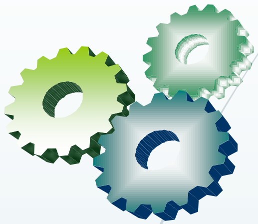
Physical Chemistry lecture



Part 2.4. The second law of thermodynamics

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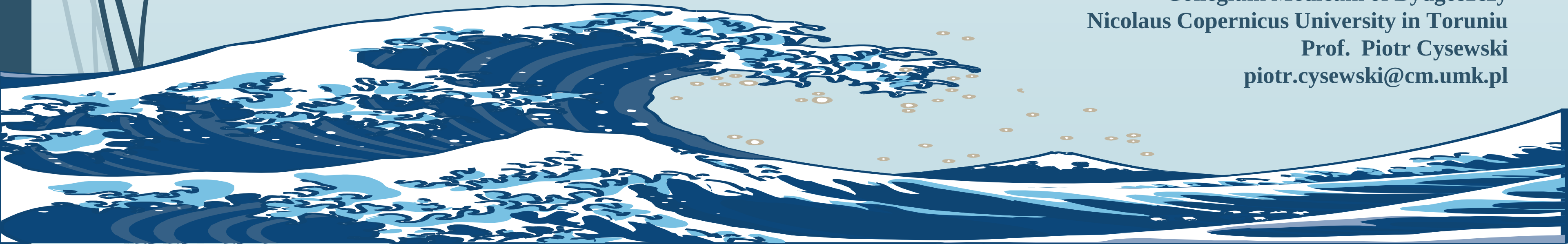
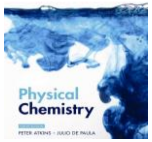




3 The Second Law

3.1 The dispersal of energy

Key point During a spontaneous change in an isolated system the total energy is dispersed into random thermal motion of the particles in the system.

3.2 Entropy

Key points The entropy acts as a signpost of spontaneous change. (a) Entropy change is defined in terms of heat transactions (the Clausius definition). (b) Absolute entropies are defined in terms of the number of ways of achieving a configuration (the Boltzmann formula). (c) The Carnot cycle is used to prove that entropy is a state function. (d) The efficiency of a heat engine is the basis of the definition of the thermodynamic temperature scale and one realization, the Kelvin scale. (e) The Clausius inequality is used to show that the entropy increases in a spontaneous change and therefore that the Clausius definition is consistent with the Second Law.

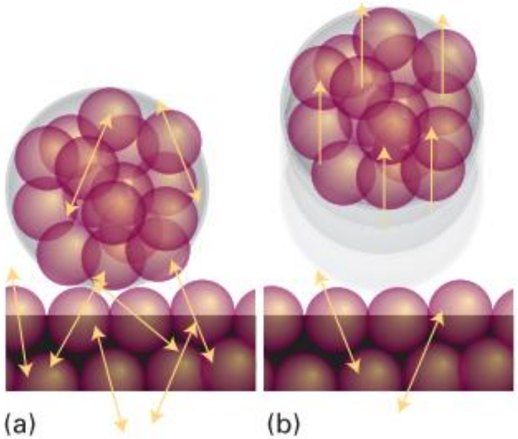


Fig. 3.3 The molecular interpretation of the irreversibility expressed by the Second Law. (a) A ball resting on a warm surface; the atoms are undergoing thermal motion (vibration, in this instance), as indicated by the arrows. (b) For the ball to fly upwards, some of the random vibrational motion would have to change into coordinated, directed motion. Such a conversion is highly improbable.

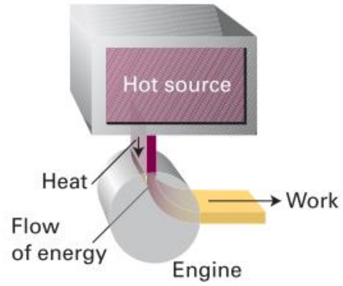


Fig. 3.1 The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change. The process is not in conflict with the First Law because energy is conserved.

Two distinct thermodynamic paths

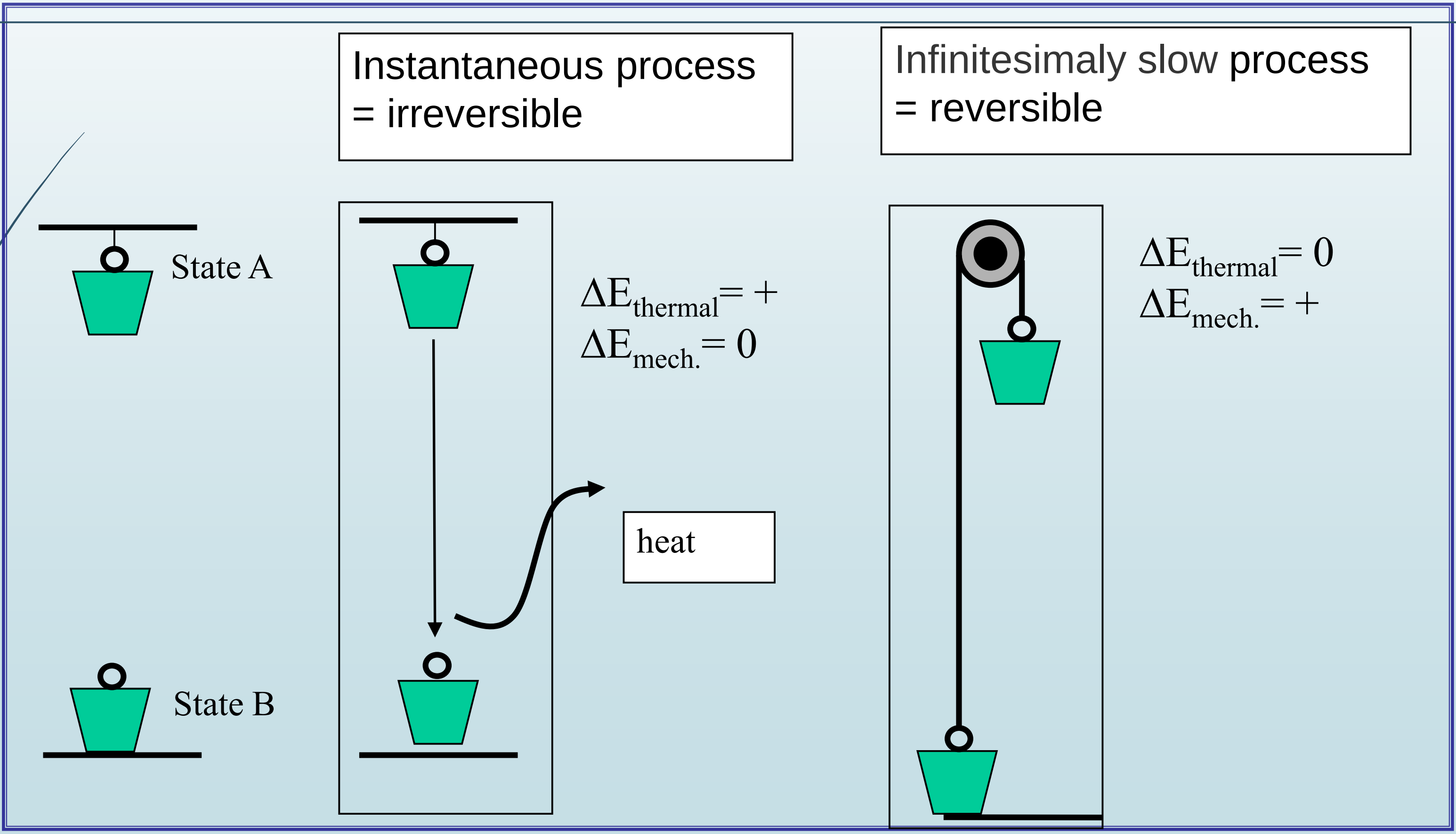
2.4. 3

Reaction Path” the way in which state parameters change over time

Reversible and irreversible thermodynamic changes

Reversible (quasistatic) – the state of the system is changed continuously by infinitesimal values along the process path. At any time, infinitesimal work can reverse the direction of the process.

Non-reversible (quasistatic) – the state of the system is changed continuously by infinitesimal values along the process path. At any time, infinitesimal work can reverse the direction of the process.



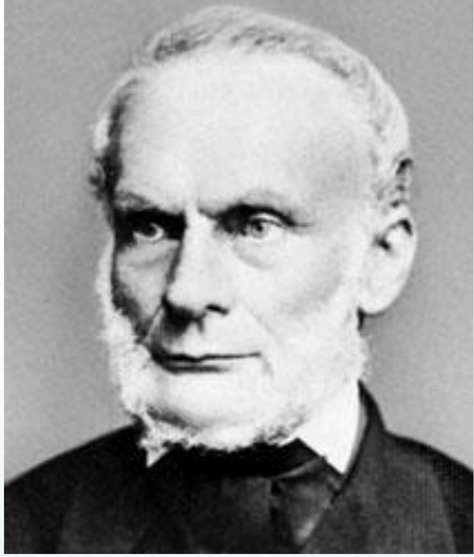
Instantaneous process
= irreversible

Infinitesimaly slow process
= reversible

$\Delta E_{thermal} = +$
$\Delta E_{mech.} = 0$

$\Delta E_{thermal} = 0$
$\Delta E_{mech.} = +$

Entropy



a concept introduced by Clausius (1852) which is an extensive thermodynamic function defining what part of the heat can be transformed into work

Each internally balanced phase is assigned an entropy value, S, - an extensive function of the phase state parameters

$$S_i = S_i\left(x_1, x_2, \ldots x_k\right)$$

the entropy is additive and for complex system is the sum of the entropies of the phases and all components

$$S = \sum_i S_i$$

Entropy

Reversible processes

$$dS = \frac{Q_{el}}{T}\left[J\cdot K^{-1}\right]$$

The total differential of the entropy of a system is equal to the ratio of the elementary amount of heat exchanged by the system as a result of an elementary reversible transformation to the temperature of the system

Irreversible processes

$$dS > \frac{Q_{el}}{T}$$

The change in the entropy of a system as a result of an elementary spontaneous process must satisfy the inequality

Entropy production

$$d_iS \overset{def}{=} dS - \frac{Q_{el}}{T} \geq 0$$

Clausius inequality

General criterion of spontaneity or equilibrium

$$\boxed{\begin{gathered} dS - \frac{Q_{el}}{T} \geq 0 \\ d_iS \geq 0 \end{gathered}}$$

CONCLUSIONS FROM THE SECOND LAW OF THERMODYNAMICS

1. The entropy of any system can change for two reasons: entropy transport from/to the surroundings: Q_{el}/T and entropy production within the system: d_iS.

$$dS = d_eS + d_iS$$

2. For reversible processes

entropy production is zero:

$$d_iS = 0 \qquad dS_{uklad} = -dS_{otoczenie}$$

the total entropy change of the system and its surroundings is zero

3. For irreversible processes

entropy production is positive:

$$d_iS > 0 \qquad dS_{system} + dS_{surr} > 0$$

the total entropy change of the system and the surrounding is positive

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4. In isolated or adiabatically isolated systems, spontaneous processes are only those that cause an increase in entropy production:

$$dS_{system} + dS_{surr} > 0$$

5. The entropy of a non-isolated system can decrease spontaneously:

$$dS_{uklad} < 0$$

provided, however, that:

$$dS_{otoczenie} >> 0$$

so as to:

$$dS_{uklad} + dS_{otoczenie} > 0$$

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6. In case of

$$dS > \frac{Q_{el}}{T}$$

this process is spontaneous. This is the basic criterion for the spontaneity of thermodynamic processes.

7. In case of

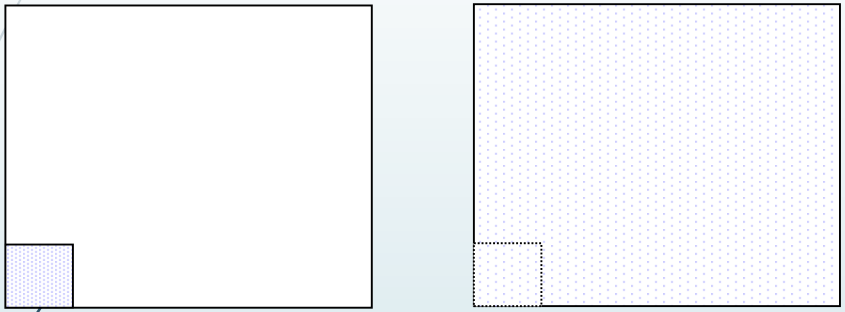
$$dS = \frac{Q_{el}}{T}$$

this process is non-spontaneous and does not occur.The opposite process also does not occur. This means that the system is in equilibrium with respect to the given process.

The physical meaning of entropy

Ludwig Boltzmann (1875)

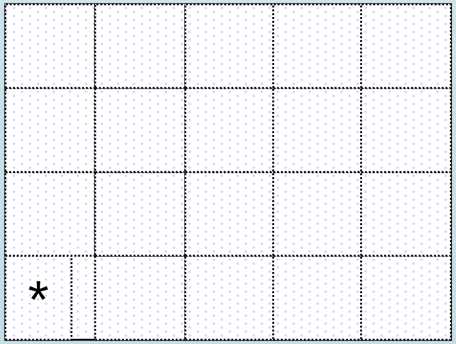
Why is the expansion of a gas spontaneous and the reverse process not?



Liczba możliwości rozmieszczenia N cząsteczek w M obszarach

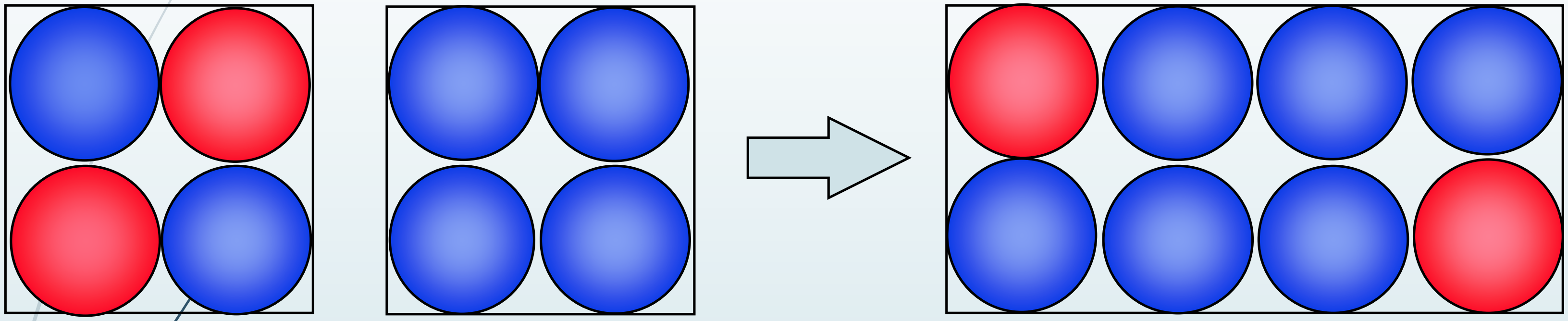
$$P \sim N^M/M!$$

$$S = k \cdot \ln(W) = (R/N_A) \cdot \ln(P)$$



Entropy is a measure of the degree of disorder in the probability of the directionality of thermodynamic processes.

Entropy at the micro level



Number of possible microstates

$N_{initial} = 6$

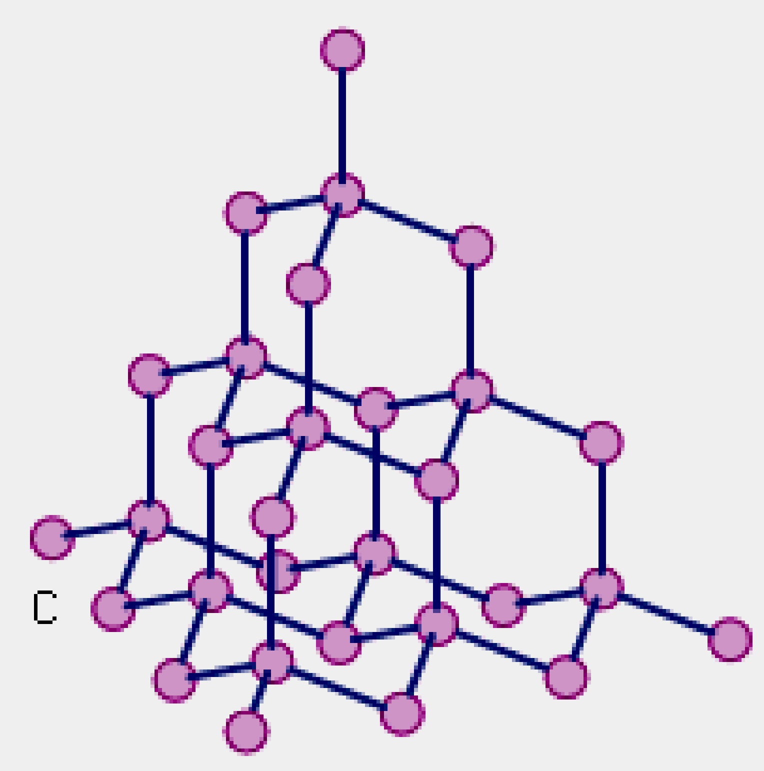
$N_{final} = 28$

$\Delta S>0$ is correlated with an increase in the probability of states

Feynman's definition of entropy

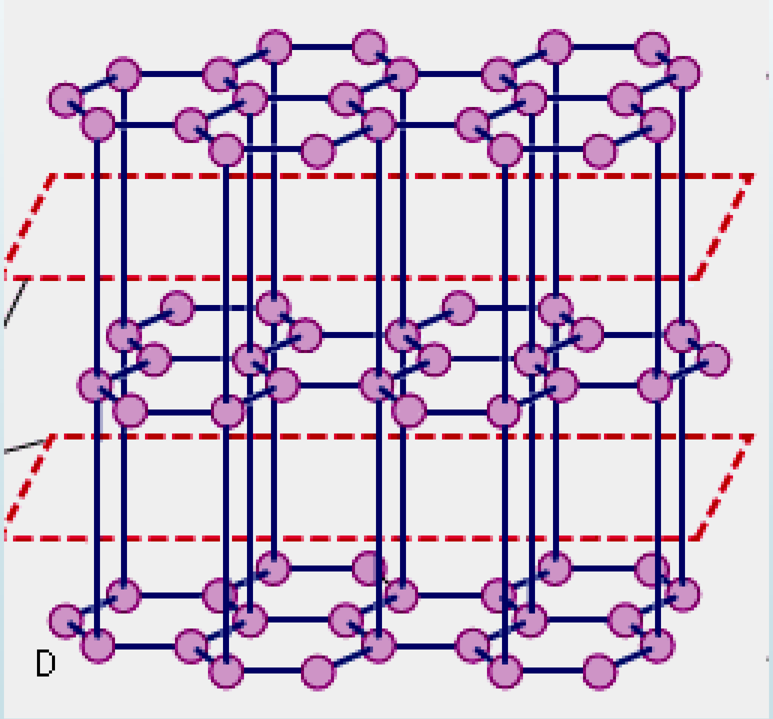
The number of ways to organize the interior of a system without changing its exterior is proportional to the entropy. Therefore, according to probability theory, the entropy of natural processes must increase.

diamond



S°298= 2.4 J/K

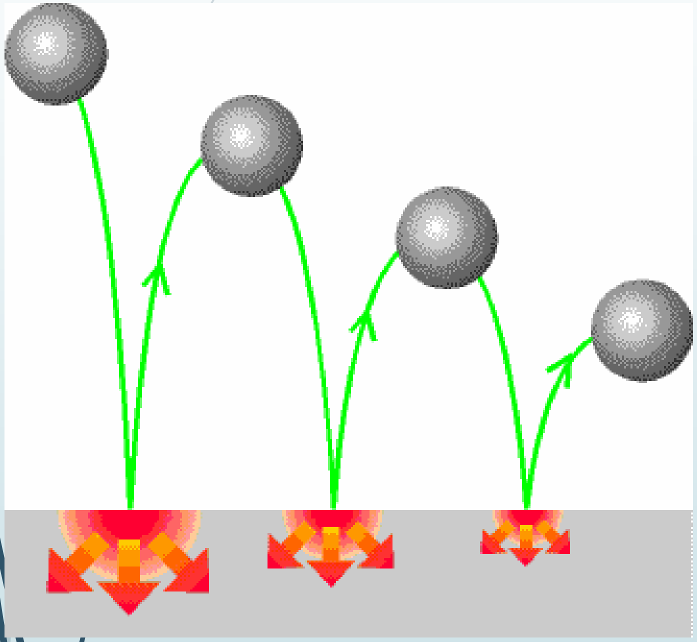
graphite



S°298= 5.7 J/K

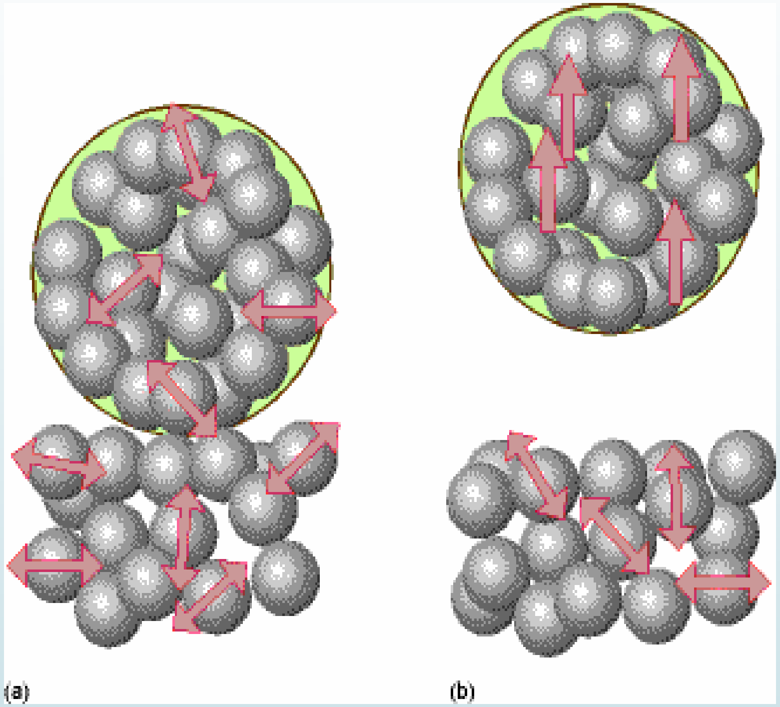
Entropy changes in physical processes

Energy dissipation from a bouncing ball



With each bounce, some of the energy is dissipated as heat from the substrate molecules and is dissipated. The reverse process is extremely unlikely

Molecular interpretation of a bouncing ball



a) **the ball molecules in contact with the surface are subject to thermal action (chaotic vibrations) in the directions shown by the arrows**
b) **for the ball moving upwards some components of the motion of the vibrating molecules must be directional. Such a conversion is highly improbable.**

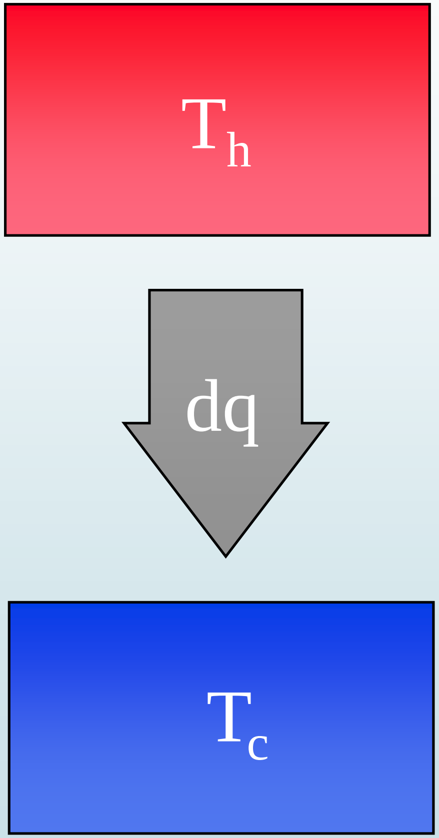
Spontaneous heat transfer

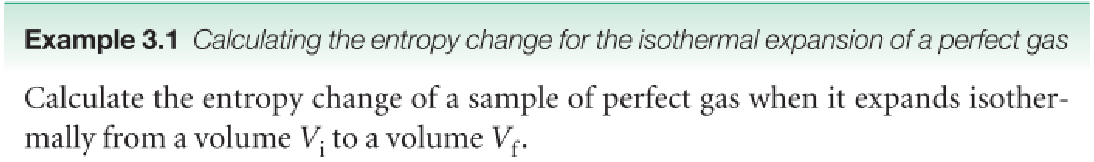
$$dS = dS_h + dS_c$$

$$dS = \frac{-dq}{T_h} + \frac{+dq}{T_c}$$

$$dS = dq\left(\frac{1}{T_c} - \frac{1}{T_h}\right)$$

$$dS > 0 \Rightarrow T_h > T_c$$





Example 3.1 *Calculating the entropy change for the isothermal expansion of a perfect gas*

Calculate the entropy change of a sample of perfect gas when it expands isothermally from a volume V_i to a volume V_f.

ΔS for the isothermal transformation of an ideal gas

$$dq = -dw = pdV$$

$$dS = \frac{pdV}{T} = nR\frac{dV}{V}$$

$$\Delta S = nR\ln\frac{V_f}{V_i}$$

ΔS phase change

- melting
  $T = T_m =$ constant
  - $q = \Delta H_m$
  - $\Delta S = \Delta H_m / T_m$
- boiling
  $T = T_b =$ constant
  - $q = \Delta H_b$
    $\Delta S = \Delta H_b / T_b$

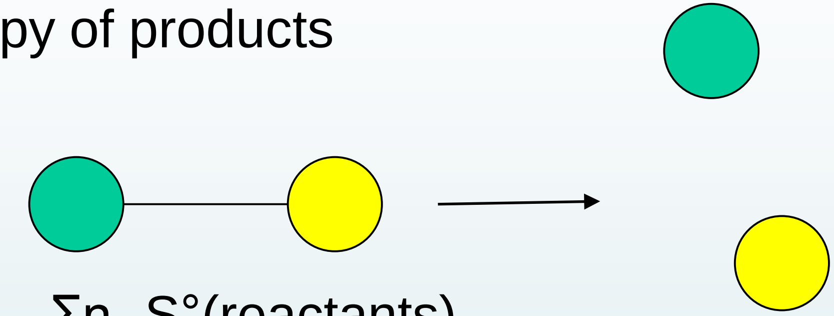
Examples of entropy change directions

increase in entropy	**decrease in entropy**
Evaporation **Melting** **Sublimation** **mixing of ingredients to form a solution**	**Condensation** **Crystallization** **resublimation**

Water example	S°298 [J/(K·mol)]
H_2O(s,ice)	44.3
H_2O(c)	69.91
H_2O(g)	188.72

Entropy change of chemical reactions

The entropy change can be calculated as the difference in entropy of products and reactants



$$\Delta S_r° = \Sigma n_p\ S°(\text{products}) - \Sigma n_s\ S°(\text{reactants})$$

n_p oraz n_s number of products and substrates

For example, for the ethane combustion reaction:

$$C_2H_{6(g)} + 7/2\ O_{2(g)} \rightarrow 2\ CO_{2(g)} + 3H_2O_{(c)}$$

$$\Delta S_r° = 2 \cdot S°_{CO2(g)} + 3 \cdot S°_{H2O(c)} - 7/2 \cdot S°_{O2(g)} - S°_{C2H6(g)}$$

Worth remembering:

Solids – high degree of ordering of atoms or molecules - low entropy. The most ordered form of matter is a perfectly crystalline body
Gases – lack of order high entropy.
Liquids – the entropy value is higher than the entropy value of solids but lower than the value corresponding to gases.

Entropy values are tabulated - see the physicochemical guide. The values in the tables are given for a temperature of 298.15 K and a pressure of 101.33 kPa (standard conditions). The unit of entropy is J / (K mol)

It is possible to determine absolute entropy values!
The molar entropy values of elements are NON-ZERO!
Example for $H_{2(g)}$
$\Delta H° = 0$ kJ/mol (by definition)
$S° = 130.58$ J/(K mol)

For a reaction taking place in the gaseous state (or involving gaseous reactants).

$$\Delta n_g > 0 \Rightarrow \Delta_r S° > 0 \text{ J/(K mol)}$$
$$\Delta n_g < 0 \Rightarrow \Delta_r S° < 0 \text{ J/(K mol)}$$
$$\Delta n_g = 0 \Rightarrow \Delta_r S° \approx 0 \text{ J/(K mol)}$$

Some Notes on Entropy

Is a mess in the traditional sense a measure of entropy? Do a tidy and an untidy room have different entropy values?

The order of macroscopic bodies is regulated by forces (wind, heat, earthquakes, people, etc.), not by the value of entropy. Disorder, or change of position, of macroscopic systems does not change the entropy of the system (e.g. an orderly or disorderly room). However, a change in entropy occurs for forces that cause the movement of macroscopic objects. Thus, the total change in entropy is positive.

Does a broken glass have more entropy than an unbroken glass?

Breaking or shattering a macroscopic object does not affect its global entropy resource.

Entropy of a glass = Entropy of a broken glass
Entropy of a standing villa = Entropy of villa destroyed by hurricane
Ford entropy in the parking lot = Ford Entropy in the Scrapyard

Some Notes on Entropy

Does grinding a crystal, e.g. NaCl, into powder change the entropy of the system?

During the grinding of a crystal, some bonds in the crystal lattice are of course broken. However, there is still a huge number of bonds that have not been broken. Grinding has only a minimal effect on increasing the entropy of the crystal.

Does dissolving a crystal, e.g. NaCl, in a solvent, e.g. water, change the entropy of the system?

During dissolution, all or almost all ionic bonds were broken. Solvation of ions changes the order, increases the volume available to ions – causing a significant increase in entropy.

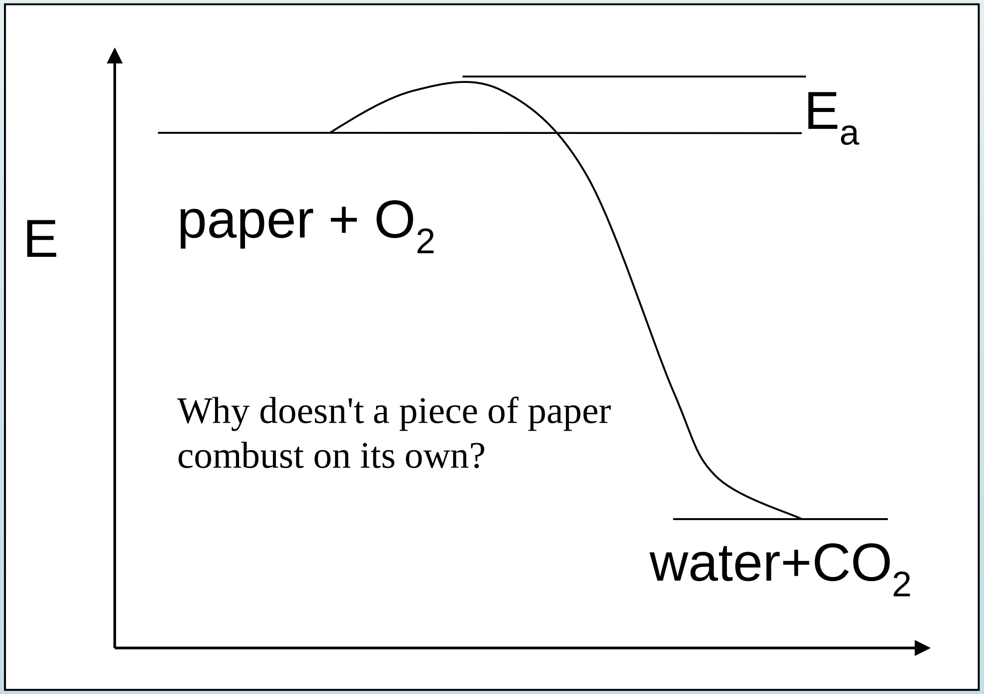
Some Notes on Entropy

Is the process of coal combustion spontaneous and accompanied by an increase in entropy?

Yes it's true

So why doesn't everything containing carbon spontaneously combust?

Because there is a barrier to free change of entropy



Why doesn't a piece of paper combust on its own?

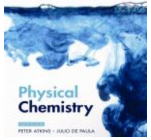
Kilka uwag dotyczących entropii

How are entropically unfavorable processes, e.g. natural, spontaneous protein biosynthesis, possible?

Non-spontaneous processes run in cycles along with spontaneous processes. The reduction in entropy in a non-spontaneous process is paid for by a much greater loss of entropy in a spontaneous reaction. Life is a clever series of reactions that use the entropy of other reactions to maintain its cycle of existence.

Can the Second Law of Thermodynamics be viewed in terms of benefits and limitations for humans?

Benefits: thanks to the 2nd law of thermodynamics, life is possible
We can eat the energy stored in food (using some of it and dissipating it to a large extent)
We can use the energy stored in fuels, using it in all areas of life, increasing its level, safety, quality, ...
We can create machines thanks to which we expand the horizons of action, seeing, being, living.



Calculating entropy changes

Calculate the change in the entropy of the expansion of an ideal gas from volume V_1 to V_2 at constant temperature if the process was carried out :

a/ quasi-statically b/ isobarically

Quasistatic transformation

$$dS = \frac{Q_{el}}{T} \qquad \Delta S = \int_1^2 \frac{Q_{el}}{T} = \frac{1}{T}\int dQ = \frac{Q}{T}$$

$$Q = -W = nRT \ln \frac{V_2}{V_1}$$

$$\boxed{\Delta S_{rev} = nR \cdot \ln \frac{V_2}{V_1}}$$

Calculating entropy changes

Calculate the change in the entropy of the expansion of an ideal gas from volume V_1 to V_2 at constant temperature if the process was carried out :

a/ quasi-statically b/ isobarically

Isobaric transformation

The formula for the first law of thermodynamics cannot be used, because the process is not reversible. However, entropy is a state function, so in this case:

$$\Delta S_{rev} = \Delta S_{irrev}$$

Heat must be calculated from the first law of thermodynamics:

$$Q = -W = p(V_2 - V_1)$$

If we were to substitute numerical values, it would turn out that for an irreversible process:

$$\Delta S > \frac{Q}{T}$$

Calculating entropy changes

Calculate the change in entropy of an ideal gas associated with heating from temperature T_1 to T_2 at constant pressure.

$$dS = \frac{Q_{el,P}}{T} \qquad Q_{el,P} = dH + PdV$$

$$dS = \frac{dH}{T} + \frac{PdV}{T}$$

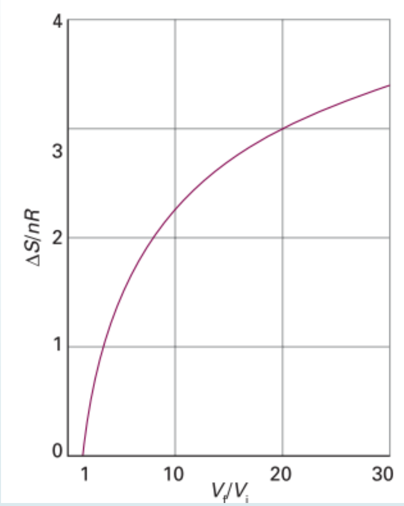
using the ideal gas equation:

$$\Delta S = S_k - S_p = \int_s^k \left(\frac{dH}{T} + \frac{PdV}{T} \right)$$

Calculating entropy changes

Calculate the change in entropy of an ideal gas associated with heating from temperature T_1 to T_2 at constant pressure.

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT + nR \ln \frac{V_2}{V_1}$$



The change in volume can be estimated from the equation of state.It is necessary to know:

$$C_p = C_p(T)$$

$$C_P = a + b \cdot T + c \cdot T^{-2}$$

Calculating entropy changes

Calculate the change in entropy of an ideal gas associated with heating from temperature T_1 to T_2 under constant volume:

$$dS = \frac{Q_{el,V}}{T}$$

$$Q_{el,V} = dU + VdP$$

$$dS = \frac{dU}{T} + \frac{VdP}{T}$$

using the ideal gas equation:

$$\Delta S = S_k - S_p = \int_s^k \left(\frac{dU}{T} + \frac{VdP}{T} \right)$$

$$\boxed{\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT - nR \ln \frac{p_2}{p_1}}$$

Knowledge is necessary about

$$C_V = C_V(T)$$

$$C_V = a + b \cdot T + c \cdot T^{-2}$$

Calculating entropy changes

Entropy of a phase change.

A phase change occurring in an isolated system is an example of a reversible process.

$$\Delta S_f = S^{\alpha} - S^{\beta} = \frac{Q_p}{T_f}$$

if the phase change process takes place under isochoric conditions then

$$\Delta S_f = \frac{\Delta H_f}{T_f} \qquad \Delta H_f = H^{\alpha} - H^{\beta}$$

phase change enthalpy

Calculating entropy changes

Entropy of phase change. Calculate the entropy change of heating water from liquid at temperature T1 to steam at temperature T2.

A cycle of transformations can be constructed

$$\begin{tikzcd}
H_2O_{(c)}[T_1] \arrow[r, "\Delta S_x"] \arrow[d, "\Delta S_1"] & H_2O_{(g)}[T_2] \\
H_2O_{(c)}[T_w] \arrow[r, "\Delta S_2"] & H_2O_{(g)}[T_w] \arrow[u, "\Delta S_3"']
\end{tikzcd}$$

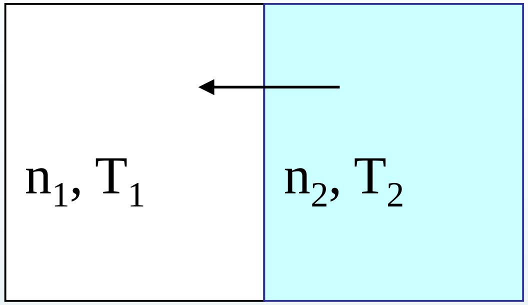
$$\boxed{\Delta S_x = \Delta S_1 + \Delta S_2 + \Delta S_3}$$

comparing the numerical values, it turns out that the greatest value has ΔS_2

Conclusion: the entropy of the phase change is dominant.

Calculating entropy changes

Calculate the entropy changes of an isolated system undergoing irreversible isochoric heat exchange between subsystems $T_2 > T_1$.



$$n_1 C_V (T_3 - T_1) + n_2 C_V (T_3 - T_2) = 0$$

$$T_3 = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}$$

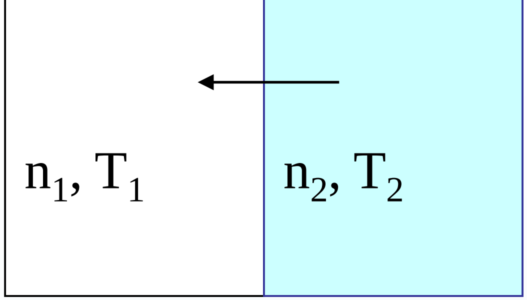
on the other hand, it has already been shown that:

$$dS = \frac{1}{T} dU + \frac{p}{T} dV$$

in isochoric conditions:

$$dU = C_V dT \qquad dS = \frac{nC_V}{T} dT$$

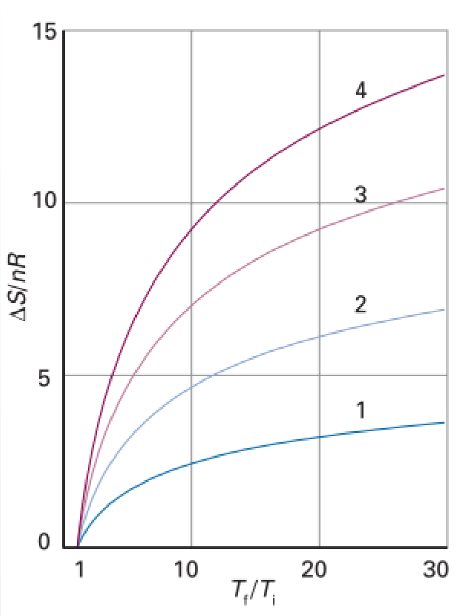
Calculating entropy changes



temperature dependence of entropy

$$\Delta S_1 = n\int_{T_1}^{T_3} \frac{C_V}{T} dT = nC_v \ln \frac{T_3}{T_1}$$

$$\Delta S_2 = n\int_{T_2}^{T_3} \frac{C_V}{T} dT = nC_v \ln \frac{T_3}{T_2}$$



The solution to the problem is the equation:

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

After substituting the numerical values, it would turn out that:

$$\Delta S_1 > 0$$

$$\Delta S_2 < 0$$

but still

$$\Delta S = \Delta S_1 + \Delta S_2 > 0$$

As a result of the temperature equalization, the entropy of one subsystem increased and the other decreased. The net value of the system's entropy, however, increased.

Entropy measurement

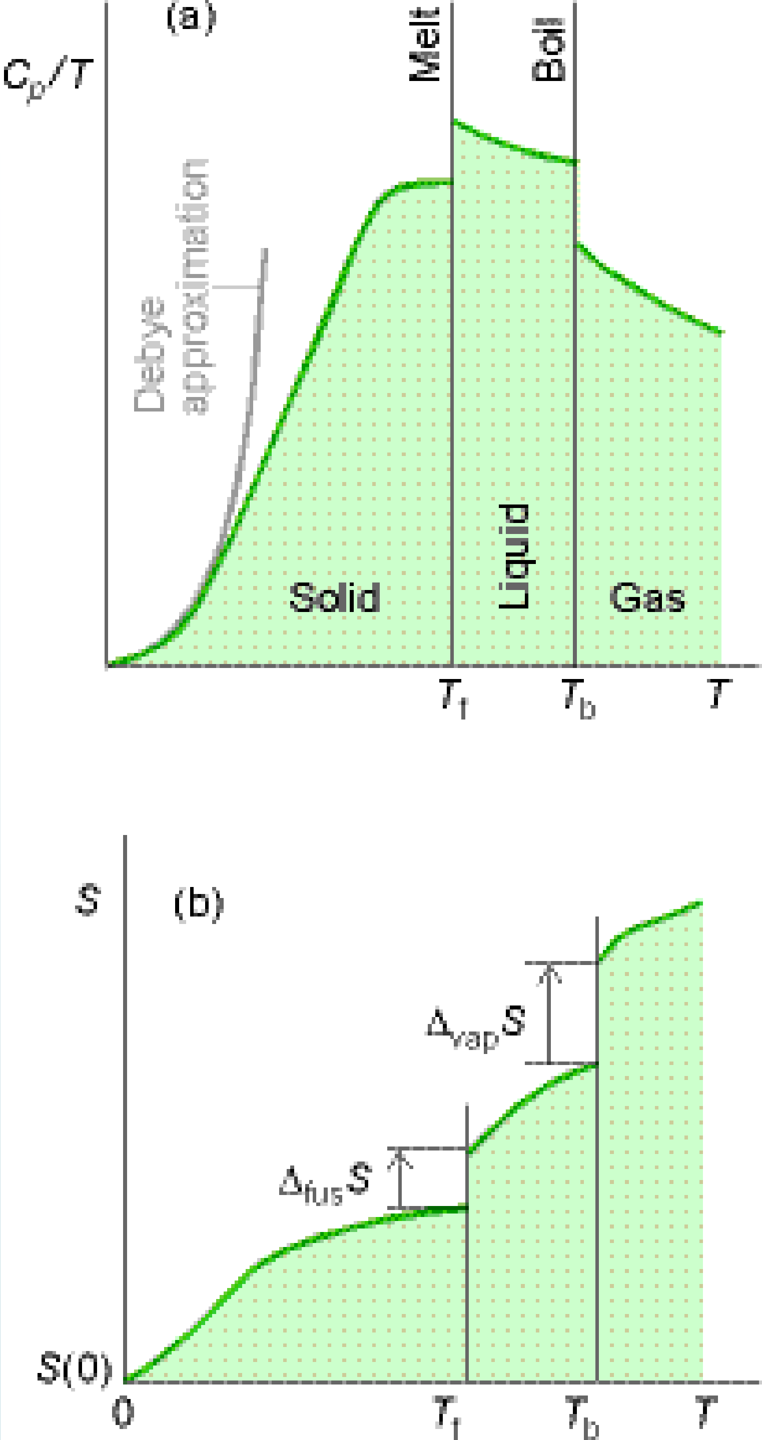
Entropy is determined experimentally based on heat capacity measurements.

$$S(T)=S(0)+\int_{0}^{T_t}\frac{C_p(s)}{T}dT+\frac{\Delta_{top}H}{T_k}+$$

$$+\int_{T_t}^{T_w}\frac{C_p(c)}{T}dT+\frac{\Delta_{par}H}{T_w}+$$

$$+\int_{T_w}^{T}\frac{C_p(g)}{T}dT$$

Debye extrapolation – bypassing the difficulties associated with very low temperature C_p measurements



Reasons for entropy changes:

What factors cause entropy change?

The simplest answer: any change in thermodynamic state:

T,V,P – physical processes
Δn – physical processes
– chemical changes
any structural change (internal degrees of freedom):
– physical: redistribution of thermal degrees of freedom
– chemical: bond redistribution, electronic degrees of freedom

Thermodynamic characteristics of a system– consequences (measures) of a change in the thermodynamic state:

$$\mathbf{Q, W, C_p \rightarrow \Delta U, \Delta H \rightarrow \Delta S}$$

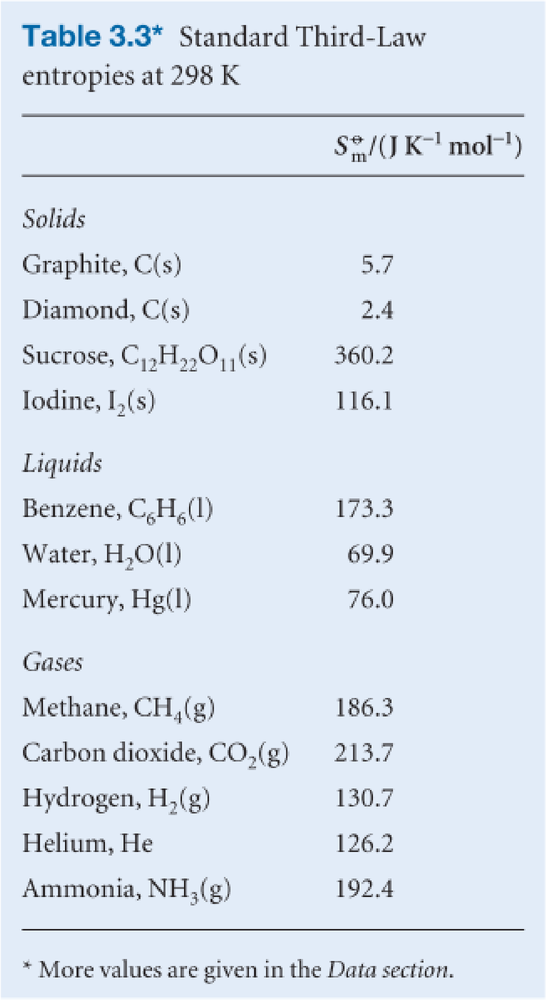


Table 3.3* Standard Third-Law entropies at 298 K

	$S_m^\ominus$/(J K^{-1} mol^{-1})
Solids	
Graphite, C(s)	5.7
Diamond, C(s)	2.4
Sucrose, $C_{12}H_{22}O_{11}$(s)	360.2
Iodine, I_2(s)	116.1
Liquids	
Benzene, C_6H_6(l)	173.3
Water, H_2O(l)	69.9
Mercury, Hg(l)	76.0
Gases	
Methane, CH_4(g)	186.3
Carbon dioxide, CO_2(g)	213.7
Hydrogen, H_2(g)	130.7
Helium, He	126.2
Ammonia, NH_3(g)	192.4

* More values are given in the *Data section*.

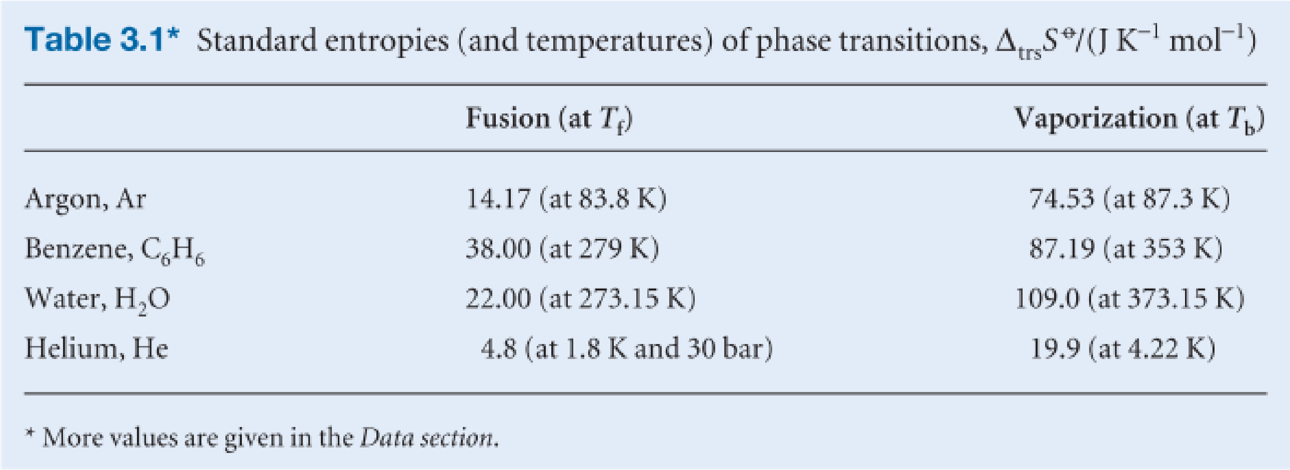


Table 3.1* Standard entropies (and temperatures) of phase transitions, $\Delta_{trs}S^\ominus$/(J K^{-1} mol^{-1})

	Fusion (at T_f)	**Vaporization (at T_b)**
Argon, Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Benzene, C_6H_6	38.00 (at 279 K)	87.19 (at 353 K)
Water, H_2O	22.00 (at 273.15 K)	109.0 (at 373.15 K)
Helium, He	4.8 (at 1.8 K and 30 bar)	19.9 (at 4.22 K)

* More values are given in the *Data section*.

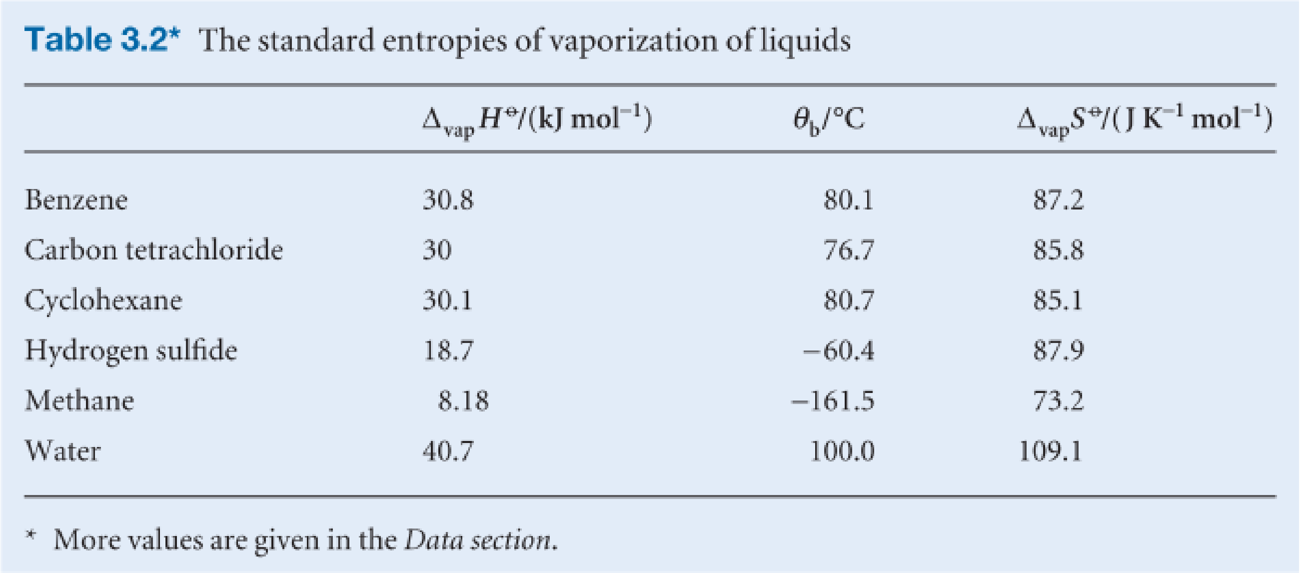
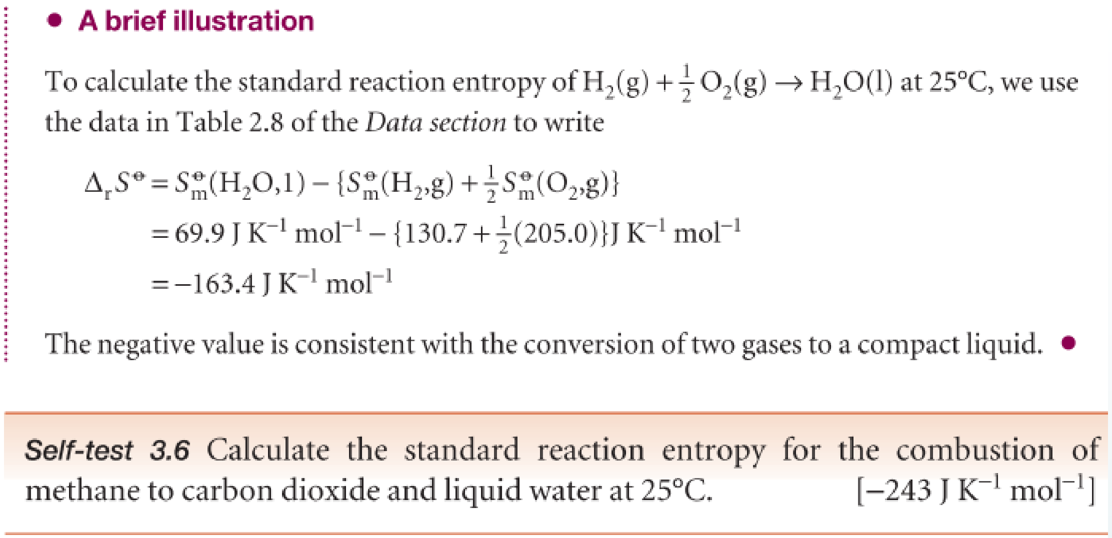


Table 3.2* The standard entropies of vaporization of liquids

	$\Delta_{vap}H^\ominus$/(kJ mol^{-1})	θ_b/°C	$\Delta_{vap}S^\ominus$/(J K^{-1} mol^{-1})
Benzene	30.8	80.1	87.2
Carbon tetrachloride	30	76.7	85.8
Cyclohexane	30.1	80.7	85.1
Hydrogen sulfide	18.7	−60.4	87.9
Methane	8.18	−161.5	73.2
Water	40.7	100.0	109.1

* More values are given in the *Data section*.

let's not forget about the excercises



A brief illustration

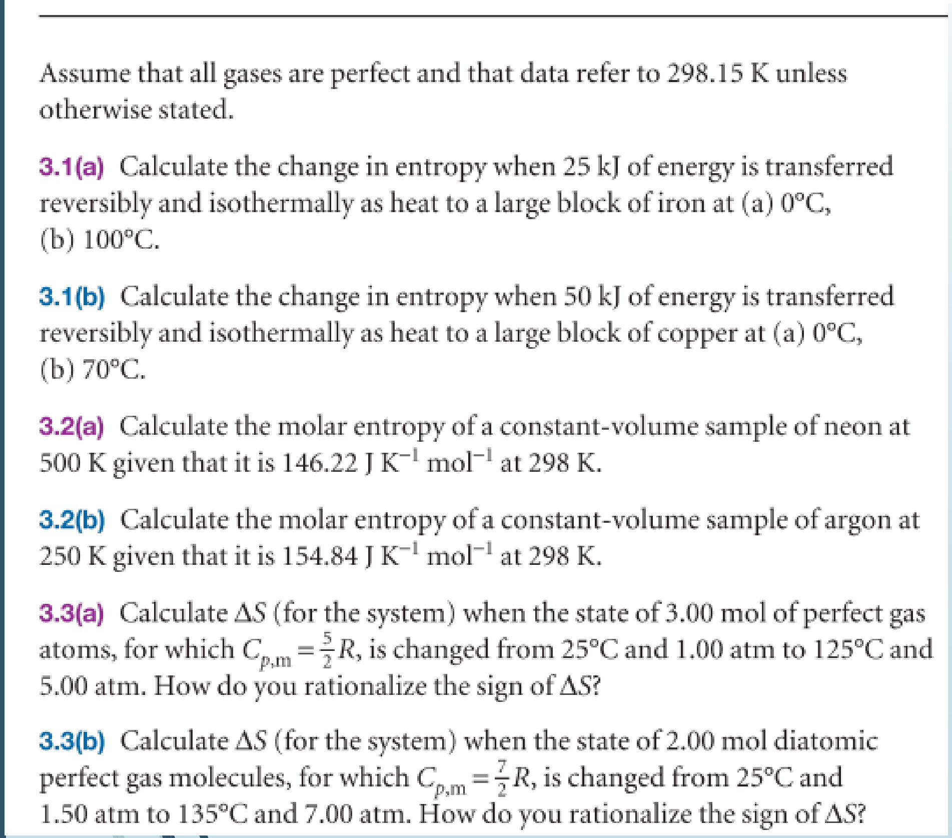
To calculate the standard reaction entropy of $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ at 25°C, we use the data in Table 2.8 of the *Data section* to write

$$\begin{aligned}\Delta_r S^\ominus &= S_m^\ominus(H_2O,l) - \{S_m^\ominus(H_2,g) + \tfrac{1}{2}S_m^\ominus(O_2,g)\}\\ &= 69.9\ \mathrm{J\,K^{-1}\,mol^{-1}} - \{130.7 + \tfrac{1}{2}(205.0)\}\ \mathrm{J\,K^{-1}\,mol^{-1}}\\ &= -163.4\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

The negative value is consistent with the conversion of two gases to a compact liquid. ●

Self-test 3.6 Calculate the standard reaction entropy for the combustion of methane to carbon dioxide and liquid water at 25°C. [$-243\ \mathrm{J\,K^{-1}\,mol^{-1}}$]

Exercises



Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

3.1(a) Calculate the change in entropy when 25 kJ of energy is transferred reversibly and isothermally as heat to a large block of iron at (a) 0°C, (b) 100°C.

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

3.2(a) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is 146.22 $\mathrm{J\,K^{-1}\,mol^{-1}}$ at 298 K.

3.2(b) Calculate the molar entropy of a constant-volume sample of argon at 250 K given that it is 154.84 $\mathrm{J\,K^{-1}\,mol^{-1}}$ at 298 K.

3.3(a) Calculate ΔS (for the system) when the state of 3.00 mol of perfect gas atoms, for which $C_{p,m} = \frac{5}{2}R$, is changed from 25°C and 1.00 atm to 125°C and 5.00 atm. How do you rationalize the sign of ΔS?

3.3(b) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = \frac{7}{2}R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of ΔS?

... and more