Physical Chemistry

Peter Atkins

(Sixth edition)

Bilingual Program

Part 1: Equilibrium

4. The Second Law: the concepts

Bilingual Program

4. The Second Law: the concepts

This chapter will explain the origin of the spontaneity of physical and chemical change. Two simple processes are examined. It shows that a property, the entropy can be defined, measured, and used to discuss spontaneous changes quantitatively. This chapter also introduces a major subsidiary thermodynamic property, the Gibbs energy.

4. The Second Law: the concepts

The direction of spontaneous change ▶

Concentrating on the system

The direction of spontaneous change

Some things happen naturally. A gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, and a chemical reaction runs in one direction rather than another.

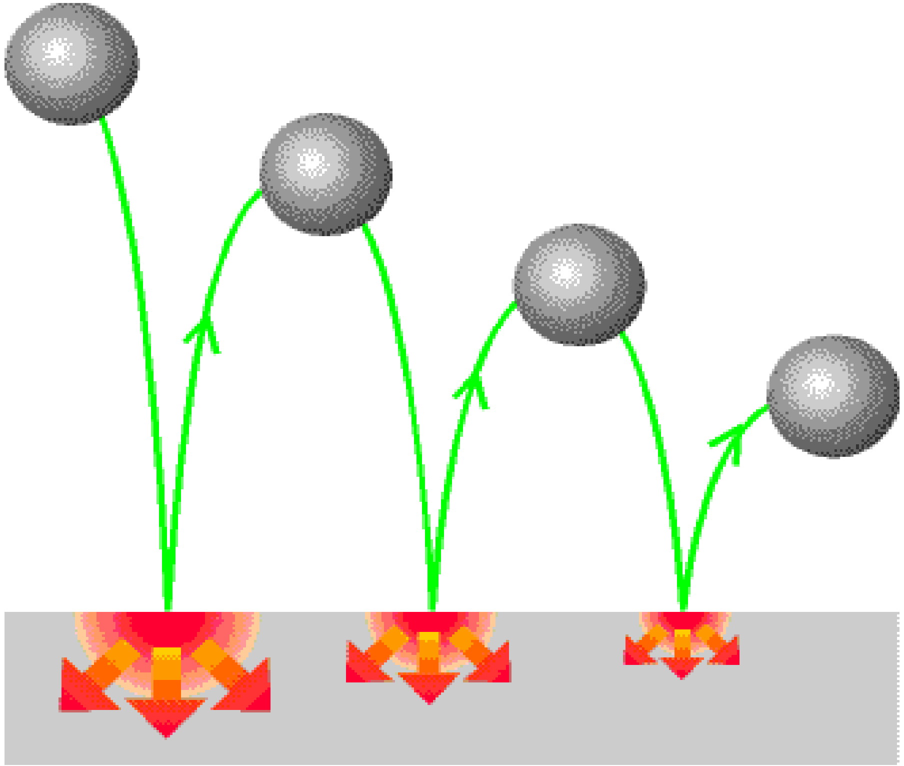
But some things don't. We can confine a gas to a smaller volume, we can cool an object with a refrigerator, and we can force some reactions to go in reverse. However, none of these processes happens spontaneously.

The direction of spontaneous change

The characteristic of these two processes, spontaneous and non-spontaneous is summarized by the Second Law of thermodynamics.

The direction of spontaneous change

4.1 The dispersal of energy

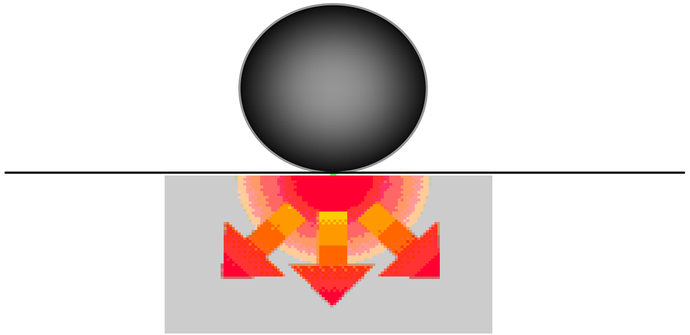


Sketch for the distribution of energy

The direction of spontaneous change

4.1 The dispersal of energy

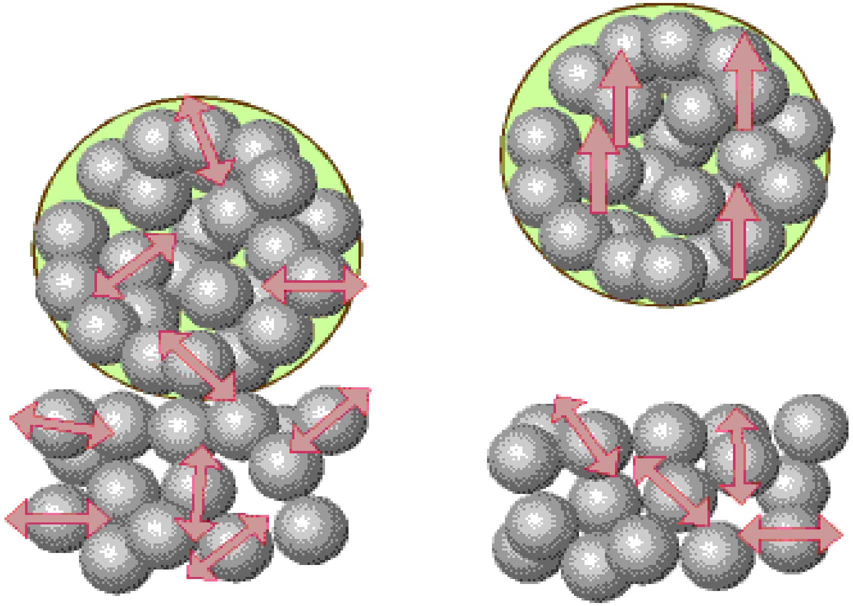
The spontaneous changes are always accompanied by a dispersal of energy into a more disordered form.



Sketch for the distribution of energy

The direction of spontaneous change

4.1 The dispersal of energy


(a) (b)

Sketch for the distribution of energy

(a) A ball resting on a warm surface; the atoms are under-going thermal motion;

(b) For the ball to fly upwards, some of the random vibra-tional motion would have to change into coordinated, directed motion.

The direction of spontaneous change

The spontaneous changes are always accompanied by a dispersal of energy into a more disordered form.

The direction of spontaneous change

4.1 The dispersal of energy

In the term of entropy

The entropy of an isolated system increases in the course of a spontaneous change:

$$\Delta S_{\mathrm{tot}} > 0$$

where S_{tot} is the total entropy of the system and its surroundings. Thermodynamically irreversible processes are spontaneous processes, and must be accompanied by an increase in entropy.

The direction of spontaneous change

The characteristic of these two process, spontaneous and non-spontaneous is summarized by the Second Law of Thermodynamics.

Statements on the Second Law of Thermodynamic

The Second Law may be expressed in terms of the entropy, a state function that lets us assess whether one state is accessible from another by a spontaneous change. the Second Law uses the entropy to identify the spontaneous changes among those permissible changes.

The First Law led to the introduction of the internal energy, a state function that lets us assess whether a change is permissible; only those change may occur for which the *U* of an isolated system remains constant. First Law uses the internal energy to identify permissible changes;

Statements on the Second Law of Thermodynamic

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

The spontaneous changes are always accompanied by a dispersal of energy into a more disordered form.

The entropy of an isolated system increases in the course of a spontaneous change:

$$\Delta S_{\mathrm{tot}} > 0$$

4. The Second Law: the concepts

The direction of spontaneous change

- 4.1 The dispersal of energy
- 4.2 Entropy ▶
- 4.3 Entropy changes accompanying specific processes
- 4.4 The Third Law of thermodynamics
- 4.5 Reaching very low temperatures

Concentrating on the system

- 4.6 The Helmholtz and Gibbs energies
- 4.7 Standard molar Gibbs energies

4.2 Entropy

1). The thermodynamic definition of entropy

a). Heat stimulates disorderly motion in the surroundings; work stimulates uniform motion of atoms in the surroundings, does not change the degree of disorder, and so does not change the entropy.

b). A change in the extent to which energy is dispersed in a disorderly manner depends on the quantity of energy transferred as heat.

4.2 Entropy

1). The thermodynamic definition of entropy

The thermodynamic definition of entropy is based on

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$$

The units of entropy: $\mathrm{J\,K^{-1}}$.

The units of Molar entropy: $\mathrm{J\,K^{-1}\,mol^{-1}}$ (the same as that of R)

4.2 Entropy

1). The thermodynamic definition of entropy

For a measurable change between two states i and f this expression integrates to:

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$$

To calculate the difference in entropy between any two states of a system, integrate the heat supplied at each stage of the path divided by the temperature at which the heat is supplied.

Example

Calculate the change in entropy when 50kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (0) ℃, and (b) 70 ℃.

Example 4.1– Calculating the entropy change for the isothermal expansion of a perfect gas

Method: $$\Delta S = \frac{1}{T}\int_{\mathrm{i}}^{\mathrm{f}} \mathrm{d}q_{\mathrm{rev}} = \frac{q_{\mathrm{rev}}}{T}$$

Answer:

(a) $$\Delta S = \frac{q_{\mathrm{rev}}}{T} = \frac{50\times10^{3}\,\mathrm{J}}{273\mathrm{K}} = 1.8\times10^{2}\,\mathrm{JK}^{-1}$$

(b) $$\Delta S = \frac{q_{\mathrm{rev}}}{T} = \frac{50\times10^{3}\,\mathrm{J}}{(70+273)\mathrm{K}} = 1.5\times10^{2}\,\mathrm{JK}^{-1}$$

4.2 Entropy

1). The thermodynamic definition of entropy

The change in entropy of the surroundings

$$\mathrm{d}S_{\mathrm{sur}} = \frac{\mathrm{d}q_{\mathrm{sur,\ rev}}}{T_{\mathrm{sur}}}$$

Because the temperature and pressure of the surroundings is commonly constant, whatever the change takes place, reversibly or irreversibly, we have

$$\mathrm{d}S_{\mathrm{sur}} = \frac{\mathrm{d}q_{\mathrm{sur}}}{T_{\mathrm{sur}}}$$

$$\Delta S_{\mathrm{sur}} = \frac{q_{\mathrm{sur}}}{T_{\mathrm{sur}}} = \frac{-q}{T_{\mathrm{sur}}}$$

4.2 Entropy

The change of entropy of the surroundings can be calculated by dividing the heat transferred by *T* at which the transfer takes place(regardless of how the change is brought about in the system).

For any adiabatic change,

$$q_{\mathrm{sur}} = 0\text{, so}$$

$$\Delta S_{\mathrm{sur}} = 0$$

Illustration

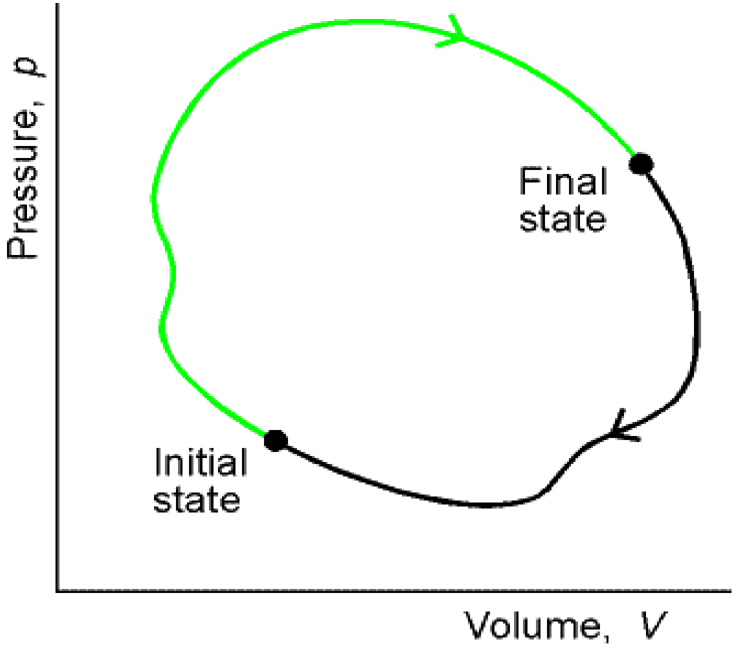
To calculate the entropy change in the surroundings when 1.00 mol $H_2O(l)$ is formed from its elements under standard conditions at 298 K, we use $\Delta H^{\ominus} = -286$ kJ from a table. The heat released is supplied to the surroundings, now regarded as being at constant pressure, so $q_{sur} = +286$ kJ. Therefore,

$$\Delta S_{sur} = \frac{2.86 \times 10^{5}\ \mathrm{J}}{298\ \mathrm{K}} = +959\ \mathrm{JK}^{-1}$$

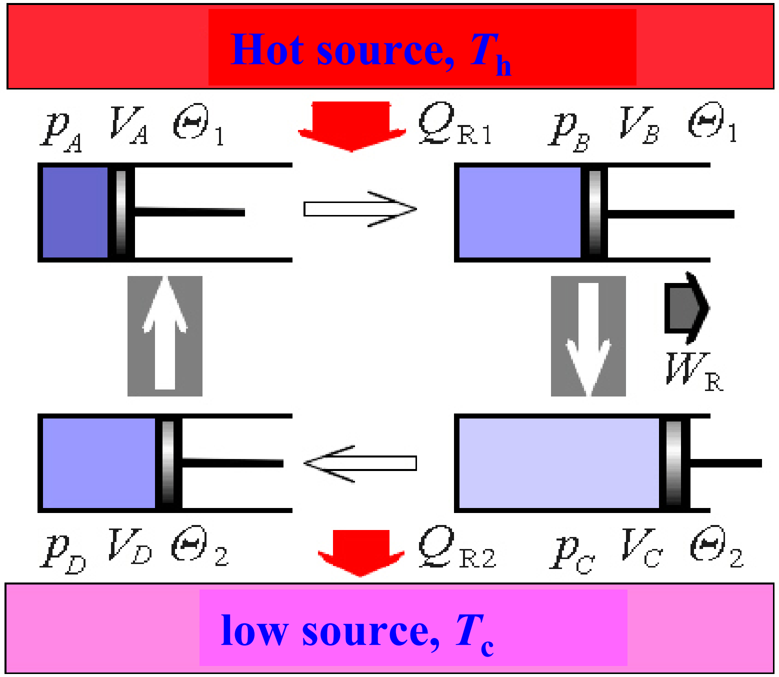
4.2 Entropy

2). The entropy as a state function

The entropy is one of the function of states, which implies that:

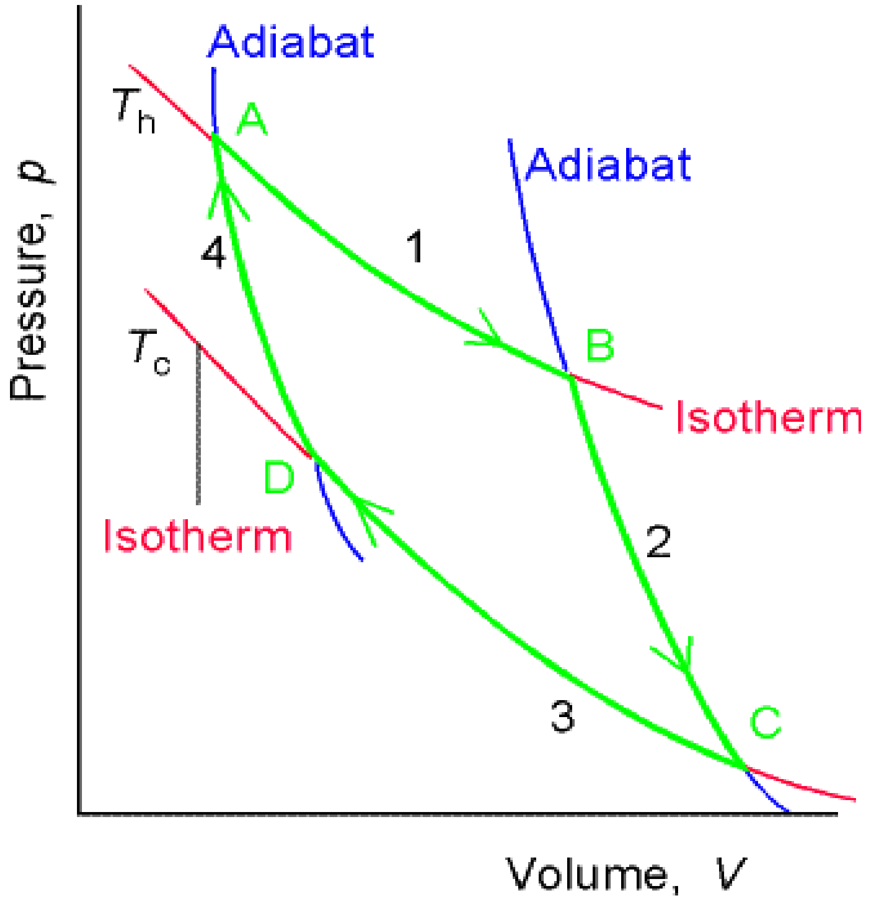


$$\oint \mathrm{d}S = 0$$



A thermodynamic cycle; the overall change in a state function is zero.

The Carnot cycle



The structure of a Carnot cycle.

Carnot cycle – four reversible stages:

1). Reversible isothermal expansion at T_h, $\Delta S_1 = q_h/T_h$, $q_h > 0$.

2). Reversible adiabatic expansion $\Delta S_2 = 0$.

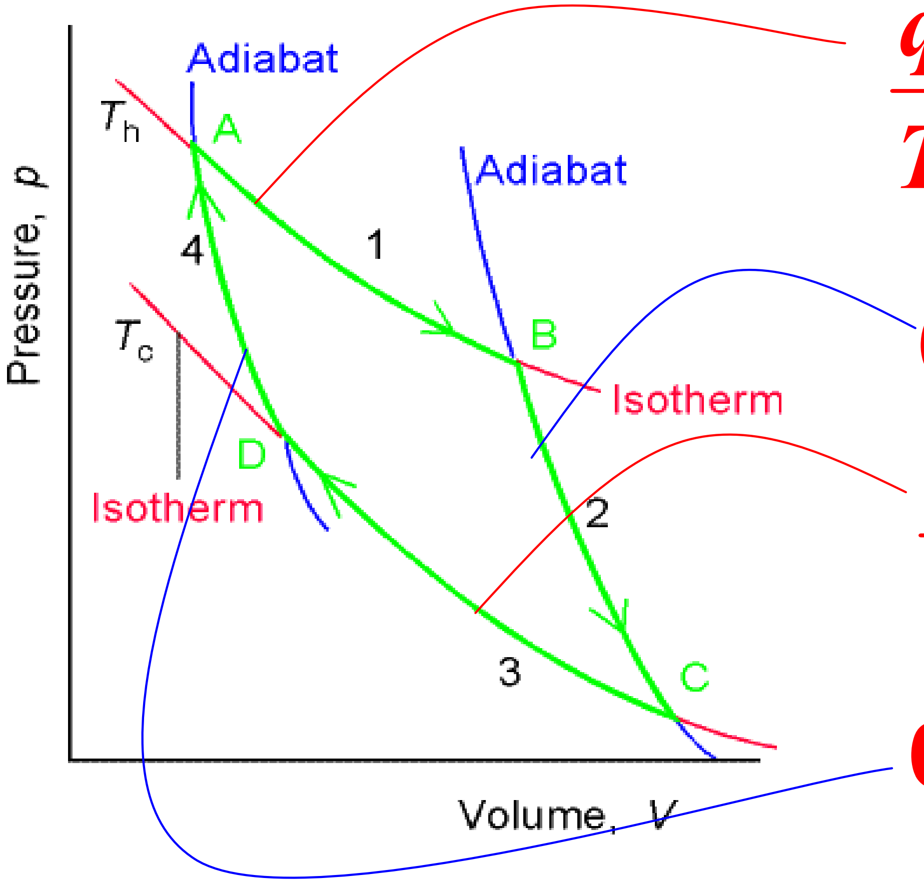
3). Reversible isothermal compression at T_c. $\Delta S_3 = q_c/T_c$, q_c is negative.

4). Reversible adiabatic compression $\Delta S_4 = 0$.

4.2 Entropy - The entropy as a state function

2). The entropy as a state function

The total change in entropy around the closed cycle is:



$$\frac{q_h}{T_h}$$

$$0$$

$$\frac{q_c}{T_c}$$

$$0$$

The structure of a Carnot cycle.

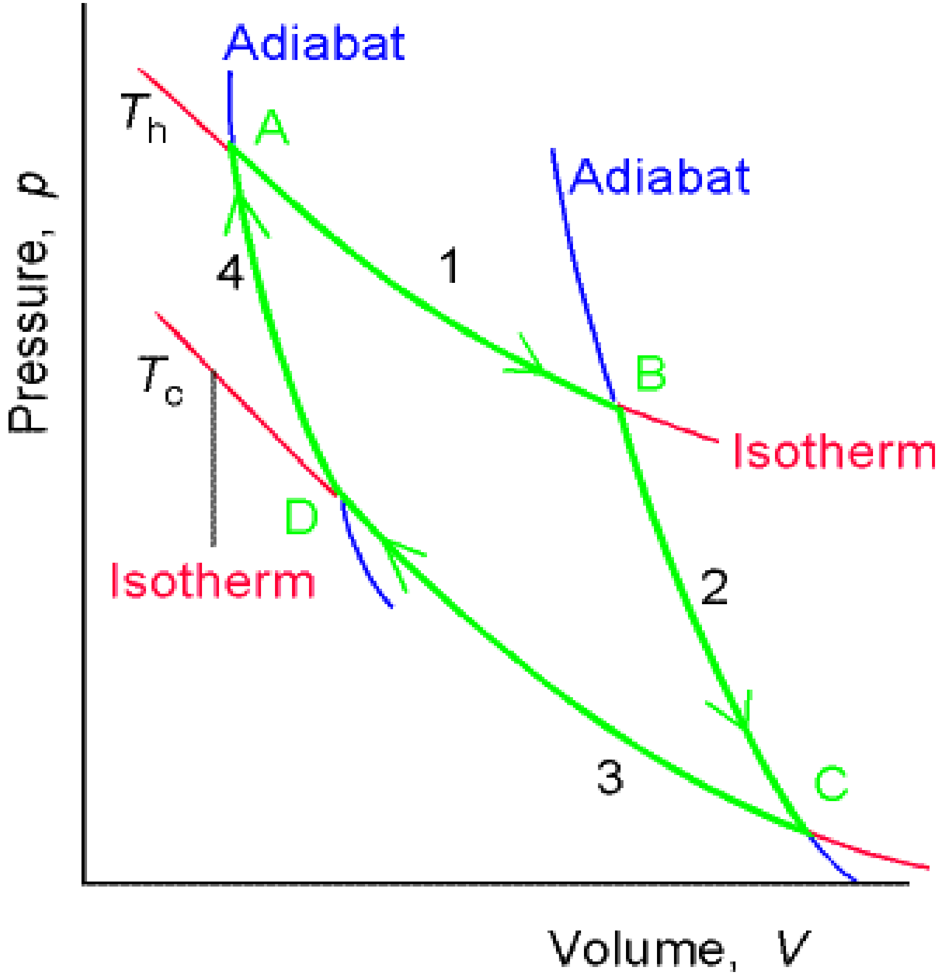
$$\oint dS = \frac{q_h}{T_h} + 0 + \frac{q_c}{T_c} + 0$$

$$= \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

since $$\frac{q_h}{q_c} = -\frac{T_h}{T_c}$$

then $$\oint dS = 0$$

4.2 Entropy - The entropy as a state function



$$q_h = nRT_h \ln\left(\frac{V_B}{V_A}\right)$$

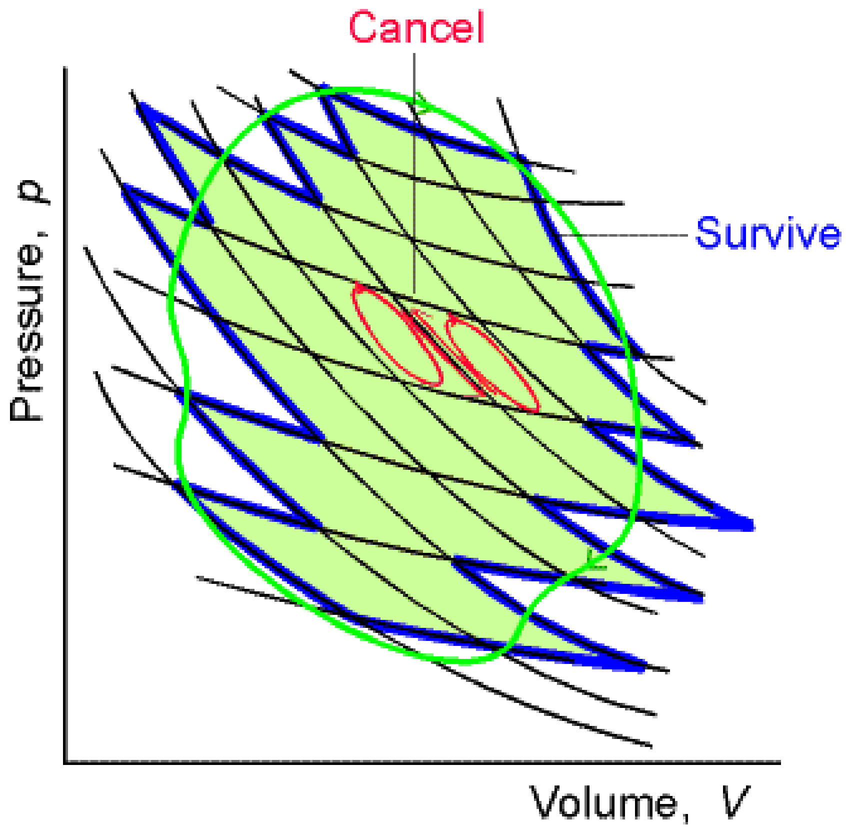
$$q_c = nRT_c \ln\left(\frac{V_A}{V_B}\right)$$

$$\frac{q_h}{q_c} = -\frac{T_h}{T_c}$$

$$\oint ds = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

4.2 Entropy

2). The entropy as a state function



$$\sum_{\text{all}} \frac{q_{\text{rev}}}{T} = \sum_{\text{perimeter}} \frac{q_{\text{rev}}}{T} = 0$$

In the limit of infinitesimal cycles, the non-canceling edges of the Carnot cycles match the overall cycle exactly; the sum becomes an integral. This result implies that d***S*** is an exact differential and ***S*** is state function.

$$\oint \mathrm{d}S = 0$$

4. The Second Law: the concepts

The direction of spontaneous change

4.1 The dispersal of energy

4.2 Entropy ▶

4.3 Entropy changes accompanying specific processes

4.4 The Third Law of thermodynamics

4.5 Reaching very low temperatures

Concentrating on the system

4.6 The Helmholtz and Gibbs energies

4.7 Standard molar Gibbs energies

Statements on the Second Law of Thermodynamic

The Second Law may be expressed in terms of the entropy, a state function that lets us assess whether one state is accessible from another by a spontaneous change. the Second Law uses the entropy to identify the spontaneous changes among those permissible changes.

The First Law led to the introduction of the internal energy, a state function that lets us assess whether a change is permissible; only those change may occur for which the *U* of an isolated system remains constant. First Law uses the internal energy to identify permissible changes;

4.2 Entropy

The thermodynamic definition of entropy

For the system

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$$

For the surroundings

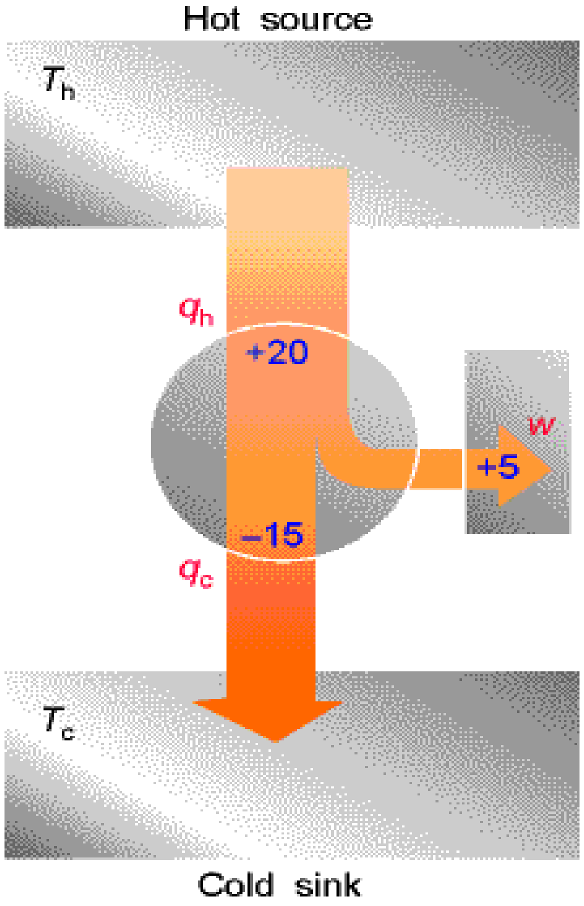
$$\mathrm{d}S_{\mathrm{sur}} = \frac{\mathrm{d}q_{\mathrm{sur,\,rev}}}{T_{\mathrm{sur}}} = -\frac{\mathrm{d}q}{T_{\mathrm{sur}}}$$

For the total

$$\Delta S_{\mathrm{tot}} = \Delta S + \Delta S_{\mathrm{sur}}$$

4.2 Entropy

The efficiency of a heat engine, ε :



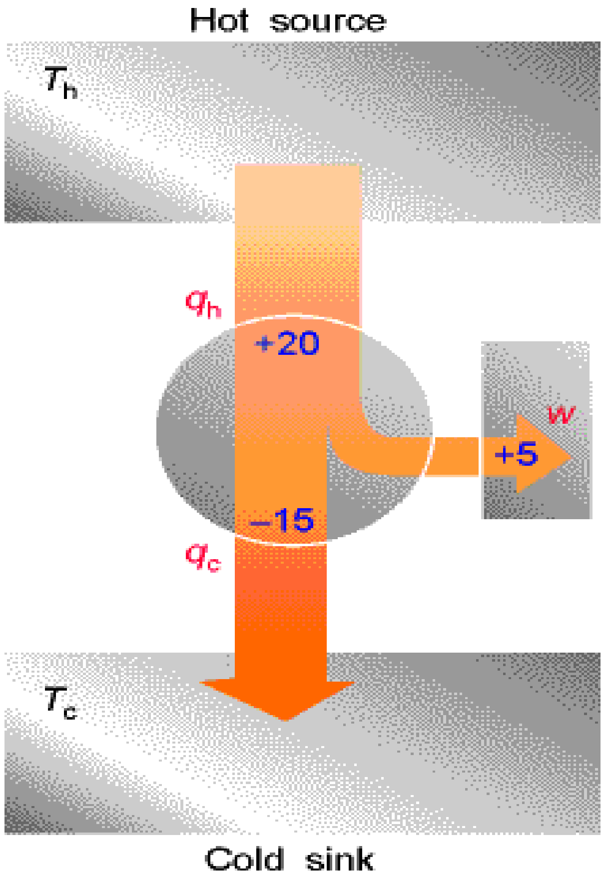
The structure of a heat engine

$$\varepsilon = \frac{\text{work performed}}{\text{heat adsorbed}} = \frac{|w|}{q_h}$$

The efficiency is the work done divided by the heat supplied from the hot source.

4.2 Entropy

The efficiency of a heat engine, ε :



The structure of a heat engine

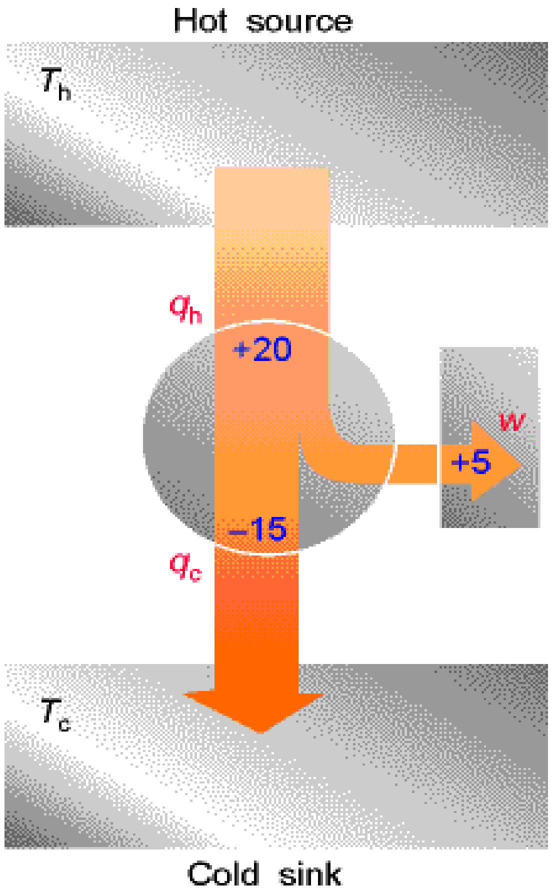
The work performed by the engine is the difference between the heat supplied by hot source and that returned to the cold sink, then:

$$\varepsilon = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

Note that $q_c<0$.

4.2 Entropy

The efficiency of a heat engine, ε :



The structure of a heat engine

For a Carnot cycle:

$$\varepsilon_{rev} = 1 - \frac{T_c}{T_h}$$

The second law of thermodynamics implies that all reversible engines have the same efficiency regardless of their construction.

4.2 Entropy

3). The thermodynamic temperature

Suppose an engine that is working reversibly between a hot source at a temperature T_h and a cold sink at a temperature T, then

$$\varepsilon = 1 - \frac{T_c}{T_h} = 1 - \frac{T}{T_h}$$

$$T = (1 - \varepsilon)T_h$$

4.2 Entropy

3). The thermodynamic temperature

$$T = (1 - \varepsilon)T_{\mathrm{h}}$$

The expression of the thermodynamic temperature scale defined by Kelvin.

1). The zero of the thermodynamic temperature scale occurs for a Carnot efficiency of 1;

2). On the Kelvin scale it is defined by setting the temperature of the triple point of water as 273.16 K exactly.

3). It is possible to measure temperature on a purely mechanical basis.

4.2 Entropy

4). The Clausius inequality

Consider a system in thermal and mechanical contact with its surroundings at the same temperature, ***T***. Any change of state is accompanied by a change in entropy of the system, d***S***, and of the surroundings, d$\boldsymbol{S}_{\text{sur}}$. Then

$$\mathrm{d}\boldsymbol{S} + \mathrm{d}\boldsymbol{S}_{\text{sur}} \geq 0 \qquad \text{or } \mathrm{d}\boldsymbol{S} \geq -\mathrm{d}\boldsymbol{S}_{\text{sur}}$$

Since $\mathrm{d}\boldsymbol{q}_{\text{sur}} = -\mathrm{d}\boldsymbol{q}$

It follows that $\mathrm{d}\boldsymbol{S}_{\text{sur}} = -\dfrac{\mathrm{d}\boldsymbol{q}}{\boldsymbol{T}} \qquad \mathrm{d}\boldsymbol{S} \geq \dfrac{\mathrm{d}\boldsymbol{q}}{\boldsymbol{T}}$

4.2 Entropy

4). The Clausius inequality

For any change, the Clausius inequality is expressed as:

$$\mathrm{d}S \geq \frac{\mathrm{d}q}{T}$$

For the isolated system:

$$\mathrm{d}S \geq 0$$

In an isolated system the entropy of the system alone cannot decrease when a spontaneous change takes place.

4.2 Entropy

4). The Clausius inequality

For the isolated system:

$$\begin{array}{l} \mathrm{d}S \geq 0 \\ \Delta S \geq 0 \end{array} \left\{ \begin{array}{l} > \ \textbf{irreversible} \\ = \ \textbf{reversible} \\ < \ \textbf{impossible} \end{array} \right.$$

4.2 Entropy

4). The Clausius inequality

$$\Delta S + \Delta S_{\mathrm{sur}} \geq 0 \quad \begin{cases} > & \textbf{spontaneous} \\ = & \textbf{equilibrorus} \\ < & \textbf{impossible} \end{cases}$$

4. The Second Law: the concepts

The direction of spontaneous change

- 4.1 The dispersal of energy
- 4.2 Entropy
- 4.3 Entropy changes accompanying specific processes ▶
- 4.4 The Third Law of thermodynamics
- 4.5 Reaching very low temperatures

Concentrating on the system

- 4.6 The Helmholtz and Gibbs energies
- 4.7 Standard molar Gibbs energies

4.3 Entropy changes accompanying specific processes

1). The entropy of phase transitions

Because a change in the degree of molecular order occurs when a substance freezes or boils, we should expect the transition to be accompanied by a change in entropy.

In a reversible process
In an irreversible process

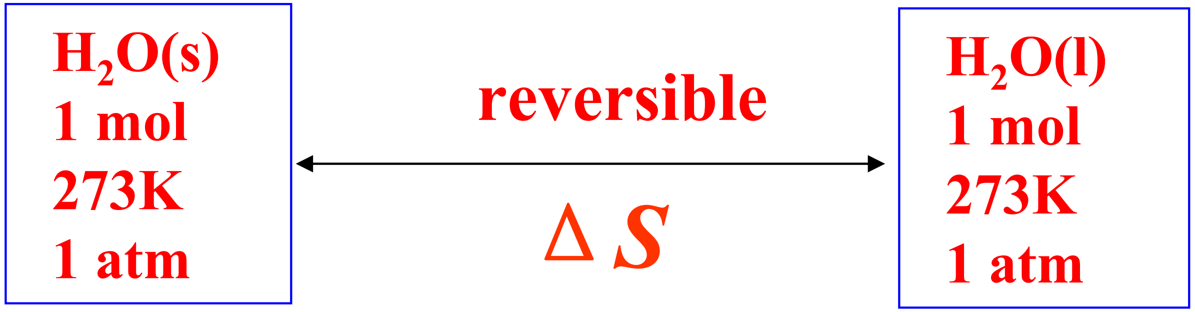
4.3 Entropy changes accompanying specific processes

ƌ The entropy of phase transition at T_{trs}, Reversible

At the normal transition temperature, T_{trs}, any transfer of heat between the system and its surroundings is reversible because the two phases in the system are in equilibrium.

Since $q = \Delta_{trs} H$ at constant *p*, the change in molar entropy of the system is

$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$



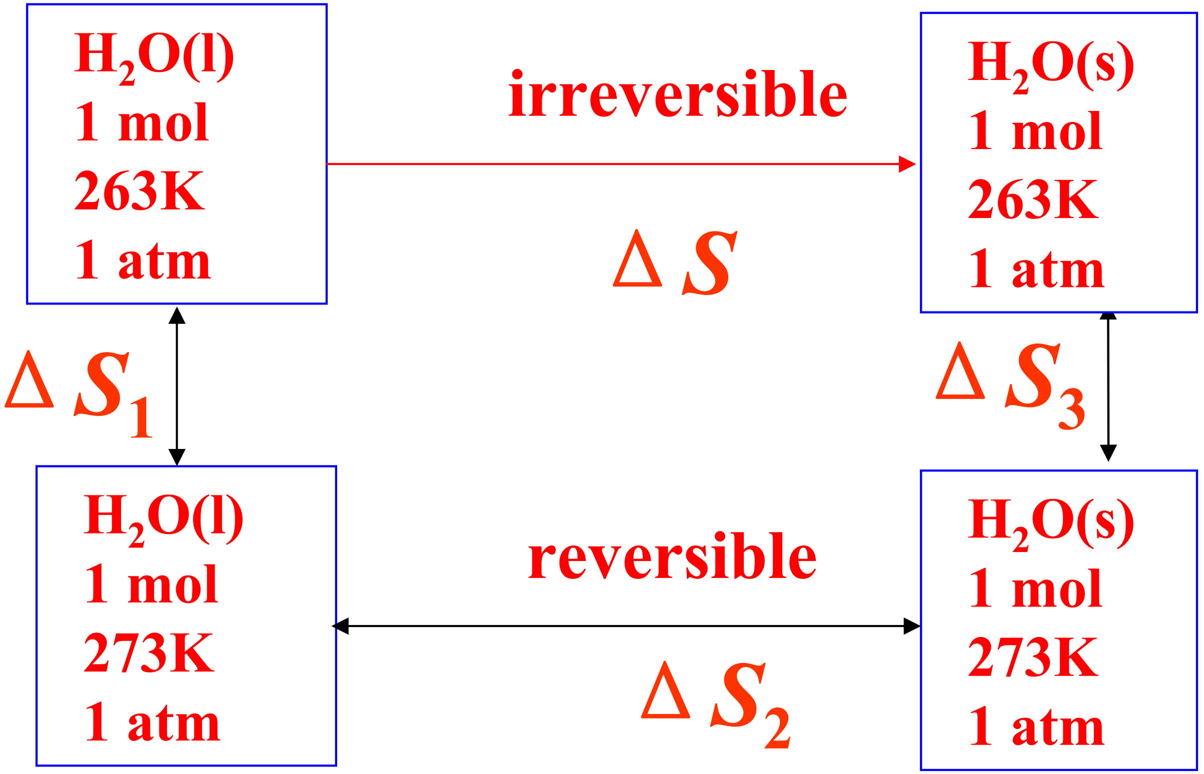
At T_{trs} =273K

$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

4.3 Entropy changes accompanying specific processes

d The entropy of transition at *T*, Irreversible

If a process changes at which the temperature deviates the normal transition temperature, T_{trs}, the process is not a reversible and the above equation can not be directly used to calculate the change in entropy.In this case

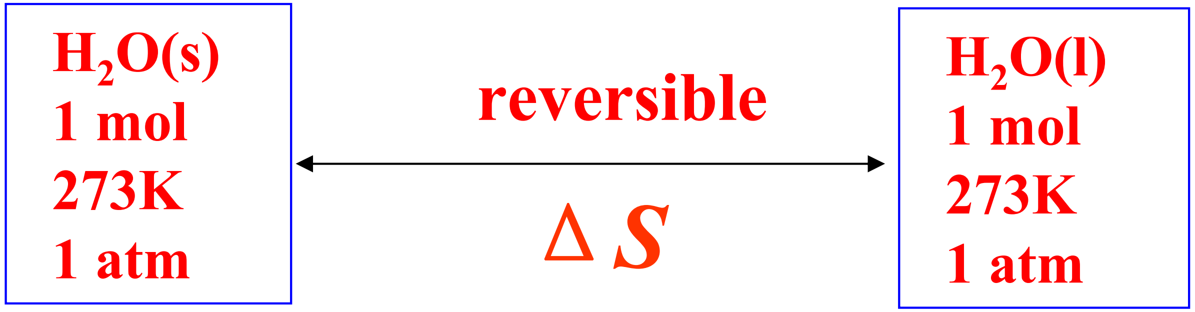


At T=263K

($T \neq T_{trs}$)

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

4.3 Entropy changes accompanying specific processes



$H_2O(s)$
1 mol
273K
1 atm

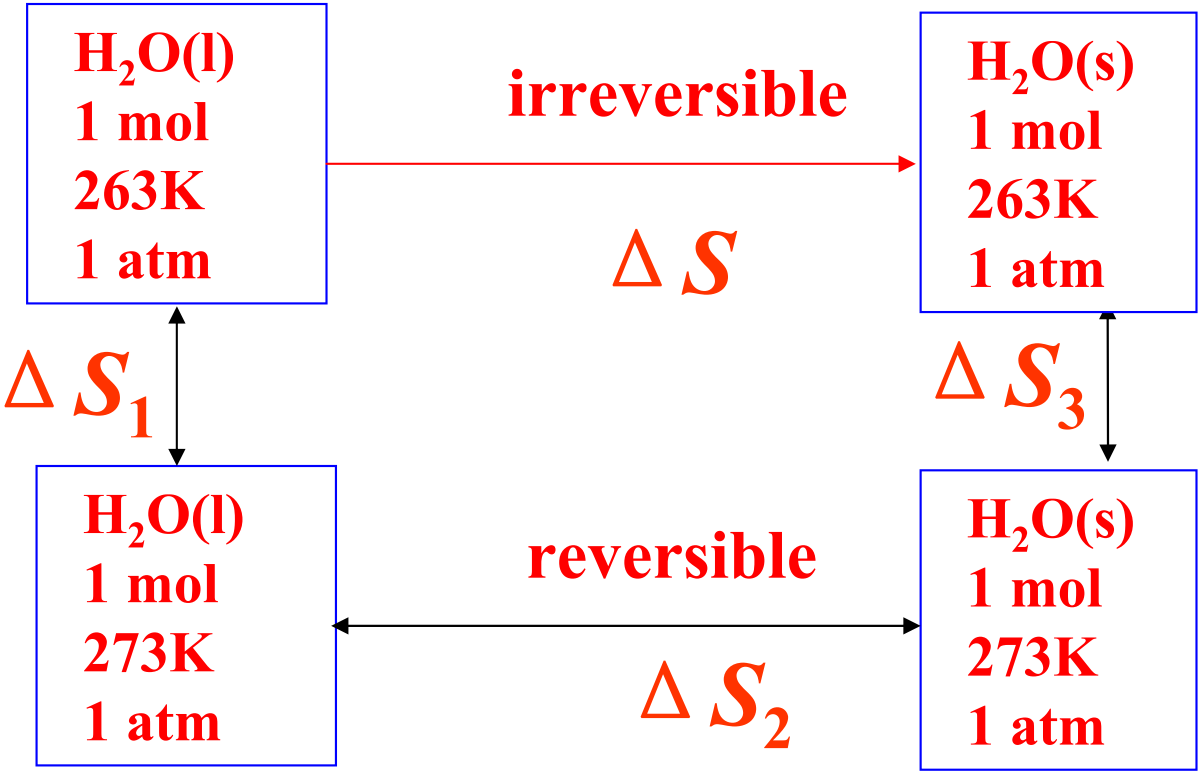
reversible

ΔS

$H_2O(l)$
1 mol
273K
1 atm

At T_{trs} =273K

$$\Delta_{trs}S=\frac{\Delta_{trs}H}{T_{trs}}$$



$H_2O(l)$
1 mol
263K
1 atm

irreversible

ΔS

$H_2O(s)$
1 mol
263K
1 atm

ΔS_1

ΔS_3

$H_2O(l)$
1 mol
273K
1 atm

reversible

ΔS_2

$H_2O(s)$
1 mol
273K
1 atm

At T=263K

$(T\neq T_{trs})$

$$\Delta S=\Delta S_1+\Delta S_2+\Delta S_3$$

4.3 Entropy changes accompanying specific processes

1). The entropy of phase transition at the T_{trs}

If the phase transition is exothermic ($\Delta_{\mathrm{trs}}H < 0$), the entropy change is negative, $\Delta_{\mathrm{trs}}S < 0$, which is consistent with the system becoming more ordered.

If the transition is endothermic($\Delta_{\mathrm{trs}}H > 0$), the entropy change is positive, $\Delta_{\mathrm{trs}}S > 0$, which is consistent with the system becoming more disordered.

4.3 Entropy changes accompanying specific processes

2). The isothermal expansion of a perfect gas

The change in entropy of a perfect gas that expands isothermally from V_i to V_f is

$$\Delta S = \frac{1}{T}\int_\mathrm{i}^\mathrm{f} \mathrm{d}q_\mathrm{rev} = \frac{q_\mathrm{rev}}{T}$$

The heat absorbed during a reversible isothermal expansion of a perfect gas can be calculated from:

$\triangle U = q + w$ **and** $\triangle U = 0.$

For a reversible change $q_\mathrm{rev} = -w_\mathrm{rev}$

4.3 Entropy changes accompanying specific processes

For a perfect gas in the isothermal process

$$w_{\mathrm{rev},T} = -nRT\int_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{\mathrm{d}V}{V} = -nRT\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$

$$q_\mathrm{rev} = -w_\mathrm{rev} = nRT\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$ **It follows that**

The change in entropy of a perfect gas that expands isothermally from V_i to V_f is

$$\Delta S = nR\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$

4.3 Entropy changes accompanying specific processes

$$\Delta S = nR \ln \frac{V_\mathrm{f}}{V_\mathrm{i}}$$

Because S is a state function, this expression applies whether the change of state occurs reversibly or irreversibly. If the change is reversible, the entropy change in the surroundings must be such as to give $\Delta S_{\mathrm{tot}} = 0$. If the expansion occurs freely ($w = 0$) and irreversibly, and if T remains constant, then $q = 0$. Consequently, $\Delta S_{\mathrm{sur}} = 0$, and the total entropy change is given by this equation. And in this case:

$$\Delta S \geq 0, \quad \text{spontaneous process}$$

4.3 Entropy changes accompanying specific processes

3). The variation of entropy with temperature

The entropy of a system at a temperature T_f from a knowle-dge of its entropy at a temperature T_i and the heat supplied to change its temperature from one value to the other:

$$\Delta S = S(T_\mathrm{f}) - S(T_\mathrm{i})$$

$$S(T_\mathrm{f}) = S(T_\mathrm{i}) + \int_\mathrm{i}^\mathrm{f} \frac{\mathrm{d}q_\mathrm{rev}}{T}$$

From the definition of constant-pressure heat capacity, so long as the system is doing no non-expansion work:

4.3 Entropy changes accompanying specific processes

3). The variation of entropy with temperature

$$\mathrm{d}q_{\mathrm{rev}} = C_p \mathrm{d}T$$

$$S(T_{\mathrm{f}}) = S(T_{\mathrm{i}}) + \int_{\mathrm{i}}^{\mathrm{f}} \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$$

$$= S(T_{\mathrm{i}}) + \int_{\mathrm{i}}^{\mathrm{f}} \frac{C_p \mathrm{d}T}{T}$$

When C_p is independent of T in the temperature range of interest:

$$S(T_{\mathrm{f}}) = S(T_{\mathrm{i}}) + C_p \ln\left(\frac{T_{\mathrm{f}}}{T_{\mathrm{i}}}\right)$$

Example – Calculating the entropy change

Calculate the entropy change when argon at 25℃ and 1.00 atm in a container of volume 500 cm^3 is allowed to expand to 1000 cm^3 and is simultaneously heated to 100 ℃.

Example – Calculating the entropy change

Method: Because *S* is a state function, we are free to choose the most convenient path from the initial state.

The first step: reversible isothermal expansion to the final volume.The entropy change in this step is

$$\Delta S_1 = nR\ln\left(V_\mathrm{f}/V_\mathrm{i}\right)$$

The second step: reversible heating at constant volume to the final temperature. The entropy change in this step is

$$\Delta S_2 = C_{V,m}\ln\left(T_\mathrm{f}/T_\mathrm{i}\right) \qquad \left(C_{V,\mathrm{m}} = C_{p,\mathrm{m}} - R\right)$$

$$\Delta S = \Delta S_1 + \Delta S_2$$

Example – **Calculating the entropy change**

Answer: The amount of Ar present is (from the perfect gas equation and the data for the initial state**):**

$$n = pV/RT = 0.0204\ \mathrm{mol}$$

$$\Delta S_1 = nR\ \ln(V_f/V_i)$$

$$= nR\ \ln(1000/500) = 0.118\mathrm{J\ \ K^{-1}}$$

From $\Delta S = C_p \ln(T_f/T_i)$ **and** $C_{p,m} - C_{V,m} = R$

$$\Delta S_2 = (0.0204\mathrm{mol})\times(12.48\mathrm{JK^{-1}mol^{-1}})\times\ln(373\mathrm{K}/298\mathrm{K})$$

$$= 0.057\mathrm{JK^{-1}}$$

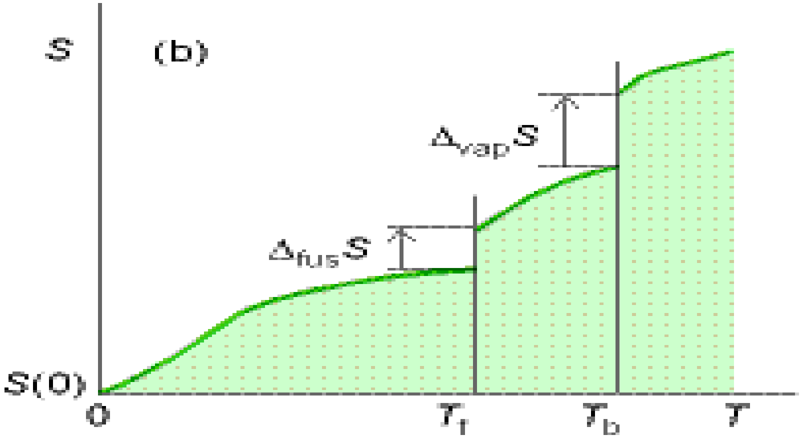
$$\Delta S = \Delta S_1 + \Delta S_2 = 0.118\mathrm{JK^{-1}} + 0.057\mathrm{JK^{-1}} = 0.175\mathrm{JK^{-1}}$$

4.3 Entropy changes accompanying specific processes

4). The measurement of entropy form heat capacity

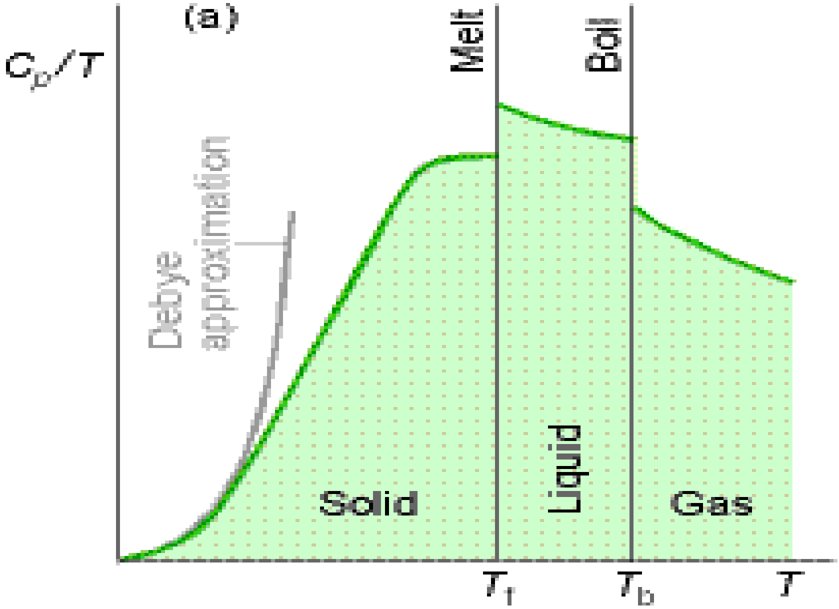
The entropy of a system at a temperature *T* based on its entropy at $T = 0$

$$S(T) = S(0) + \int_0^{T_\mathrm{f}} \frac{C_p(\mathrm{s})\mathrm{d}T}{T} + \frac{\Delta_\mathrm{fus}H}{T_\mathrm{f}} + \int_{T_\mathrm{f}}^{T_b} \frac{C_p(\mathrm{l})\mathrm{d}T}{T} + \frac{\Delta_\mathrm{vap}H}{T_\mathrm{b}} + \int_{T_\mathrm{b}}^{T} \frac{C_p(\mathrm{g})\mathrm{d}T}{T}$$



The entropy is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

4.3 Entropy changes accompanying specific processes



The variation of C_p/T with the temperature

Debye extrapolation

Theoretically, the heat capacity is proportional to T^3 when T is low:

$$C_p = aT^3$$

4. The Second Law: the concepts

The direction of spontaneous change

4.1 The dispersal of energy

4.2 Entropy

4.3 Entropy changes accompanying specific processes

4.4 The Third Law of thermodynamics ▶

4.5 Reaching very low temperatures

Concentrating on the system

4.6 The Helmholtz and Gibbs energies

4.7 Standard molar Gibbs energies

4.4 The Third Law of thermodynamics

1). The Nernst heat theorem

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero:

$$\Delta S_{T \to 0\,\mathrm{K}} = 0$$

4.4 The Third Law of thermodynamics

2). The Third Law thermodynamics

If the entropy of every element in its most stable state at T=0 is taken as zero, then every substance has a positive entropy which at T=0 may become zero, and which does become zero for all perfect crystalline substances, including compounds.

S**(0K) = 0, for all perfect crystalline substances**

The Third Law does not state that entropies are zero at T = 0; it merely implies that all perfect materials have the same entropy at that temperature. Choosing this common value as zero is then a matter of convenience.

4.4 The Third Law of thermodynamics

3). Third-Law entropies

The Third-Law entropy, standard entropy, $S^{\ominus}:(T)$

On the basis of $S(0\text{K}) = 0$ for all perfect crystals, the entropy of the substance in its standard state at the Temperature T is denoted $S^{\ominus}(T)$

4.4 The Third Law of thermodynamics

The standard reaction entropy, $\Delta_r S^\ominus$: the difference between the molar entropies of the pure, separated products and the pure, separated reactants, all substances being in their standard states at the specified temperature.

$$\Delta_r S^\ominus = \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus$$

$$\Delta_r S^\ominus = \sum_J \nu_J S_m^\ominus (J)$$

ν-stoichiometric coefficient

Illustration

Calculate the standard reaction entropy of the following reaction at 25 ℃:

$$H_2(g)+\tfrac{1}{2}O_2(g)\rightarrow H_2O(l)$$

$$\Delta_r S^\ominus = \underbrace{\sum \nu S_m^\ominus}_{\text{Products}} - \underbrace{\sum \nu S_m^\ominus}_{\text{Reactants}}$$

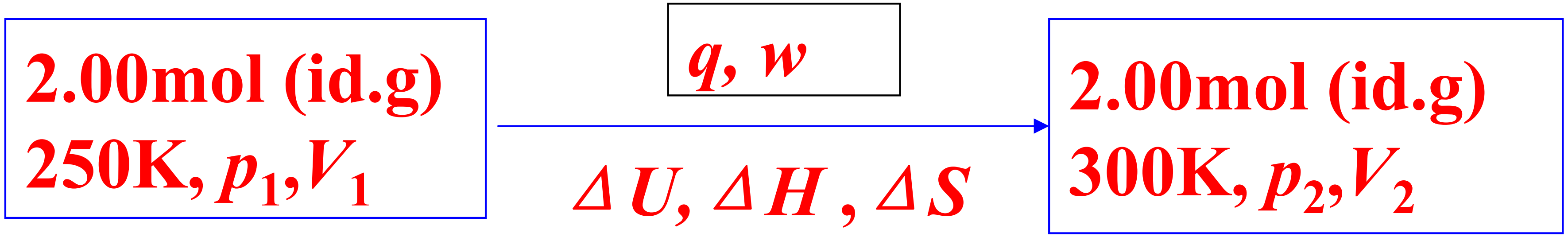
$$\Delta_r S^\Theta = S_m^\Theta(H_2O,l) - \left\{S_m^\Theta(H_2,g) + \tfrac{1}{2}S_m^\Theta(O_2,g)\right\}$$

$$= 69.9 - \left\{130.7 + \tfrac{1}{2}(205.0)\right\} JK^{-1}mol^{-1} = -163.3 JK^{-1}mol^{-1}$$

Example

- A sample consisting of 2.00 mol of a diatomic perfect gas at 250K is compressed reversibly and adiabatically until its temperature reaches 300K. Calculate *q*, *w*, ΔU, ΔH and ΔS. Given that $C_{V,\mathrm{m}}$=27.5 $\mathrm{K^{-1}\ mol^{-1}}$.

Example



2.00mol (id.g)
250K, p_1,V_1

q, w

ΔU, ΔH , ΔS

2.00mol (id.g)
300K, p_2,V_2

Answer: **Because the compression process is reversible and adiabatic, it follows that**

$$q = q_{\text{rev}} = 0$$

$$\Delta S = \int_{\text{i}}^{\text{f}} \frac{\mathrm{d}q_{\text{rev}}}{T} = 0$$

Example

$$\Delta U = nC_{V,\mathrm{m}}\Delta T$$

$$= (2.0\,\mathrm{mol}) \times (27.5\,\mathrm{JK^{-1}mol^{-1}}) \times (300 - 250)\,\mathrm{K}$$

$$= 2750\ \mathrm{J} = +2.75\,\mathrm{kJ}$$

$$w = \Delta U - q = \Delta U = 2.75\ \mathrm{kJ}$$

Since $\Delta H = nC_{p,\mathrm{m}}\Delta T$ and

$$C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R = (27.5 + 8.314)\mathrm{JK^{-1}mol^{-1}} = 35.814\mathrm{JK^{-1}mol^{-1}}$$

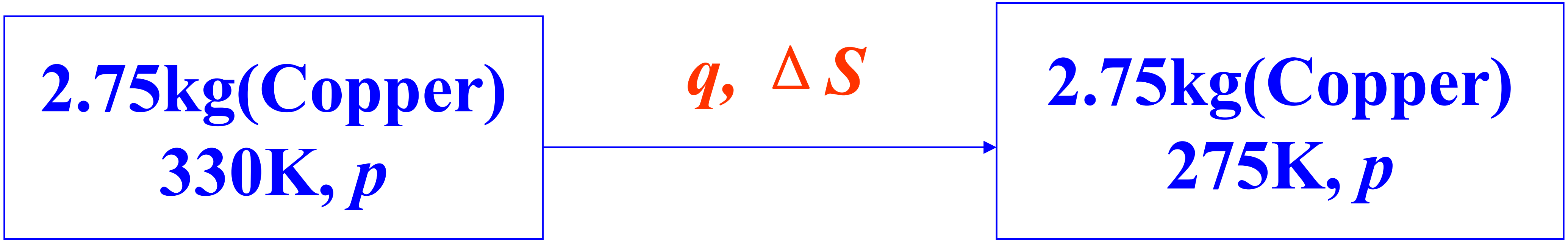
then

$$\Delta H = (2.0\mathrm{mol}) \times (35.814\mathrm{JK^{-1}mol^{-1}}) \times (300 - 250)\mathrm{K}$$

$$= 3581.4\mathrm{J} = 3.58\mathrm{kJ}$$

Example

A sample of copper of mass 2.75 kg is cooled at constant pressure from 330K to 275K. Calculate (a) the energy that must be removed as heat, and (b) the change in entropy of the sample.



2.75kg(Copper)
330K, p

q, ΔS

2.75kg(Copper)
275K, p

Example

Answer: The heat released is

$$q = C_p \Delta T = nC_{p,\mathrm{m}} \Delta T$$

$$= \left(\frac{2.75\mathrm{kg}}{63.54 \times 10^{-3}\,\mathrm{kgmol}^{-1}}\right) \times (24.44\mathrm{JK}^{-1}\mathrm{mol}^{-1}) \times (275 - 330)\mathrm{K}$$

$$= -58.2 \times 10^{3}\,\mathrm{J}$$

Example

(b)

$$\Delta S=\int\frac{\mathrm{d}q_{\text{rev}}}{T}=\int\frac{C_p\mathrm{d}T}{T}=nC_{p,\mathrm{m}}\ln\frac{T_f}{T_i}$$

$$=\left(\frac{2.75\,\text{kg}}{63.54\times10^{-3}\,\text{kg}\,\text{mol}^{-1}}\right)\times(24.44\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\times\ln\frac{275}{330}$$

$$=-193\,\text{J}\,\text{K}^{-1}$$

4. The Second Law: the concepts

The direction of spontaneous change

4.1 The dispersal of energy
4.2 Entropy
4.3 Entropy changes accompanying specific processes
4.4 The Third Law of thermodynamics
4.5 Reaching very low temperatures

Concentrating on the system

4.6 The Helmholtz and Gibbs energies
4.7 Standard molar Gibbs energies

4. The Second Law: the concepts

Concentrating on the system

Entropy is the basic concept for discussing the direction of natural change, but to use it we have to analyze changes in both the system and its surroundings. We have seen that it is always very simple to calculate the entropy change in the surroundings, and we shall now see that it is possible to devise a simple method for taking that contribution into account automatically. This approach focuses our attention on the system and simplifies discussions.

4.6 The Helmholtz and Gibbs energies

1) The Helmholtz and Gibbs energies

For a system in thermal equilibrium with its surroundings at a temperature *T*, when a change in the system occurs and there is a transfer of energy as heat between the system and the surroundings, the Clausius inequality is

$$\mathrm{d}S - \frac{\mathrm{d}q}{T} \geq 0$$

This inequality can be developed in two ways according to the conditions of (a) constant volume, and (b) constant pressure under which the process occurs

4.6 The Helmholtz and Gibbs energies

(a) Heat transfer at constant volume, zero of non-expansion work: $\mathrm{d}q_V = \mathrm{d}U$

$$\mathrm{d}S - \frac{\mathrm{d}U}{T} \geq 0$$

$$T\mathrm{d}S \geq \mathrm{d}U \qquad \text{(constant } p\text{, no non-expanision work)}$$

The criterion for spontaneous change is expressed solely in terms of the state functions of the system.

At either constant internal energy ($\mathrm{d}U = 0$) or constant entropy ($\mathrm{d}S = 0$):

$$\mathrm{d}S_{U,V} \geq 0 \qquad \mathrm{d}U_{S,V} \leq 0$$

4.6 The Helmholtz and Gibbs energies

$$\mathrm{d}S_{U,V} \geq 0 \qquad \mathrm{d}U_{S,V} \leq 0$$

The first inequality states that, in a system at constant *V* and constant *U*, the entropy increases in a spontaneous change. The second inequality should be interpreted that, if the entropy of the system is unchanged, then there must be an increase in entropy of the surroundings, which can be achieved only if the energy of the system decreases as energy flows out as heat.

4.6 The Helmholtz and Gibbs energies

(b) Heat transfer at constant pressure, zero of non-expansion work: $\mathrm{d}q_p = \mathrm{d}H$

$$T\mathrm{d}S \geq \mathrm{d}H \quad (\text{constant } p, \text{no non-expanision work})$$

At either constant enthalpy ($\mathrm{d}H = 0$) or constant entropy ($\mathrm{d}S = 0$):

$$\mathrm{d}S_{H,p} \geq 0 \qquad \mathrm{d}H_{S,p} \leq 0$$

The entropy of the system at constant *p* must increase if its enthalpy remains constant; the enthalpy must decrease if the entropy of the system is constant.

4.6 The Helmholtz and Gibbs energies

c) The definition of the Helmholtz and Gibbs energies

The Helmholtz energy, A: $A = U - TS$

The Gibbs energy, G: $G = H - TS$

When the state of the system changes at constant T:

$$\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S \qquad \mathrm{d}G = \mathrm{d}H - T\mathrm{d}S$$

4.6 The Helmholtz and Gibbs energies

1) The Helmholtz and Gibbs energies

$$T\mathrm{d}S \geq \mathrm{d}U \quad (\text{constant } p, \text{no non-expanision work})$$

$$T\mathrm{d}S \geq \mathrm{d}H \quad (\text{constant } p, \text{no non-expanision work})$$

$$\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S \qquad \mathrm{d}G = \mathrm{d}H - T\mathrm{d}S$$

From $\mathrm{d}U - T\mathrm{d}S \leq 0$ **and** $\mathrm{d}H - T\mathrm{d}S \leq 0$

the criterion for spontaneous change is then:

$$\mathrm{d}A_{T,V} \leq 0 \quad \mathrm{d}G_{T,p} \leq 0 \quad \begin{cases} < 0 \text{ spontaneous} \\ = 0 \text{ equilibrorus} \end{cases}$$

at constant T,V
$w_e = 0$

at constant T, p
$w_e = 0$

4.6 The Helmholtz and Gibbs energies

2) Maximum work, $w_{\max}$

The Clausius inequality: $T\mathrm{d}S \geqslant \mathrm{d}q$ and

the First Law: $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$, it then follows that

$$\mathrm{d}U \leqslant T\mathrm{d}S + \mathrm{d}w \qquad \text{or} \qquad \mathrm{d}w \geqslant \mathrm{d}U - T\mathrm{d}S$$

The maximum energy that can be obtained from the system as work in a reversible change is then given by

$$\mathrm{d}w_{\max} = \mathrm{d}U - T\mathrm{d}S$$

Since $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S$ ⬇

4.6 The Helmholtz and Gibbs energies

2) Maximum work

$$\mathrm{d}w_{\max} = \mathrm{d}A$$

$$w_{\max} = \Delta A$$

The change in the Helmholtz energy is equal to the maximum work accompanying a process.

A **is also called the ‘maximum work function’, or the ‘work function’ .**

(*A*, Arbeit is the German word for work)

Example - Calculating the maximum available work

When 1mol $C_6H_{12}O_6$ (glucose) is oxidized to carbon dioxide and water at 25 ℃ according to the equation

$$C_6H_{12}O_6(s) + 6O_2\ (g) \rightarrow 6CO_2\ (g) + \rightarrow 6H_2O\ (l)$$

How much of this energy change can be extracted as (a) heat at constant pressure, (b) work? Given that

$$\Delta_r U^{\ominus} = -2808\text{kJmol}^{-1}, \Delta_r S = +182.4\text{JK}^{-1}\text{mol}^{-1}$$

Example - Calculating the maximum available work

Method: We know that the heat released at constant pressure is equal to the value of ΔH, so we need to relate $\Delta_r H^\ominus$ to $\Delta_r U^\ominus$, which is given. Suppose that all the gases involved are perfect and the equation is

$$\Delta_r H = \Delta_r U + \Delta n_g RT$$

For the maximum available from the process,

$$w_{\max} = \Delta A$$

Example - Calculating the maximum available work

Answer: (a) Because $\Delta n_g = 0$, so

$$\Delta_r H^\ominus = \Delta_r U^\ominus = -2808\text{kJmol}^{-1}$$

Therefore, at constant pressure, the energy available as heat is 2808 kJmol^{-1}.

(b) Because $T = 298$ K, the value of $\Delta_r A$

$$\Delta_r A^\ominus = \Delta_r U^\ominus - T\Delta_r S^\ominus = -2862\text{kJmol}^{-1}$$

Therefore, the combustion of 1.000 mol $C_6H_{12}O_6$ can be used to produce up to 2862 kJ of work.

4.6 The Helmholtz and Gibbs energies

3). Maximum non-expansion work at constant *T&p*

From the definition that $H = U + PV$

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + \mathrm{d}(pV)$$

For a reversible change

$$\mathrm{d}w = \mathrm{d}w_{\mathrm{rev}} \quad \text{and} \quad \mathrm{d}q = \mathrm{d}q_{rev} = T\mathrm{d}S$$

so $\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S$

$$= \cancel{T\mathrm{d}}S + \mathrm{d}w_{\mathrm{rev}} + \mathrm{d}(pV) - \cancel{T\mathrm{d}}S$$

$$= \mathrm{d}w_{\mathrm{rev}} + \mathrm{d}(pV)$$

⬇

$\mathrm{d}w_{\mathrm{rev}}$ consists of expansion work ($-p\mathrm{d}V$) and non-expansion work($\mathrm{d}w_{\mathrm{e}}$)

4.6 The Helmholtz and Gibbs energies

4). Maximum non-expansion work at constant *T*&*p*

$$\mathrm{d}G = \mathrm{d}w_{\mathrm{rev}} + \mathrm{d}(pV)$$

$$\mathrm{d}G = (-p\mathrm{d}V + \mathrm{d}w_{\mathrm{e,rev}}) + p\mathrm{d}V + V\mathrm{d}p$$

$$= \mathrm{d}w_{\mathrm{e,rev}} + V\mathrm{d}p$$

For the reversible change at constant *p* and *T*

$$\mathrm{d}G = \mathrm{d}w_{\mathrm{e,rev}}$$

At constant temperature and pressure the maximum non-expansion work is equal to the change in Gibbs energy.

Example - Calculating the maximum non-expansion work of a reaction

How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mol of glucose molecules under standard conditions at 37℃ (blood temperature)?

Given that The standard entropy of reaction is +182.4 JK^{-1} mol^{-1}and the $\Delta_r H^{\ominus}$ is −2808 kJmol^{-1}

Example - Calculating the maximum non-expansion work of a reaction

Method: The non-expansion work available from the reaction is equal to the change in standard Gibbs energy for the reaction.

$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

The standard reaction Gibbs energy is then:

$$\begin{aligned}\Delta_r G^{\ominus} &= -2808\ \mathrm{kJmol^{-1}} - (310\ \mathrm{K}) \times (18204\ \mathrm{JK^{-1}mol^{-1}}) \\ &= -2865\ \mathrm{kJmol^{-1}}\end{aligned}$$

Example - Calculating the maximum non-expansion work of a reaction

$w_{\mathrm{e,\,max}} = -2865\ \mathrm{kJ}$

for the combustion of 1 mol glucose molecules, and the reaction can be used to do up to 2865 kJ of non-expansion work.

A person of mass 70 kg would need to do 2.1 kJ of work to climb vertical through 3.0 m; therefore, at least 0.13 g of glucose is needed to complete the task.

4. The Second Law: the concepts

The direction of spontaneous change

Concentrating on the system

4.7 Standard molar Gibbs energies

☐ The standard Gibbs energies of reaction

The standard Gibbs energy of reaction can be based on the standard entropies and enthalpies of reaction:

$$\Delta_{\mathrm{r}} G^{\ominus} = \Delta_{\mathrm{r}} H^{\ominus} - T\Delta_{\mathrm{r}} S^{\ominus}$$

☐ The standard Gibbs energies of formation

The standard Gibbs energy of formation is the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states.

$$\Delta_{\mathrm{r}} G^{\ominus} = \sum_{\text{Products}} \nu \Delta_{\mathrm{f}} G^{\ominus} - \sum_{\text{Reactants}} \nu \Delta_{\mathrm{f}} G^{\ominus}$$

4.7 Standard molar Gibbs energies

$$\Delta_{\mathrm{r}} G^{\ominus} = \sum_{\text{Products}} \nu \Delta_{\mathrm{f}} G^{\ominus} - \sum_{\text{Reactants}} \nu \Delta_{\mathrm{f}} G^{\ominus}$$

Standard Gibbs energies o formation of the elements in their reference states are zero, because their formation is 'null' reaction.

Illustration: To calculate the standard Gibbs energy of the reaction $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$ at 25℃:

$$\Delta_{\mathrm{r}} G^{\ominus} = \Delta_{\mathrm{f}} G^{\ominus}(\mathrm{CO}_2, \mathrm{g}) - \left\{\Delta_{\mathrm{f}} G^{\ominus}(\mathrm{CO}, \mathrm{g}) + \tfrac{1}{2} \Delta_{\mathrm{f}} G^{\ominus}(\mathrm{O}_2, \mathrm{g})\right\}$$

$$= -3394.4 - \left\{-(137.2) + \tfrac{1}{2}(0)\right\} = -257.2\,\mathrm{kJ\,mol}^{-1}$$

Part 1: Equilibrium

1. The properties of gases
2. The First Law: the concepts
3. The First Law: the machinery
4. The Second Law: the concepts
5. The Second Law: the machinery
6. Physical transformations of pure substances
7. Simple mixtures
8. Phase diagrams
9. Chemical equilibrium
10. Electrochemistry

版权所有：华东理工大学物理化学教研室