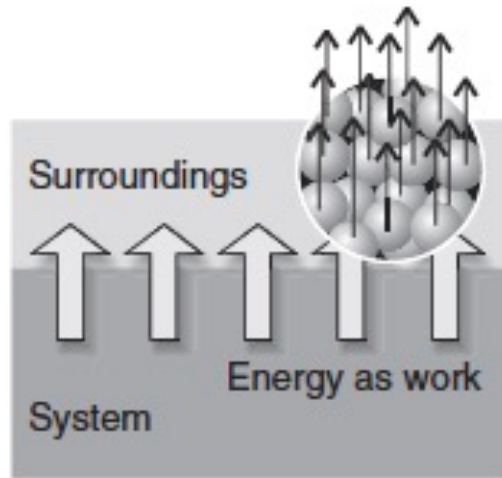
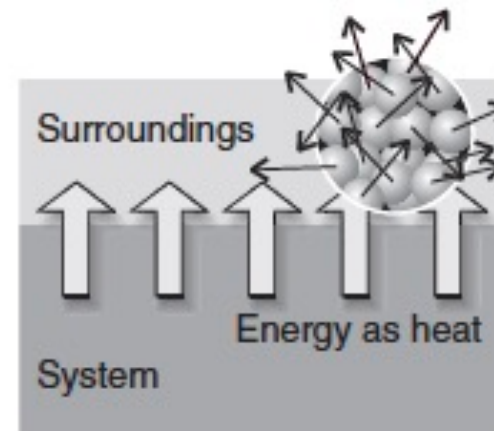


Introdução à Química-Física

Aula 5



Work is transfer of energy that causes or utilizes uniform motion of atoms in the surroundings. For example, when a weight is raised, all the atoms of the weight (shown magnified) move in unison in the same direction.



Heat is the transfer of energy that causes or utilizes random motion in the surroundings. When energy leaves the system (the shaded region), it generates random motion in the surroundings (shown magnified).

$$dU = C_v dT \quad (\text{at constant volume})$$

$$\Delta U = C_v \Delta T \quad (\text{at constant volume})$$

$$q_v = C_v \Delta T \quad \text{is the constant-volume heat capacity of the sample}$$

$$dH = C_p dT \quad (\text{at constant pressure})$$

$$\Delta H = C_p \Delta T \quad (\text{at constant pressure})$$

$$q_p = C_p \Delta T$$

This expression shows us how to measure the heat capacity of a sample: a measured quantity of energy is supplied as heat under conditions of constant pressure (as in a sample exposed to the atmosphere and free to expand), and the temperature rise is monitored

Quando uma substância é aquecida, a sua temperatura aumenta.

Para um dado valor de energia, q , transferida, a variação de temperatura, ΔT , depende da capacidade calorífica, C , da substância.

$$C = \frac{q}{\Delta T}$$

expressa em J K^{-1}
ou $\text{J }^{\circ}\text{C}^{-1}$

Energia fornecida
na forma de calor

Variação de
temperatura

Pode ser expressa em
Kelvin (DT)
ou em grau Celsius
($\Delta\theta$)

C_p Capacidade calorífica a
pressão constante

C_v Capacidade calorífica a
volume constante

$$C_s = \frac{C}{m}$$

calor específico (specific heat capacity)
 $\text{J K}^{-1} \text{g}^{-1}$

$$C_m = \frac{C}{n}$$

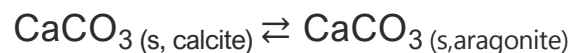
calor específico molar (molar heat capacity)
 $\text{J K}^{-1} \text{mol}^{-1}$

$C_{p,m}$ Calor específico molar a pressão constante
 $\text{J K}^{-1} \text{mol}^{-1}$

$C_{v,m}$ Calor específico molar a volume constante
 $\text{J K}^{-1} \text{mol}^{-1}$

Relacionando ΔH e ΔU

Quando 1.0 mol CaCO_3 na forma de calcite se converte em aragonite, a variação de energia interna é +0.21 kJ. Calcule a variação de entalpia se a transformação se der à pressão de 1.0 bar sabendo que as densidades das duas formas sólidas são 2.71 g cm^{-3} e 2.93 g cm^{-3} , respectivamente.



Resolução:

$$\Delta H = H(\text{aragonite}) - H(\text{calcite})$$

$$= \{U(\text{a}) + pV(\text{a})\} - \{U(\text{c}) + pV(\text{c})\}$$

$$= \Delta U + p\{V(\text{a}) - V(\text{c})\} = \Delta U + p\Delta V$$

Cálculo do volume de 1 mol de calcite

$$\rho = M/V_m \quad \Leftrightarrow \quad V_m = M/\rho$$

$$V = n M/\rho$$

$$V = 1 \text{ mol} \times 100 \text{ g mol}^{-1} / 2,93 \text{ g cm}^{-3}$$

$$= 34 \text{ cm}^3$$

Cálculo do volume de 1 mol de aragonite

$$\rho = M/V_m \quad \Leftrightarrow \quad V_m = M/\rho$$

$$V = n M/\rho$$

$$V = 1 \text{ mol} \times 100 \text{ g mol}^{-1} / 2,71 \text{ g cm}^{-3}$$

$$= 37 \text{ cm}^3$$

$$p\Delta V = (1.0 \times 10^5 \text{ Pa}) \times (34 - 37) \times 10^{-6} \text{ m}^3 = -0.3 \text{ J}$$

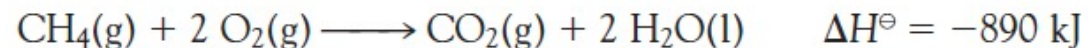
$$\Delta H - \Delta U = p\Delta V = -0,3 \text{ J}$$

A entalpia de um gás perfeito pode ser relacionada com a sua energia interna utilizando a equação dos gases perfeitos

$$H = U + pV = U + nRT \quad \text{ou seja} \quad \Delta H = \Delta U + \Delta n_g RT$$

Enthalpies of combustion

An example is the combustion of methane in a natural gas flame:



The standard enthalpy of combustion, $\Delta_c H^\ominus$, is the standard change in enthalpy per mole of combustible substance

In this example, we would write $\Delta_c H^\ominus(\text{CH}_4, \text{g}) = -890 \text{ kJ mol}^{-1}$

Note that $\Delta_c H^\ominus$ is a molar quantity and is obtained from the value of ΔH^\ominus by dividing by the amount of organic reactant consumed (in this case, by 1 mol CH_4)

According to what we said before and the relation $\Delta U = q_v$

the energy transferred as heat at constant volume is equal to the change in internal energy, ΔU , not ΔH

To convert from U to H , we need to note that the molar enthalpy of a substance is related to its molar internal energy by $H_m = U_m + pV_m$

For condensed phases, pV_m is so small, it may be ignored. For example, the molar volume of liquid water is $18 \text{ cm}^3 \text{ mol}^{-1}$, and at 1.0 bar

$$\begin{aligned} pV_m &= (1.0 \times 10^5 \text{ Pa}) \times (18 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) = 1.8 \text{ Pa m}^3 \text{ mol}^{-1} \\ &= 1.8 \text{ J mol}^{-1} \end{aligned}$$

However, the molar volume of a gas, and therefore the value of pV_m , is about 1000 times greater and cannot be ignored. For gases treated as perfect, pV_m may be replaced by RT .

If in the chemical equation the difference (products - reactants) in the stoichiometric coefficients of gas phase species is $\Delta \nu_{\text{gas}}$, we can write

$$\Delta_c H = \Delta_c U + \Delta \nu_{\text{gas}} RT$$

Note that gas. $\Delta \nu_{\text{gas}}$ is a dimensionless number

Converting between ΔH and ΔU

The energy released as heat by the combustion of the iso-octane is 5461 kJ mol^{-1} , at 298.15 K , so $\Delta_c H = -5461 \text{ kJ mol}^{-1}$.
From the chemical equation



$$\Delta v_{\text{gas}} = (16 - 25) = -9$$

$$\Delta_c H = \Delta_c U + \Delta v_{\text{gas}} RT \quad \Leftrightarrow \quad \Delta_c U = \Delta_c H - \Delta v_{\text{gas}} RT$$

$$\Delta_c U = -5461 \text{ kJ mol}^{-1} - (-9) \times 8,314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298,15 \text{ K}$$

$$\Delta_c U = - 5439 \text{ kJ mol}^{-1}$$

Standard enthalpy changes

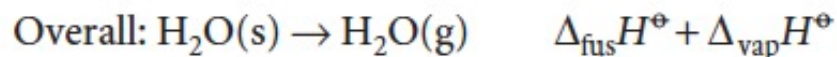
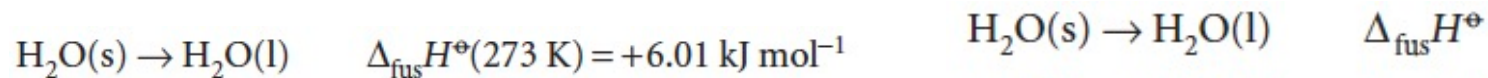
The standard state of a substance at a specified temperature is its pure form at 1 bar

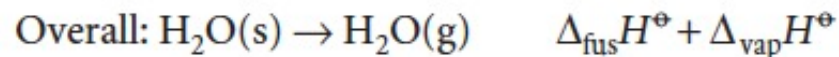
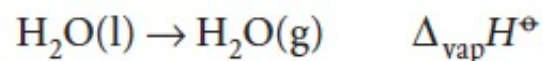
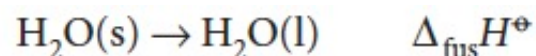
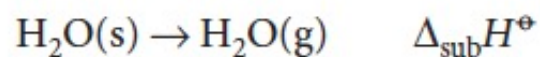
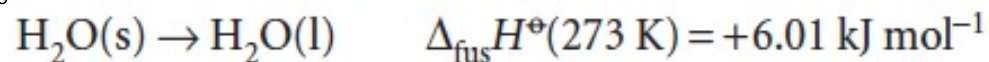
the standard enthalpy of vaporization, $\Delta_{\text{vap}}H^\circ$, is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar



The standard enthalpies may be reported for any temperature.

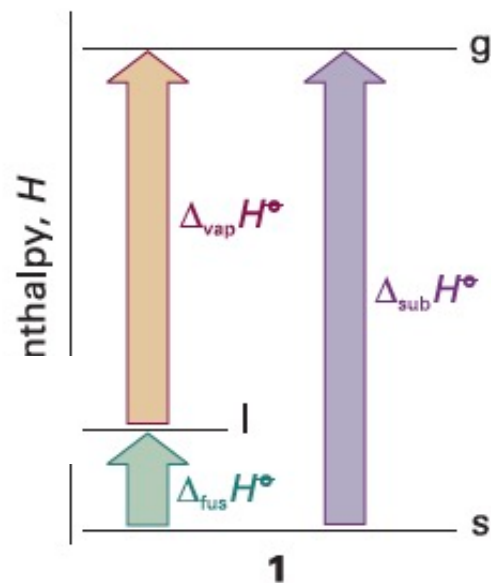
However, the conventional temperature for reporting thermodynamic data is 298.15 K (corresponding to 25.00°C). Unless otherwise mentioned, all thermodynamic data in this text will refer to this conventional temperature.



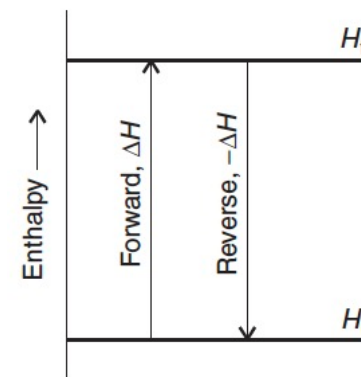


$$\Delta_{\text{sub}}H^\ominus = \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus$$

The standard enthalpy changes of a forward process and its reverse differ in sign



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

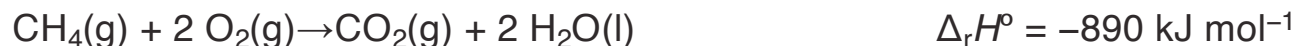


Thermochemical equation

ΔH° is the change in enthalpy when reactants in their standard states change to products in their standard states:



The standard reaction enthalpy, $\Delta_r H^\circ$



For the reaction $2 \text{A} + \text{B} \rightarrow 3 \text{C} + \text{D}$

the standard reaction enthalpy is $\Delta_r H^\circ = \{3H_m^\circ(\text{C}) + H_m^\circ(\text{D})\} - \{2H_m^\circ(\text{A}) + H_m^\circ(\text{B})\}$

H_m° (J) is the standard molar enthalpy of species J at the temperature of interest

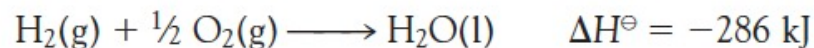
$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus$$

H_m^\ominus are molar quantities and the stoichiometric coefficients are pure numbers, the units of $\Delta_r H^\ominus$ are kilojoules per mole

The standard reaction enthalpy is the change in enthalpy of the system when the reactants in their standard states (pure, 1 bar) are completely converted into products in their standard states (pure, 1 bar), with the change expressed in kilojoules per mole of reaction as written.

The standard enthalpy of formation, $\Delta_f H^\ominus$ of a substance is the standard enthalpy (per mole of the substance) for its formation from its elements in their reference states.

The standard enthalpy of formation of liquid water (at 25°C, as always in this text) is obtained from the thermochemical equation.

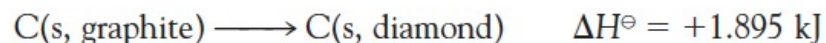


With the introduction of standard enthalpies of formation, we can write

$$\Delta_r H^\ominus = \sum \nu \Delta_f H^\ominus(\text{products}) - \sum \nu \Delta_f H^\ominus(\text{reactants})$$

The first term on the right is the enthalpy of formation of all the products from their elements; the second term on the right is the enthalpy of formation of all the reactants from their elements

The standard enthalpies of formation of elements in their reference states are zero by definition (because their formation is the null reaction: element \rightarrow element). Note, however, that the standard enthalpy of formation of an element in a state other than its reference state is not zero:



$$\Delta_f H^\ominus(\text{C, graphite}) = 0, \Delta_f H^\ominus(\text{C, diamond}) = +1.895 \text{ kJ mol}^{-1}$$

The variation of reaction enthalpy with temperature

We need to know how to predict reaction enthalpies of biochemical reactions at different temperatures, even though we may have data at only one temperature.

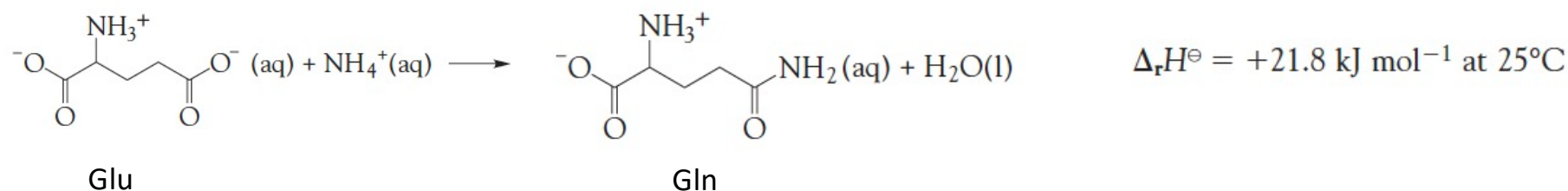
Kirchhoff's law

$$\Delta_r H^\ominus(T') = \Delta_r H^\ominus(T) + \Delta_r C_p^\ominus \times (T' - T)$$

where $\Delta_r C_p^\ominus$ is the difference between the weighted sums of the standard molar heat capacities of the products and the reactants

$$\Delta_r C_p^\ominus = \sum \nu C_{p,m}^\ominus(\text{products}) - \sum \nu C_{p,m}^\ominus(\text{reactants})$$

Using Kirchhoff's law



Estimate the value of the reaction enthalpy at 60°C

Data: the standard molar constant-pressure heat capacities of $\text{H}_2\text{O}(\text{l})$ and $\text{NH}_4^+(\text{aq})$ are $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $79.9 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

$$\begin{aligned}
 \Delta_r C_p^\ominus &= \{C_{p,m}^\ominus(\text{Gln, aq}) + C_{p,m}^\ominus(\text{H}_2\text{O, l})\} - \{C_{p,m}^\ominus(\text{Glu, aq}) + C_{p,m}^\ominus(\text{NH}_4^+, \text{aq})\} \\
 &= \{(187.0 \text{ J K}^{-1} \text{ mol}^{-1}) + (75.3 \text{ J K}^{-1} \text{ mol}^{-1})\} - \{(177.0 \text{ J K}^{-1} \text{ mol}^{-1}) + (79.9 \text{ J K}^{-1} \text{ mol}^{-1})\}
 \end{aligned}$$

$$T' - T = +35 \text{ K}$$

$$\begin{aligned}
 \Delta_r H^\ominus(333 \text{ K}) &= (+21.8 \text{ kJ mol}^{-1}) + (5.4 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (35 \text{ K}) \\
 &= (+21.8 \text{ kJ mol}^{-1}) + (0.19 \text{ kJ mol}^{-1}) \\
 &= +22.0 \text{ kJ mol}^{-1}
 \end{aligned}$$

Table 1.8 Standard enthalpies of formation at 298.15 K*

| Substance | $\Delta_f H^\ominus / (\text{kJ mol}^{-1})$ | Substance | $\Delta_f H^\ominus / (\text{kJ mol}^{-1})$ |
|--|---|--|---|
| <i>Inorganic compounds</i> | | <i>Organic compounds</i> | |
| Ammonia, $\text{NH}_3(\text{g})$ | -46.11 | Adenine, $\text{C}_5\text{H}_5\text{N}_5(\text{s})$ | +96.9 |
| Carbon monoxide, $\text{CO}(\text{g})$ | -110.53 | Alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}(\text{s})$ | -604.0 |
| Carbon dioxide, $\text{CO}_2(\text{g})$ | -393.51 | Benzene, $\text{C}_6\text{H}_6(\text{l})$ | +49.0 |
| Hydrogen sulfide, $\text{H}_2\text{S}(\text{g})$ | -20.63 | Butanoic acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}(\text{l})$ | -533.8 |
| Nitrogen dioxide, $\text{NO}_2(\text{g})$ | +33.18 | Ethane, $\text{C}_2\text{H}_6(\text{g})$ | -84.68 |
| Nitrogen monoxide, $\text{NO}(\text{g})$ | +90.25 | Ethanoic acid, $\text{CH}_3\text{COOH}(\text{l})$ | -484.3 |
| Sodium chloride, $\text{NaCl}(\text{s})$ | -411.15 | Ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$ | -277.69 |
| Water, $\text{H}_2\text{O}(\text{l})$ | -285.83 | α -D-Glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ | -1268 |
| $\text{H}_2\text{O}(\text{g})$ | -241.82 | Guanine, $\text{C}_5\text{H}_5\text{N}_5\text{O}(\text{s})$ | -183.9 |
| | | Glycine, $\text{CH}_2(\text{NH}_2)\text{COOH}(\text{s})$ | -528.5 |
| | | N-Glycylglycine, $\text{C}_4\text{H}_8\text{N}_2\text{O}_3(\text{s})$ | -747.7 |
| | | Hexadecanoic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}(\text{s})$ | -891.5 |
| | | Leucine, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}(\text{s})$ | -637.4 |
| | | Methane, $\text{CH}_4(\text{g})$ | -74.81 |
| | | Methanol, $\text{CH}_3\text{OH}(\text{l})$ | -238.86 |
| | | Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$ | -2222 |
| | | Thymine, $\text{C}_5\text{H}_6\text{N}_2\text{O}_2(\text{s})$ | -462.8 |
| | | Urea, $(\text{NH}_2)_2\text{CO}(\text{s})$ | -333.1 |