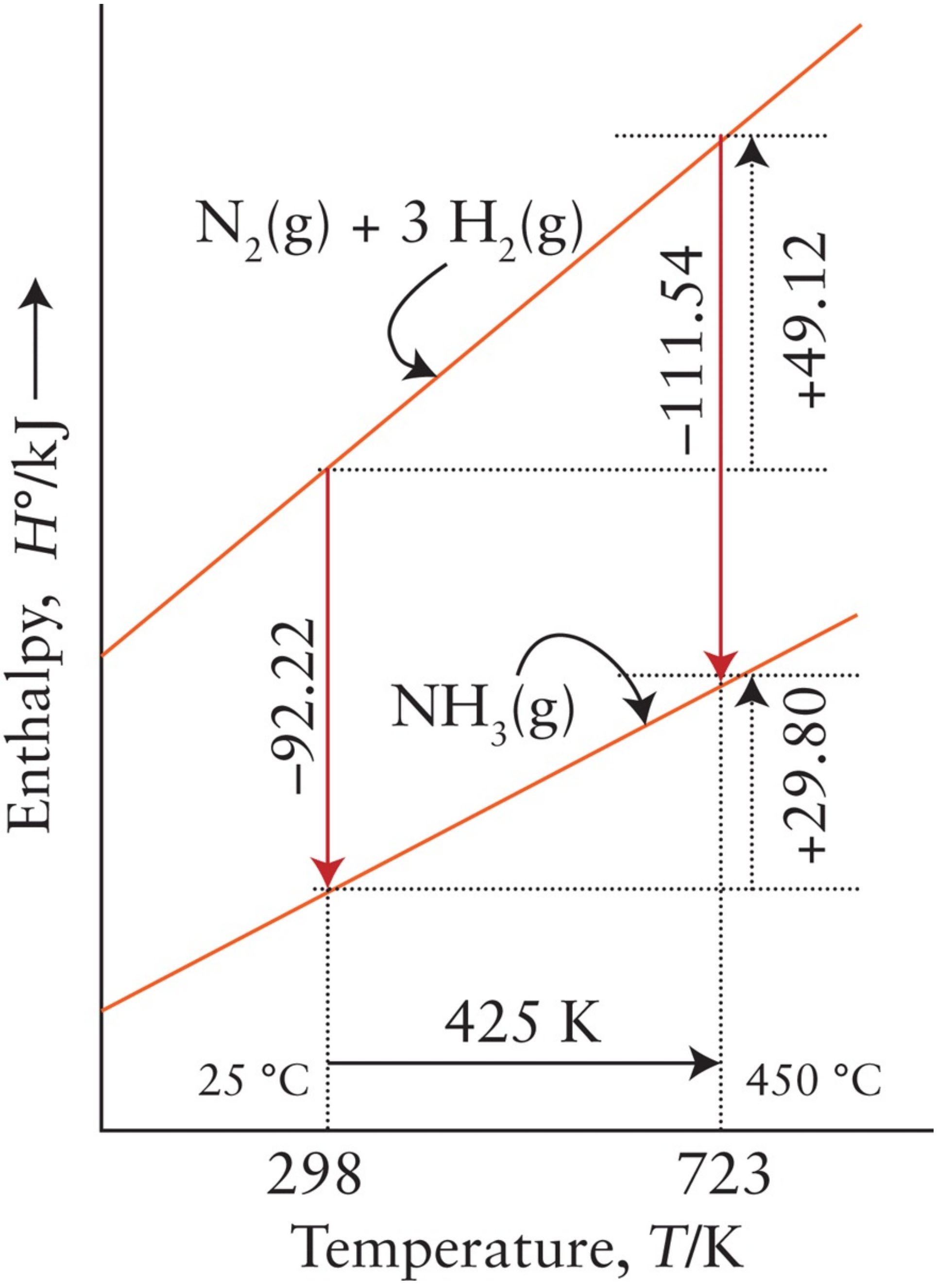


FIGURE 8.35 If the heat capacity of the reactants is larger than that of the products, the enthalpy of the reactants will increase more sharply with increasing temperature. If the reaction is exothermic, the reaction enthalpy will become more negative, as shown here.

$\Delta H_{298} = -92.22$ kJ/mol

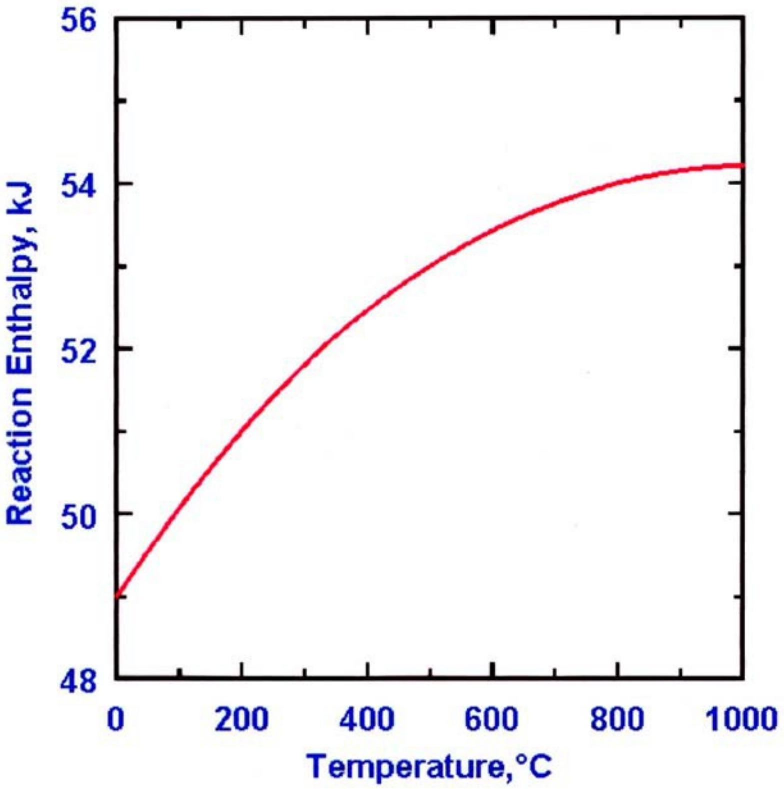
$\Delta H_{723} = -111.54$ kJ/mol



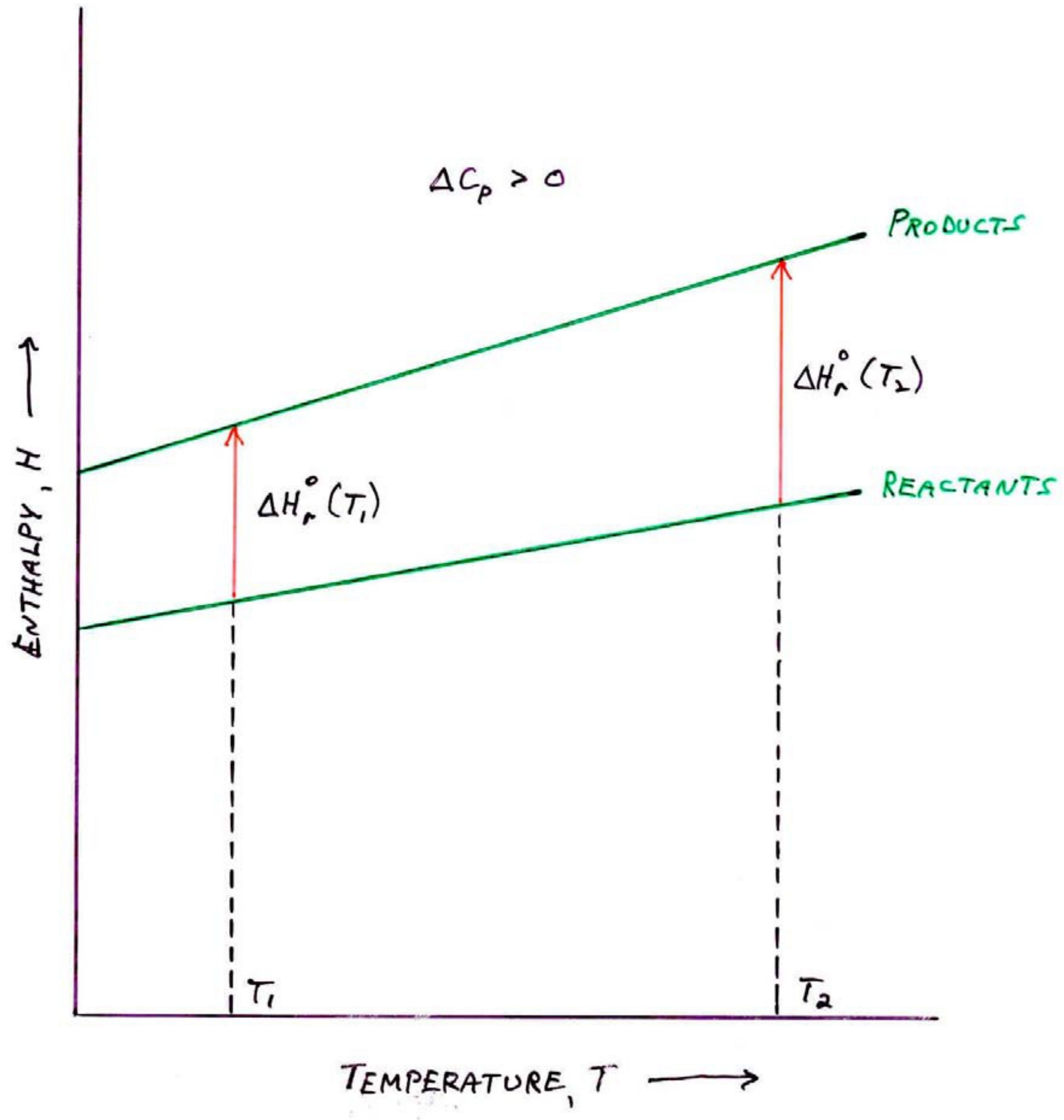
For the reaction

$CH_4\ (g) + H_2O\ (g) \rightleftarrows CO\ (g) + 3\ H_2\ (g)$ $\Delta H^\circ_{298} = +49.2\ kJ$

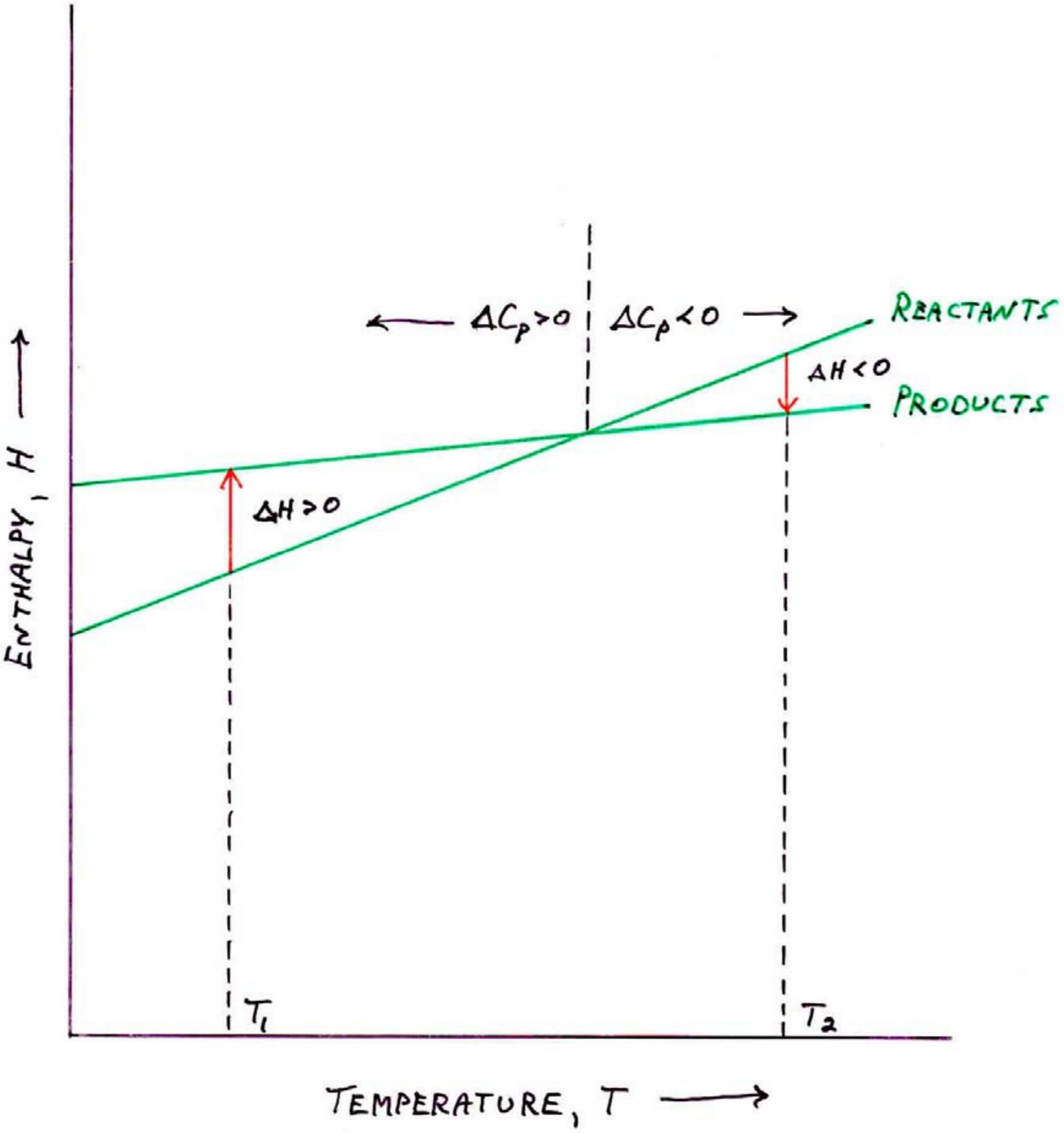
$\Delta C_p = -[35.3 + 35.6] + [29.1 + 3(28.8)] = +44.6\ J/K$



Since $\Delta H = nC_p\Delta T$, and because the total heat capacity of the products of the above reaction is greater than that of the reactants, then ΔH becomes increasingly more positive with increasing temperature.



Depending on the values of the heat capacities of reactants and products, a reaction can change between endothermic and exothermic at a particular temperature:


ΔCp>0
ΔCp<0
REACTANTS
PRODUCTS
ΔH<0
ΔH>0
ENTHALPY, H
T1
T2
TEMPERATURE, T