Enthalpy of Reaction

By

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Chemical metallurgy

- **Chemical metallurgy encompasses the extraction and refining of metals, liquid metal treatments, and the corrosion protection and surface treatment of metals.**
- **Thermodynamics is the study of the energies involved in a reaction and, therefore, provides information regarding the driving force behind a reaction.**
- **By studying the energy requirements it is possible to determine the optimum conditions necessary to provide the desired reaction.**

Thermochemistry

- Thermochemistry is the study of heat energies, *H*, in a reaction and as such provides important information regarding heat balances and fuel requirements in a metallurgical process. The unit of heat energy is the joule or kilojoule (J or kJ).

Exothermic and endothermic reactions

Every known chemical reaction involves an energy change; most reactions occur with an evolution of heat and are called *exothermic reactions,* a few reactions (which will normally only take place at high temperatures) absorb heat and are called *endothermic reactions.*

If heat is lost by the system, i.e. given out to the surroundings (exothermic reaction) a negative sign (-) is placed in front of the stated quantity of heat.

Conversely if the system gains heat from the surroundings (endothermic reaction) a positive sign is used. Two examples are given below:

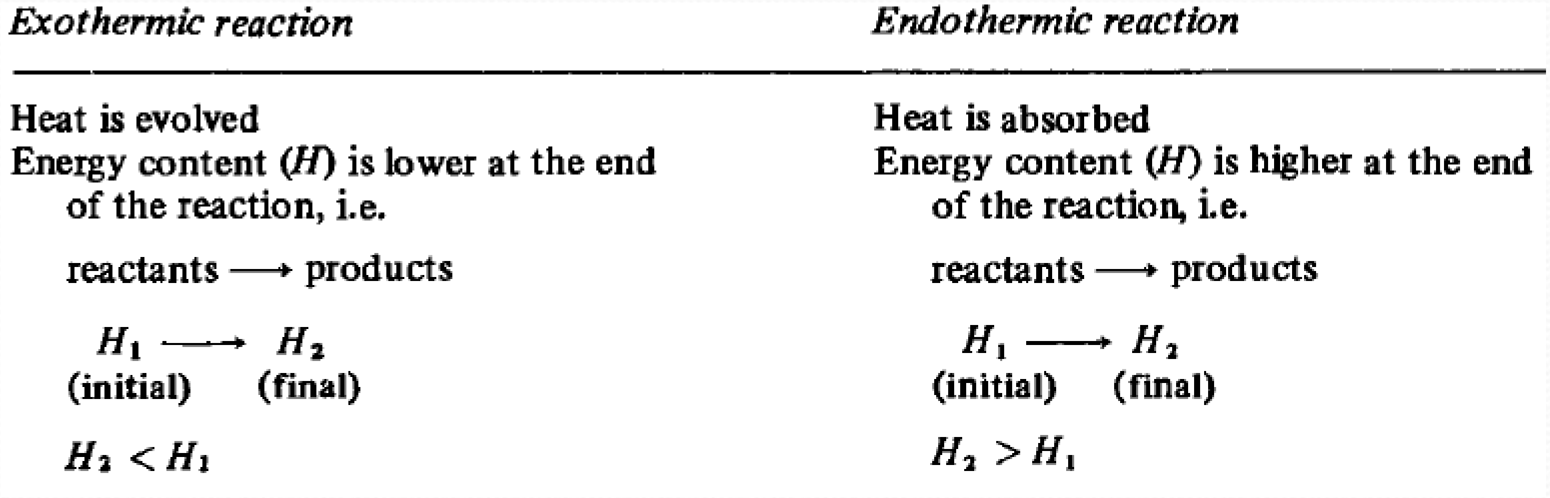
The top of a mould into which metal is cast may be made of a material (e.g. powdered aluminium and an oxidising agent) which evolves heat when in contact with a source of heat such as molten metal.

$$2Al + \frac{3}{2}O_2 \xrightarrow{298K} Al_2O_3; \qquad -1700\ kJ\ mol^{-1}$$

This extraction reaction for zinc needs to overcome the difficulties of heat supply and conservation in order to be commercially operable at 1373 K

$$ZnO + C \xrightarrow{1373K} Zn + CO; \qquad +350\ kJ\ mol^{-1}$$

Standard enthalpy change for a reaction

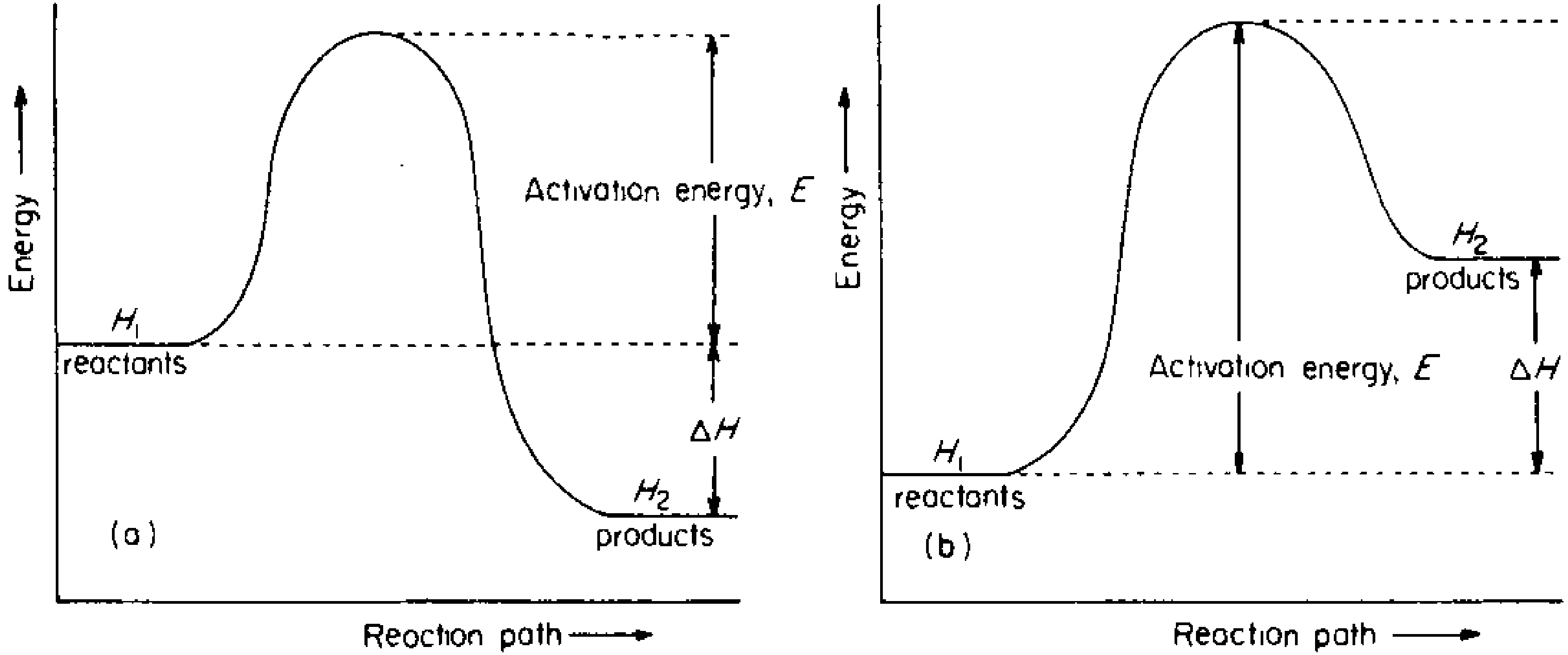


Exothermic reaction	*Endothermic reaction*
Heat is evolved	Heat is absorbed
Energy content (H) is lower at the end of the reaction, i.e.	Energy content (H) is higher at the end of the reaction, i.e.
reactants ⟶ products	reactants ⟶ products
$H_1 \longrightarrow H_2$ (initial) (final)	$H_1 \longrightarrow H_2$ (initial) (final)
$H_2 < H_1$	$H_2 > H_1$

Now the change in enthalpy, ΔH, is given by

$$\Delta H = H_2 - H_1$$
$$= H_{products} - H_{reactants}$$

Fig. below gives typical heat energy profiles for exothermic and endothermic reactions. Before a reaction can occur energy is required, called *activation energy (E),* to surmount an initial energy barrier; without this energy the reaction cannot proceed



- The enthalpy change for a reaction ΔH is dependent upon: (a) temperature; (b) pressure; (c) physical states of reactants and products; (d) amounts of substances reacting.
- The standard enthalpy change for a reaction, $\Delta H°$, is defined as the change in enthalpy referring to the masses (in moles) of the reactants and products shown in the equation for the reaction at 101 325 Pa (1atm) and at a stated temperature, T.
- For example, $\Delta H°_{298}$ refers to the enthalpy change at standard pressure (1 atm) and a temperature of 298 K.

There are various ways in which enthalpy changes for reactions may be stated more specifically:

(i) Standard enthalpy change of formation for a compound, $\Delta H°_f$

This is the change in enthalpy when *one mole of a compound* is formed from its elements under standard conditions.

$$\mathrm{C(graphite)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \qquad \Delta H^{\ominus}_{298} = -393\ \mathrm{kJ\ mol^{-1}}$$

(i) Standard enthalpy change of combustion, ΔH°_c , of a substance

This is the enthalpy change when *one mole of a substance* is completely burned in oxygen under standard conditions, e.g.

$$\mathrm{Mg(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{MgO(s)};$$

$$\Delta H^{\ominus}_{\mathrm{c}\,298}[\mathrm{Mg(s)}] = -605\ \mathrm{kJ\ mol^{-1}}$$

Obtaining ΔH°_c values for elements and compounds by use of the bomb calorimeter.

(iii) Enthalpy change of atomisation, ΔH°_A , for an element

This is the enthalpy change occurring when *one mole of gaseous atoms* is formed from the element in the defined physical state under standard conditions, e.g.

$$\tfrac{1}{2}\mathrm{H_2(g)} \longrightarrow \mathrm{H(g)}; \quad \Delta H^{\ominus}_{\mathrm{A}}[\mathrm{H_2(g)}] = +218\ \mathrm{kJ\ mol^{-1}}$$

(iv) Standard enthalpy change of transformation, ΔH°_{trans} ,

This is the change in enthalpy when *one mole of a substance* undergoes a specific physical change, e.g. melting, evaporating, allotropic transformation, under standard conditions.

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn(l)}; \quad \Delta H^{\ominus}_{\mathrm{trans}\ 693} = +7.14\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{Zn(l)} \longrightarrow \mathrm{Zn(g)}; \quad \Delta H^{\ominus}_{\mathrm{trans}\ 1180} = +114.7\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{C(diamond)} \longrightarrow \mathrm{C(graphite)}; \quad \Delta H^{\ominus}_{\mathrm{trans}\ 2273} = -2.0\ \mathrm{kJ\ mol^{-1}}$$

$$\mathrm{Ti}(\alpha, \mathrm{hcp}) \longrightarrow \mathrm{Ti}(\beta, \mathrm{bcc}); \quad \Delta H^{\ominus}_{\mathrm{trans}\ 1153} = +3.36\ \mathrm{kJ\ mol^{-1}}$$

(v) Standard enthalpy change of solution, ΔH°_{sol}

This is the change in enthalpy when *one mole of a solute* is dissolved in a given amount of solvent, under standard conditions. For example

$$\mathrm{NaCl(s)} + 200\mathrm{H_2O(l)} \rightarrow \mathrm{NaCl.200H_2O(aq)}$$

$$\Delta H^{\ominus}_{\mathrm{sol}} = +4.26\ \mathrm{kJ\ mol^{-1}}$$

(vi) Standard enthalpy change of dilution, ΔH°_{dil}

This is the enthalpy change when further solvent is added to a solution of specified concentration under standard conditions.

(vii) Standard enthalpy change of neutralisation ΔH°_{neut}

This is the enthalpy change when an acid and a base react together to give *one mole of water.* For a strong acid and a strong base the enthalpy change of neutralisation is effectively constant at -56.9 kJ/mole when considering infinite dilution.

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

In this reaction, as in any other strong acid-strong base reactions, the sole reaction is the formation of molecular water,

$$\underbrace{H^+(aq)}_{\text{from acid}} + \underbrace{OH^-(aq)}_{\text{from base}} \longrightarrow H_2O(l); \qquad \Delta H^\ominus_{neut} = -56.9\ \text{kJ mol}^{-1}$$

Calculating enthalpies and enthalpy changes

$$\Delta H^\circ = H^\circ_{products} - H^\circ_{reactants}$$

The enthalpy of an element, by convention, is taken to be zero at the reference temperature (usually 298 K), providing the element is in its normal physical state under the conditions considered, and becomes finite at any other temperature. For example

$$H^\ominus_{298}[\mathrm{C(graphite)}] = 0; \qquad H^\ominus_{298}[\mathrm{O_2(g)}] = 0$$

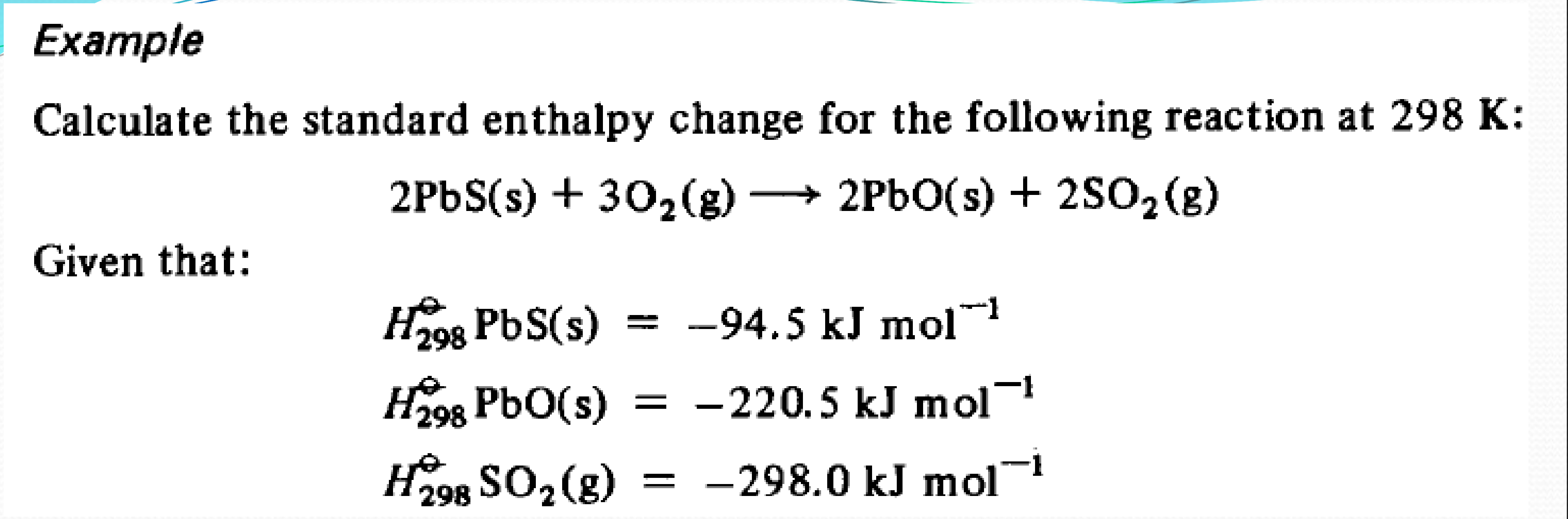
$$H^\ominus_{298}[\alpha\mathrm{Fe(s)}] = 0; \qquad H^\ominus_{298}[\mathrm{Hg(l)}] = 0$$

But

$$H^\ominus_{298}[\mathrm{Hg(g)}] = +60.84\ \mathrm{kJ\ mol^{-1}}$$

since, under the specified conditions, mercury is a liquid rather than a gas, i.e.

$$\mathrm{Hg(l)} \longrightarrow \mathrm{Hg(g)}; \qquad \Delta H^\ominus_{298} = +60.8\ \mathrm{kJ\ mol^{-1}}$$



Example

Calculate the standard enthalpy change for the following reaction at 298 K:

$$2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$$

Given that:

$$H^{\ominus}_{298}\,PbS(s) = -94.5\ kJ\ mol^{-1}$$

$$H^{\ominus}_{298}\,PbO(s) = -220.5\ kJ\ mol^{-1}$$

$$H^{\ominus}_{298}\,SO_2(g) = -298.0\ kJ\ mol^{-1}$$

Hess's law

Hess's law states that the enthalpy change for a reaction is the same whether it takes place in one or several stages (i.e. ΔH for a reaction depends only on the initial and final states).

The great utility of this law is in calculating enthalpy changes for reactions which cannot be carried out experimentally.

Example (1)

The standard enthalpy change of formation for carbon monoxide is required. The reaction is represented as:

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta H^{\ominus}_{I} = ? \qquad (2.I)$$

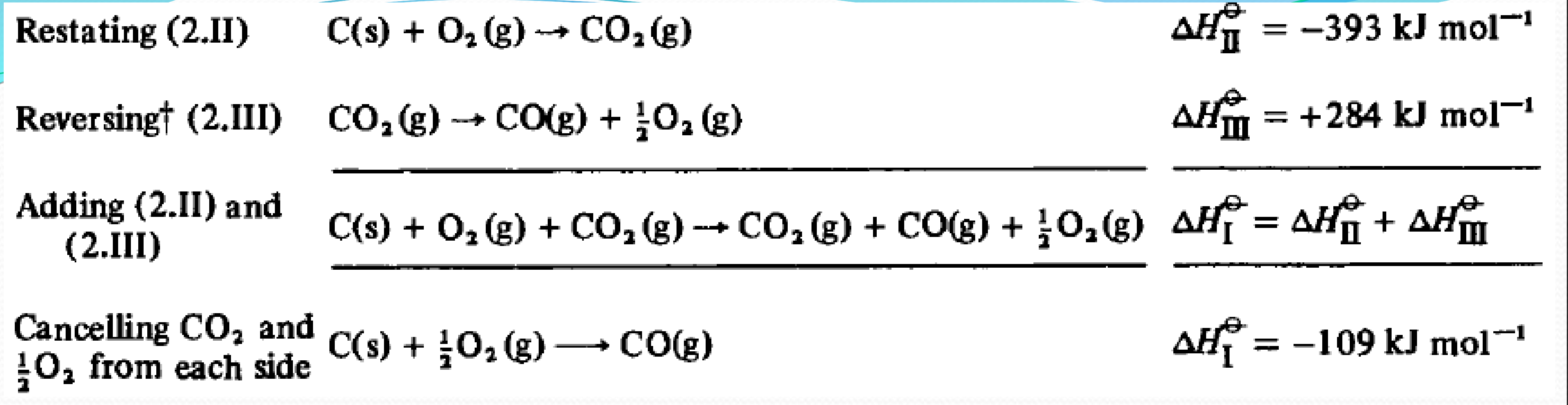
but cannot occur stoichiometrically because of the tendency of the carbon to form carbon dioxide giving rise to a mixture of products (CO and CO2) .

However, standard enthalpy values are experimentally obtainable for the following reactions:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^{\ominus}_{II} = -393\ \text{kJ mol}^{-1}\ \text{(bomb calorimeter)} \quad (2.II)$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^{\ominus}_{III} = -284\ \text{kJ mol}^{-1}\ \text{(gas calorimeter)} \quad (2.III)$$

These reactions may be manipulated (e.g. reversed, added, subtracted, multiplied) to represent the change occurring in reaction (2.1), hence making it possible to calculate $\boldsymbol{\Delta H^{\circ}_{I}}$



Restating (2.II)	$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H^\ominus_{II} = -393\ \text{kJ mol}^{-1}$
Reversing† (2.III)	$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$	$\Delta H^\ominus_{III} = +284\ \text{kJ mol}^{-1}$
Adding (2.II) and (2.III)	$C(s) + O_2(g) + CO_2(g) \rightarrow CO_2(g) + CO(g) + \frac{1}{2}O_2(g)$	$\Delta H^\ominus_{I} = \Delta H^\ominus_{II} + \Delta H^\ominus_{III}$
Cancelling CO_2 and $\frac{1}{2}O_2$ from each side	$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	$\Delta H^\ominus_{I} = -109\ \text{kJ mol}^{-1}$

Example (2)

Methane cannot be synthesized by direct combustion of carbon and hydrogen:

$$C(s) + 2H_2(g) \longrightarrow CH_4(g); \qquad \Delta H^\ominus_{IV} = ?$$

but its enthalpy of formation, ΔH°_f, can be calculated from the enthalpies of combustion of methane, carbon and hydrogen by application of Hess's law:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\ominus_{I} = -890\ \text{kJ mol}^{-1} \qquad (I)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\ominus_{II} = -393\ \text{kJ mol}^{-1} \qquad (II)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\ominus_{III} = -287\ \text{kJ mol}^{-1} \qquad (III)$$

Reverse reaction I , multiply reaction III by 2 and add all three together

$$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \qquad \Delta H^\ominus_{I} = +890\ \text{kJ mol}^{-1}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\ominus_{II} = -393\ \text{kJ mol}^{-1}$$

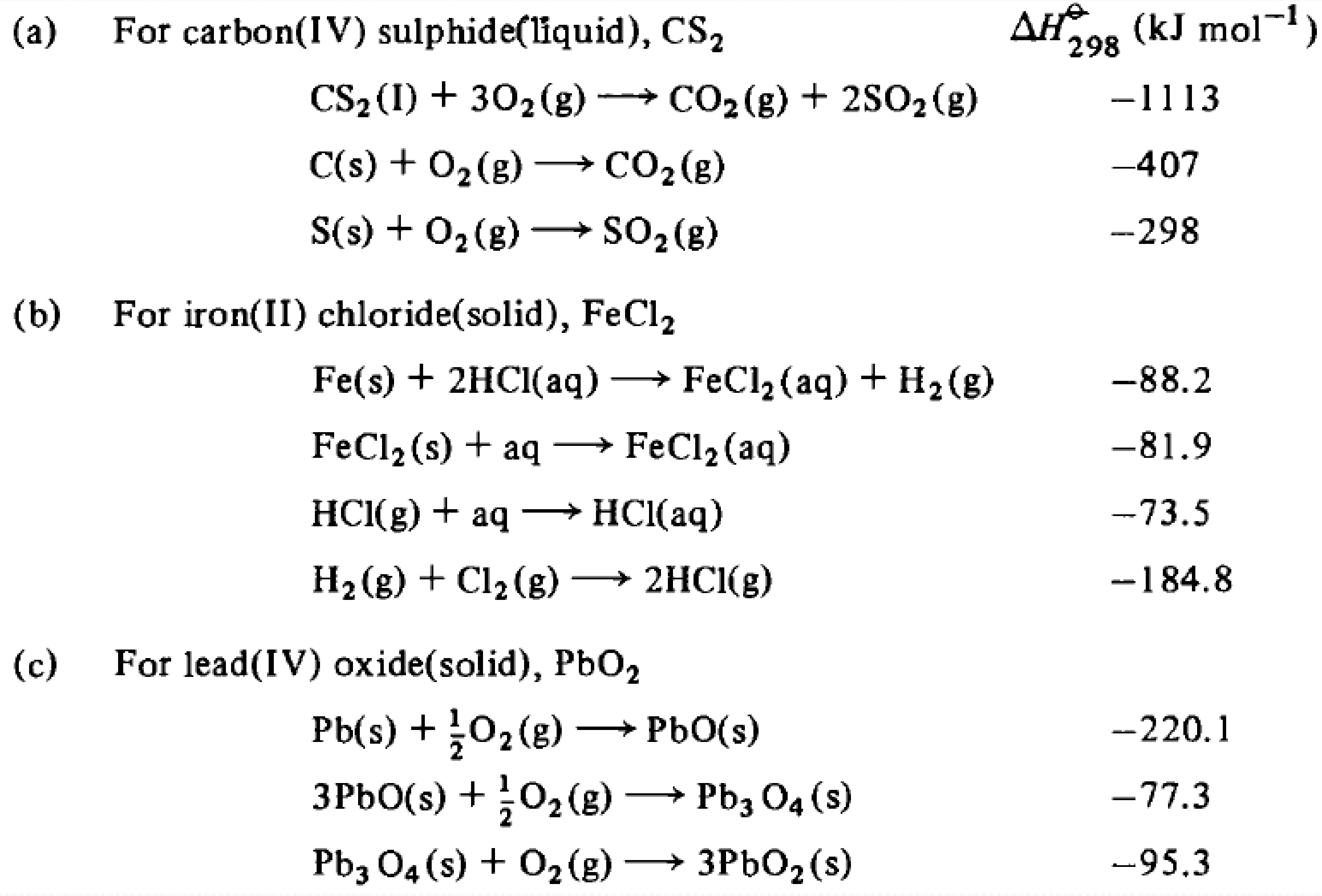
$$2H_2(g) + O_2(g) \longrightarrow 2H_2O\ (l) \qquad 2\Delta H^\ominus_{III} = -574\ \text{kJ mol}^{-1}$$

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H^\ominus_{IV} = \Delta H^\ominus_{I} + \Delta H^\ominus_{II} + 2\Delta H^\ominus_{III}$$

$$\Delta H^\ominus_{IV} = -79\ \text{kJ mol}^{-1}$$

Homework

1) Calculate the standard enthalpy changes of formation at 298 K for the stated compounds from the data supplied in each case:



		$\Delta H^\ominus_{298}$ (kJ mol^{-1})
(a)	For carbon(IV) sulphide(liquid), CS_2	
	$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$	-1113
	$C(s) + O_2(g) \longrightarrow CO_2(g)$	-407
	$S(s) + O_2(g) \longrightarrow SO_2(g)$	-298
(b)	For iron(II) chloride(solid), $FeCl_2$	
	$Fe(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g)$	-88.2
	$FeCl_2(s) + aq \longrightarrow FeCl_2(aq)$	-81.9
	$HCl(g) + aq \longrightarrow HCl(aq)$	-73.5
	$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$	-184.8
(c)	For lead(IV) oxide(solid), PbO_2	
	$Pb(s) + \frac{1}{2}O_2(g) \longrightarrow PbO(s)$	-220.1
	$3PbO(s) + \frac{1}{2}O_2(g) \longrightarrow Pb_3O_4(s)$	-77.3
	$Pb_3O_4(s) + O_2(g) \longrightarrow 3PbO_2(s)$	-95.3

(2) The standard enthalpy changes of combustion at 298 K for $H_2(g)$, CO(g) and $CH_3OH(l)$ are −286, −283 and −714 kJ mol^{-1} respectively. Make use of these data to calculate the value of $\Delta H^\ominus$ at the same temperature for the reaction:

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$$

(3) In the iron blast furnace iron(III) oxide is reduced to iron. Coke (carbon) is charged with the ore and air (oxygen) is blown into the furnace, the overall reaction at 1600 °C possibly being:

$$Fe_2O_3 + 3C + \tfrac{3}{2}O_2 \longrightarrow 2Fe + 3CO_2$$

Calculate $\Delta H^\ominus$ for this reaction at 1600 °C given that the following may be feasible intermediate stages:

$$\tfrac{3}{2}C + \tfrac{3}{2}O_2 \longrightarrow CO_2 \qquad \Delta H^\ominus = -593.3\ \text{kJ}$$

$$\tfrac{3}{2}CO_2 + \tfrac{3}{2}C \longrightarrow 3CO \qquad \Delta H^\ominus = +259.6\ \text{kJ}$$

$$Fe_2O_3 + \tfrac{1}{3}CO \longrightarrow \tfrac{2}{3}Fe_3O_4 + \tfrac{1}{3}CO_2 \qquad \Delta H^\ominus = -17.6\ \text{kJ}$$

$$\tfrac{2}{3}Fe_3O_4 + \tfrac{8}{3}CO \longrightarrow 2Fe + \tfrac{8}{3}CO_2 \qquad \Delta H^\ominus = -10.5\ \text{kJ}$$

Enthalpy changes: the effect of temperature

Kirchoff's equation

The heat capacity of a given substance usually alters with temperature change. It is this variation in heat capacity of products and reactants which gives rise to variation of *ΔH* values for reactions as temperature changes,

i.e. in the generalized reaction shown below there are two alternative pathways which may be considered:

(i) shown by solid arrows

(ii) shown by broken arrows

$$\begin{tikzcd}
\text{Reactants (R)} \arrow[r, "\Delta H_1", "(i)"'] \arrow[d, dashed, "(ii)"', "C_p^R(T_2-T_1)"] & \text{Products (P)} \arrow[d, dashed, "(i)"', "C_p^P(T_2-T_1)"] & \text{at temperature } T_1 \\
\text{Reactants (R)} \arrow[r, dashed, "\Delta H_2", "(ii)"'] & \text{Products (P)} & \text{at temperature } T_2
\end{tikzcd}$$

As in both (i) and (ii) the initial and final states are identical then, according to Hess's law, the heat exchange for each process will be the same, i.e.

$$\Delta H_1 + C_p^{\mathrm{P}}(T_2 - T_1) = \Delta H_2 + C_p^{\mathrm{R}}(T_2 - T_1)$$

$$\Delta H_2 - \Delta H_1 = (C_p^{\mathrm{P}} - C_p^{\mathrm{R}})(T_2 - T_1)$$

This is only applicable when using mean values of C_p for the temperature interval T_1 - T_2 .This can be rewritten as:

$$\frac{\mathrm{d}(\Delta H)}{\mathrm{d}T} = \Delta C_p$$

i.e. change of ΔH with T is equal to change in C_p .This is known as Kirchoff's equation

This equation is useful in the integrated form as in the case of high-temperature conditions which normally apply to metallurgical reactions. Integrating Kirchoff's equation between T_2 and T_1 yields:

$$\int_{\Delta H_{T_1}}^{\Delta H_{T_2}} \mathrm{d}(\Delta H) = \Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_p \, \mathrm{d}T \qquad (2\text{-}3)$$

This may be expressed more usefully:

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p \, \mathrm{d}T$$

To calculate ΔH_{T2} from this equation it is necessary to consider how C_p varies with temperature.

$$C_p = a + bT + cT^{-2} + \ldots \qquad (2\text{-}4)$$

Therefore, the enthalpy change for a reaction at any temperature, ΔH_T may be calculated if the enthalpy change for the reaction at another specified temperature, usually 298 K, is known and molar heat capacity data are available,

i.e. equation (2.3) may be rewritten (considering standard conditions):

$$\Delta H_T^{\ominus} = \Delta H_{298\,\mathrm{K}}^{\ominus} + \int_{298}^{T} \Delta C_p \, \mathrm{d}T \pm \text{latent heats} \qquad (2\text{-}5)$$

Molar latent heats are added if products transform ; subtracted if reactants transform.

In the simplest case it may be assumed that the molar heat capacities of the reactants and products do not alter appreciably with change of temperature, i.e. C_p values at 298 K from data sources may be used directly. Equation (2.5) then becomes:

$$\Delta H_T^{\ominus} = \Delta H_{298\,\mathrm{K}}^{\ominus} + \Delta C_p(T_2 - T_1) \qquad \textbf{(2-6)}$$

and ΔC_p is simply calculated as follows:

$$\Delta C_p = \sum C_p^{\mathrm{P}} - \sum C_p^{\mathrm{R}} \qquad \textbf{(2-7)}$$

e.g. for the generalised reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta C_p = (cC_{p_C} + dC_{p_D}) - (aC_{p_A} + bC_{p_B})$$

For more accurate values of ΔH_T it is necessary to calculate ΔCp using Cp values for reactants and products at the required temperature deduced from the type of empirical equation illustrated by equation (2.4) such that:

$$\Delta C_p = \Delta a + \Delta bT + \Delta cT^{-2} + \ldots$$

If the heat capacity of a substance differs in the various states considered, the calculation must be performed separately for each state, i.e.

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_f} \Delta C_p \, \mathrm{d}T + L_f + \int_{T_f}^{T_2} \Delta C_p \, \mathrm{d}T$$

where T_f and L_f are the melting point and latent heat of fusion of the product respectively.

Latent heat of transformation and melting and boiling points must also be considered in the above equation if the reactants or products go through a phase transformation.

Example

Does the enthalpy change of formation of water vapour increase or decrease with rise in temperature?

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H^\ominus \text{ is negative at 298 K}$$

Using Kirchoff's equation (2.6)

$$\begin{aligned}\Delta H_T^\ominus &= \Delta H_{298}^\ominus + \Delta C_p(T_2 - T_1)\\ &= (-) \quad + \Delta C_p(T_2 - T_1)\end{aligned}$$

and from equation (2.7) and *Table 2.3*

$$\Delta C_p = \{C_p(H_2O) - [C_p(H_2) + \tfrac{1}{2}C_p(O_2)]\}$$

i.e.,

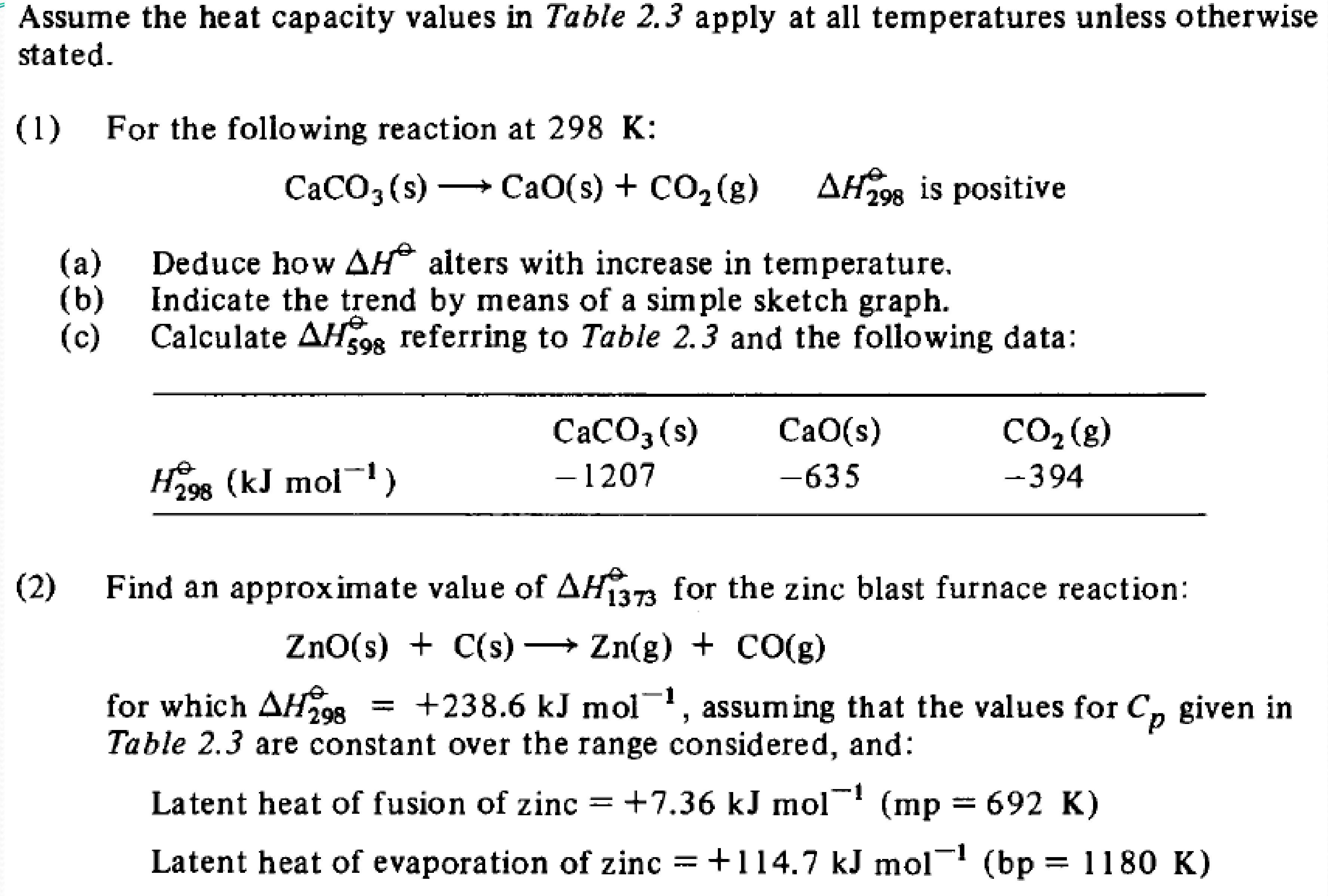
$$\begin{aligned}\Delta C_p &= [33.5 - (28.9 + 14.7)]\\ &= 33.5 - 43.6\\ &= -10.1 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Substituting this value for ΔC_p in equation (2.6) we have

$$\begin{aligned}\Delta H_T^\ominus &= (-) + (-10.1)(T_2 - T_1)\\ &= (-) - 10.1(T_2 - T_1)\end{aligned}$$

So $\Delta H_T^\ominus$ is more negative than $\Delta H_{298}^\ominus$.

Homework



Assume the heat capacity values in *Table 2.3* apply at all temperatures unless otherwise stated.

(1) For the following reaction at 298 K:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H^\ominus_{298} \text{ is positive}$$

(a) Deduce how $\Delta H^\ominus$ alters with increase in temperature.
(b) Indicate the trend by means of a simple sketch graph.
(c) Calculate $\Delta H^\ominus_{598}$ referring to *Table 2.3* and the following data:

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
$H^\ominus_{298}$ (kJ mol^{-1})	−1207	−635	−394

(2) Find an approximate value of $\Delta H^\ominus_{1373}$ for the zinc blast furnace reaction:

$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$$

for which $\Delta H^\ominus_{298} = +238.6$ kJ mol^{-1}, assuming that the values for C_p given in *Table 2.3* are constant over the range considered, and:

Latent heat of fusion of zinc = +7.36 kJ mol^{-1} (mp = 692 K)

Latent heat of evaporation of zinc = +114.7 kJ mol^{-1} (bp = 1180 K)

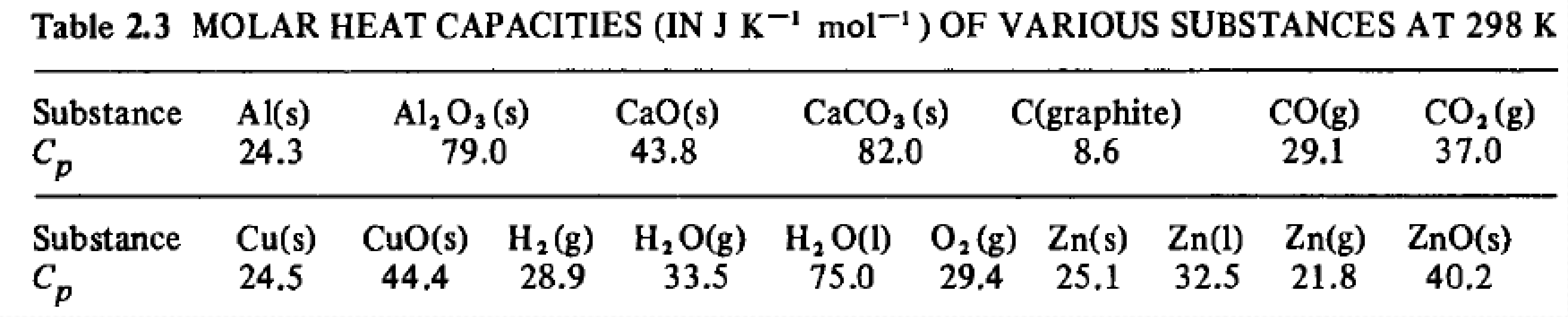


Table 2.3 MOLAR HEAT CAPACITIES (IN J K^{-1} mol^{-1}) OF VARIOUS SUBSTANCES AT 298 K

Substance	Al(s)	Al_2O_3(s)	CaO(s)	$CaCO_3$(s)	C(graphite)	CO(g)	CO_2(g)
C_p	24.3	79.0	43.8	82.0	8.6	29.1	37.0

Substance	Cu(s)	CuO(s)	H_2(g)	H_2O(g)	H_2O(l)	O_2(g)	Zn(s)	Zn(l)	Zn(g)	ZnO(s)
C_p	24.5	44.4	28.9	33.5	75.0	29.4	25.1	32.5	21.8	40.2

(3) For the reaction:

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

Calculate the standard enthalpy change at 473 K given that the standard enthalpy changes of formation (in kJ mol^{-1}) at 298 K are −110.50 for CO and −393.50 for CO_2. Molar heat capacities, C_p (in J K^{-1} mol^{-1}), are:

CO(g), $C_p = 30.0 + 0.0041T$

O_2(g), $C_p = 28.5 + 0.0042T$

CO_2(g), $C_p = 44.2 + 0.0088T$