

THERMODYNAMICS



Lecturer: A/Prof Steve Colbran

$$dU = T dS - \sum_i X_i dx_i + \sum_j \mu_j dN_j$$

$$dH = TdS + Vdp + \sum_i \mu_i dN_i$$

$$dG = Vdp - SdT + \sum_{i=1}^k \mu_i dN_i - \sum_{i=1}^n X_i da_i + \dots$$

$$\mu_i = \left(\frac{\partial U}{\partial N_i} \right)_{S,V,N_j \neq i} \quad \oint \frac{\delta Q}{T} = 0 \quad dS = \frac{\delta Q}{T}$$

* a simplified version developed from lecture slides prepared by Dr Ron Haines
(all the good stuff is his, all of the errors & bad jokes are entirely mine!)

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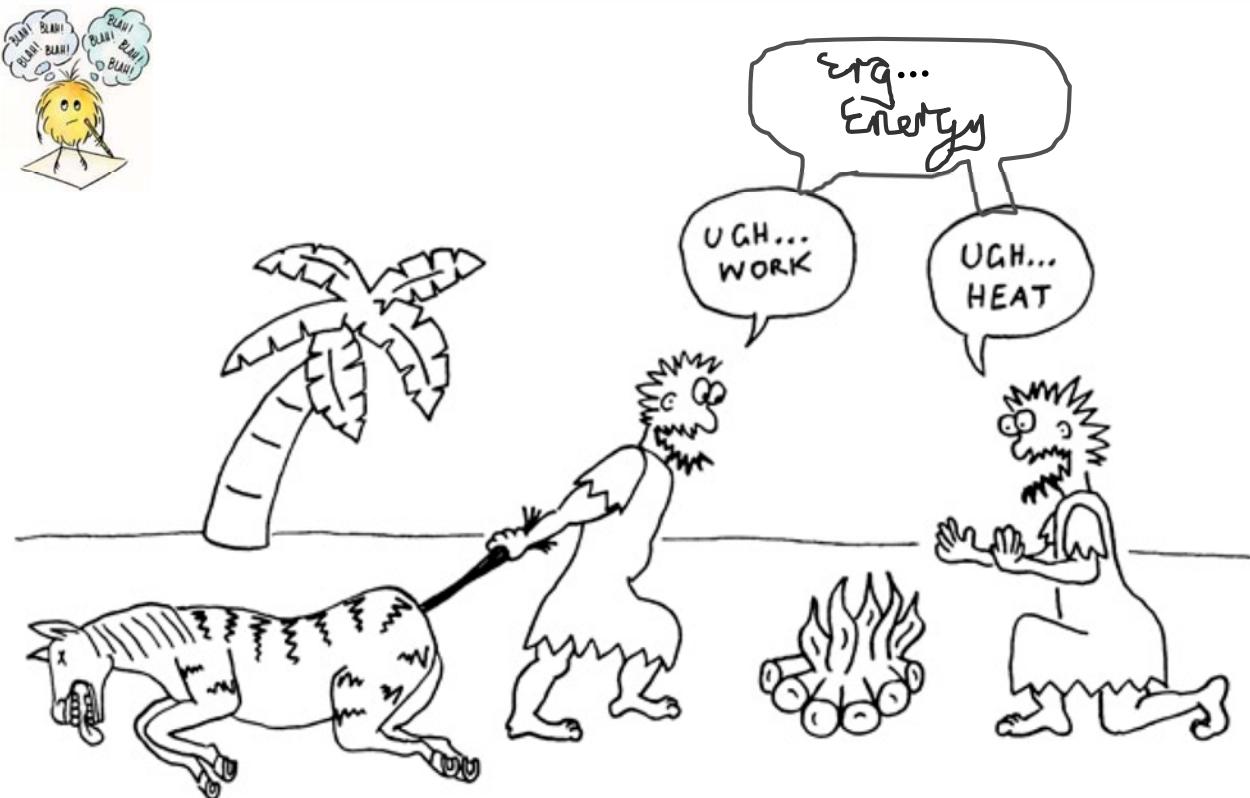
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an early history of thermodynamics



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THERMODYNAMICS

Thermodynamics is the study of
transformations of heat to and from other forms of energy



Thermodynamics is applied in:

- chemistry and the chemical industry
- geology and geophysics
- material science
- engineering
- biochemistry and biology
- physics

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Energy

Doing work: Hmm...
a difficult concept



Energy is the capacity to do work (*w*)

- Kinetic energy (motion)
- Potential energy (position)
- Chemical energy (rearrangement of bonds)
- Radiant energy (photons)
- Thermal (random motion of atoms)

Measured in Joules (1 J = 1 N m = 1 kg m² s⁻²; 1 kJ = 10³ J)

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Heat

[Blackman 8.2]

Heat is (thermal) energy transfer
due to a **temperature difference**



\$^§∞£ Ouch!!...
just kidding,
its not so hot

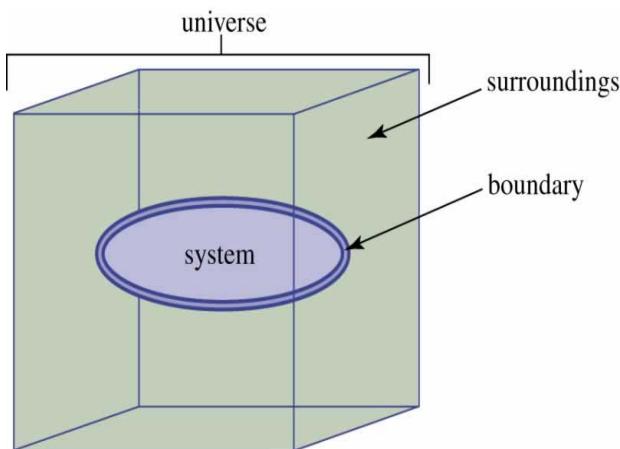
why not ?
we'll see later

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more terminology... The System

In thermodynamics:

the **system** is what is under study;
everything else is called the **surroundings**



system = inside
the testtube

surroundings =
outside the
testtube

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Types of system

Isolated system:

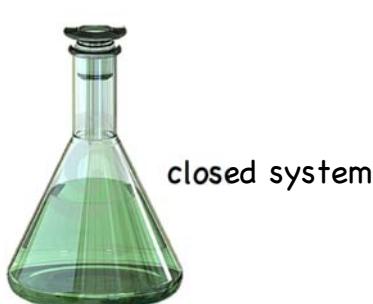
can't exchange matter or energy with the surroundings

Closed system:

can exchange energy but not matter with the surroundings

Open system:

can exchange matter and energy with the surroundings



closed system



open system

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Extensive and Intensive Properties

For a thermodynamic system:

Extensive properties – depend on how much matter makes up the system, e.g. volume, mass, total energy.

Intensive properties – are independent of the amount of matter in the system e.g. density, temperature.

Intensive properties are often calculated by dividing an extensive property by the amount of matter in the system,

$$\text{e.g. density} = \text{mass/volume} \text{ or } \rho = m/V$$

In chemistry,

the amount of a substance in a system is often expressed in moles, and energy changes in chemical reactions are usually expressed as Joules per mole (J/mol or J mol^{-1}) or kiloJoules per mole (kJ/mol or kJ mol^{-1}).

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some more on... Heat

For any thermodynamic system,
the direction of **heat** flow depends on the temperature of the system and its surroundings.

Heat (q) always flows spontaneously from higher to lower temperature

exothermic processes: $q < 0$; heat flows out of the system

endothermic processes: $q > 0$; heat flows in to the system

thermal equilibrium: $q = 0$; no net heat flow between the system and its surroundings

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Heat Capacity

The heat associated with simply heating or cooling a system depends on:

- the amount of substance that is heated or cooled,
- the temperature change (ΔT), and
- the **heat capacity (C)*** of the substance(s) that make up the system



* heat capacity is an intrinsic property of a substance and depends on whether the process occurs at *constant pressure* or *constant volume*

in the lab, you do everything under constant .pressure.



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Heat Capacity... 2. C_p & C_v

Heat for process at constant pressure...

$$q_p = n \times C_p \times \Delta T \quad \text{where } C_p = \text{heat capacity at constant } P$$

Heat for process at constant volume...

$$q_v = n \times C_v \times \Delta T \quad \text{where } C_v = \text{heat capacity at constant } V$$

- the most common units for heat capacity are $J K^{-1} mol^{-1}$ or $J K^{-1} g^{-1}$...
if C_p or C_v is expressed with units $J K^{-1} mol^{-1}$ then n must be in mol;
if C_p or C_v is expressed with units $J K^{-1} g^{-1}$ then n must be in g.
- $C_p \approx C_v$ for solids and liquids, but they differ for gases.

*in the lab, most processes happen at constant pressure and so the heat you measure is called q_p .

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Heat Capacity

EXAMPLE QUESTION

Q: Calculate the heat required to raise 100 g of iron (atomic mass = 55.85 g mol⁻¹) from 25°C to its melting point (1535 °C) at constant pressure using $C_p = 0.45 \text{ J K}^{-1} \text{ g}^{-1}$ (SI Chem. Data, table 4) and $C_p = 25 \text{ J K}^{-1} \text{ mol}^{-1}$ (SICD, table 5).

A: Using the first heat capacity:

$$q_p = n C_p \Delta T =$$

=

Note: ΔT is the same in °C and in K.

Using the second heat capacity, first convert 100 g of Fe to moles:

$$n = m/M =$$

$$q_p = n C_p \Delta T =$$

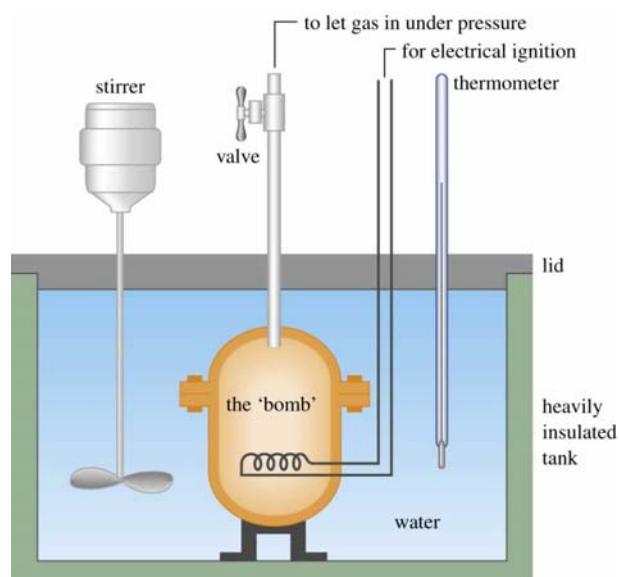
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KJ.

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Calorimetry

Calorimetry is a technique for measuring energy changes in chemical reactions by carrying out the reaction in a thermally insulated vessel and measuring the consequent temperature change of the system including the enclosing vessel.



A '**bomb**' calorimeter keeps all the reactants and products in a constant volume (thermally insulated) container during the reaction.

Bomb calorimetry is used to measure the heat released in many types of combustion processes; e.g. burning coal or coke, or foodstuff such as flour and breakfast cereal.

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Bomb Calorimetry

If we consider a bomb calorimeter and its contents to be the system and heat does not flow in or out of the system then:

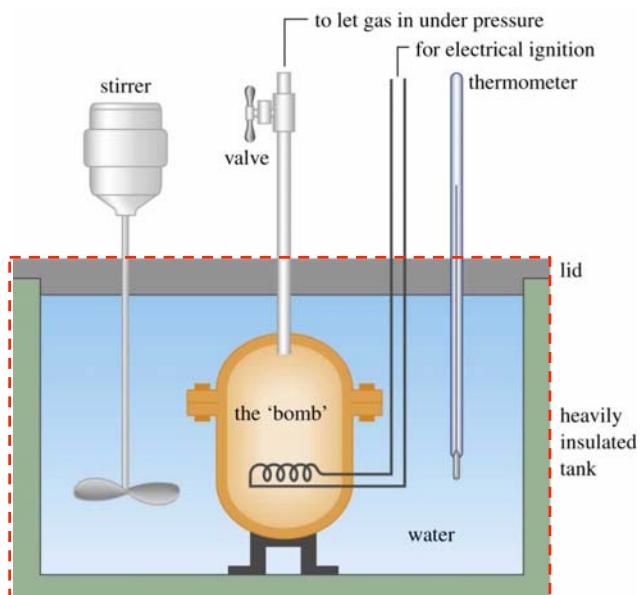
$$q_{\text{sys}} = 0 \\ = q_{\text{reaction}} + (q_{\text{calorimeter}} + q_{\text{contents}}).$$

Hence

$$q_{\text{reaction}} = - (q_{\text{calorimeter}} + q_{\text{contents}}) \\ = - (C_{\text{calorimeter}} \\ + n_{\text{contents}} C_{\text{contents}}) \Delta T.$$

Heat released: $q_r < 0$

Heat absorbed: $q_r > 0$



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Bomb Calorimetry

EXAMPLE QUESTION

Q: 1.435g of naphthalene ($C_{10}H_8$) was burned in a bomb calorimeter to produce $CO_2(g)$ and $H_2O(l)$. The bomb had a heat capacity of $1.800 \times 10^3 \text{ J K}^{-1}$ and was immersed in 2000 g of water ($C = 4.184 \text{ J K}^{-1} \text{ g}^{-1}$). The temperature of the water and calorimeter rose 5.670 K. Calculate the heat released per mole of naphthalene burned.

A:
$$q = -(C_{\text{cal}} \Delta T + mC_{\text{water}} \Delta T) \\ = -(1.800 \times 10^3 \text{ JK}^{-1} \times 5.670 \text{ K} + 2000 \text{ g} \times 4.184 \text{ JK}^{-1} \text{ g}^{-1} \times 5.670 \text{ K}) \\ = \text{J}$$

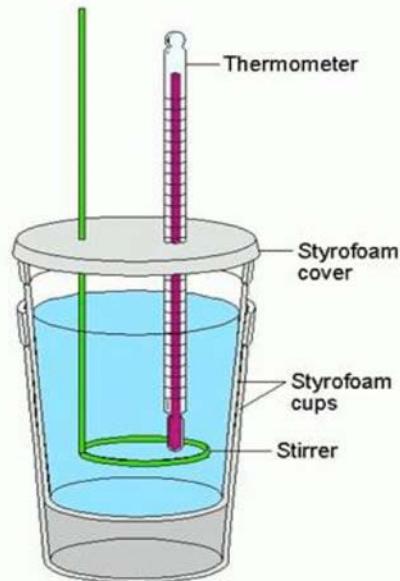
Heat per mole:

Amount of naphthalene burnt = $n/M = \text{mol}$

$$q = -5.151 \times 10^6 \text{ J mol}^{-1}$$
$$= -5151 \text{ kJ mol}^{-1}$$

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A cheaper calorimeter



Provided no gases are involved, the reaction is 'insulated' in the cups (an isolated system) & occurs at constant pressure...

$$\text{So: } q_{\text{system}} = 0 = q_r + q_{\text{solution}}$$

And, if contents the are dilute, then the solution's heat capacity & density approximate those of pure water...

$$\begin{aligned} \text{So: } q_{\text{reaction}} &= -q_{\text{solution}} \\ &= -(m_{\text{soln}} \times C_{\text{soln}} \times \Delta T) \end{aligned}$$

Firewalking & burnt feet

Need to consider

- heat capacity

$$C(\text{amorphous}) < 0.7 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\text{water (@ 25 }^{\circ}\text{C)} = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$$



- thermal conductivity (how fast heat is transferred by a substance)

$$C(\text{amorphous}) \sim 0.04 - 0.18 \text{ W m}^{-1} \text{ K}^{-1}$$

$$\text{water} \sim 0.56 - 0.60 \text{ W m}^{-1} \text{ K}^{-1}$$

- vascularisation of human feet



Work

Work (**w**) is done when an object is moved (by Δx) against an opposing force (**F**).

$$w = F \times \Delta x$$

Opposing forces could include:

- gas pressure on a piston (pV work),
- electrostatic force on a charged object,
- gravitational force on a mass,
- spring tension acting on a mass,
- the surface tension of a liquid.



"We're frequent rowers.
Any chance of an upgrade?"

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pV work

Consider a massless and frictionless piston. The gas (the system) expands the piston moves through a distance d against a constant pressure p_{ext} .

Force on the piston is

$$F = p_{\text{ext}} \times A$$

The gas does work (by expanding against p).

$$w = F \times d = p_{\text{ext}} \times A \times d$$

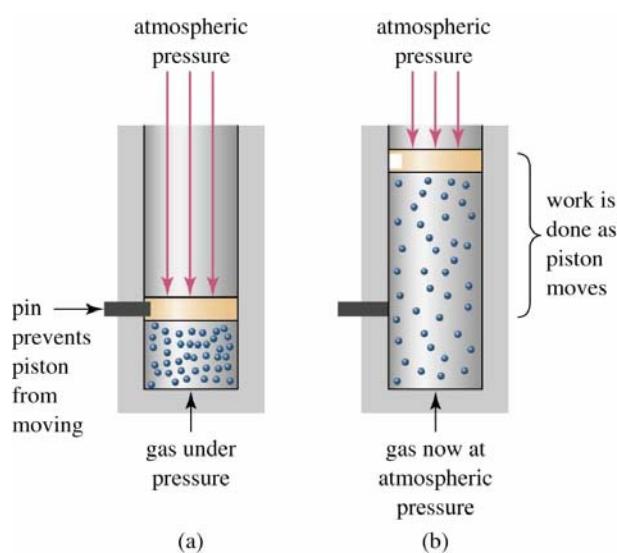
$$= p_{\text{ext}} \times \Delta V$$

where $\Delta V = V_{\text{final}} - V_{\text{initial}}$

and $\Delta V > 0$ if the system expands

In this case, work is formally defined as:

$$w = -p_{\text{ext}} \Delta V$$



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First Law of Thermodynamics

The energy of an isolated system is a constant

Energy can neither be created nor destroyed

There is no free lunch...



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Internal Energy

[Blackman 8.3]

internal energy (U) of a system ...

is the energy associated with all chemical species*
in the system including their kinetic, thermal and
chemical energies

U will usually depend on the temperature, pressure and composition of a system and will change if we change the temperature of a system or if a chemical reaction occurs in the system.

Internal energy changes are symbolised by ΔU ,

where $\Delta U = U_{\text{final}} - U_{\text{initial}}$

and *initial* and *final* refer to the system before and after a specified process has occurred.

*atoms, ions, molecules, electrons

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State Functions

State functions depend on the **state** of a system, not its history.

So state functions are independent of the path taken for the system to reach a specific 'state'



the height of the summit of Dhauligiri above sea level is a state function;
the route taken or the distance travelled to the top are not (they are path functions)

Internal energy (U) is a **state function**.

Heat and work are not state functions, but path functions

- they depend on the route followed from initial to final state

First Law of Thermodynamics

The internal energy (U) of a system can be changed by:

transferring heat (q) in or out of the system, and/or

by the system doing work (w) or having work (w) done on it.

The First Law of Thermodynamics:

$$\Delta U = q + w$$

When the system exchanges heat, particles in the surroundings change motions in a random way

When the system does work, particles in the surroundings change kinetic energy in an organised way.

Enthalpy

Enthalpy is defined as:

$$H = U + pV$$

Interesting – pV
must have the
units of energy ?



So, for a change

$$\Delta H = \Delta U + \Delta(pV)$$

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

For a reaction:
final = products
initial = reactants



Enthalpy... an alternative view

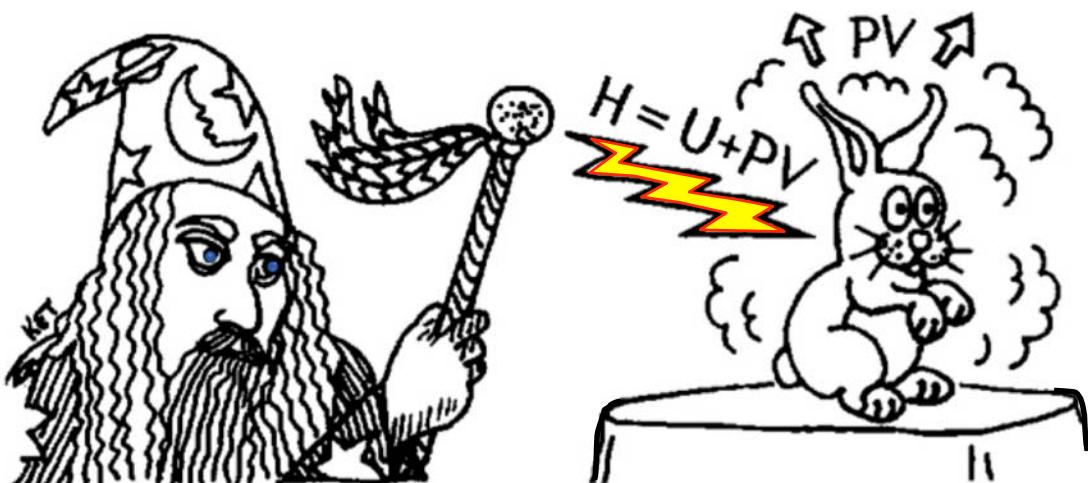


Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV , to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$.

Enthalpy and Thermochemistry

For any process (e.g. a reaction)

$$\Delta H = \Delta U + \Delta(pV)$$

Ah ha! – the **enthalpy of reaction** is just the **heat of reaction** (in the lab, $p = 1 \text{ atm}$)
SO VERY USEFUL

If the pressure of the system remains constant (e.g. the experiment is done at 1.0 bar)



$$\begin{aligned} \text{then } \Delta H &= \Delta U + p\Delta V = q_p + w_p + p\Delta V \\ &= q_p \quad (\text{since } w_p = -p\Delta V \text{ at const. } p) \end{aligned}$$

$$\Delta H = q_p$$

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Enthalpy and Thermochemistry

The enthalpy change of a reaction is the heat change at constant pressure (q_p) (ie. under everyday lab conditions)



$$\Delta H = q_p$$

ΔH is easy to measure because q_p is easy to measure (by calorimetry).

For reactions where all the reactants and products are solids and/or liquids, $p\Delta V \ll \Delta U$ and so $\Delta H \approx \Delta U$.

If gases are produced or consumed, $p\Delta V$ can be calculated from the change in the number of moles of gas in the process, assuming the gases behave ideally ($pV = nRT$); in this case:

$$p\Delta V = \Delta n_{\text{gas}} RT$$

where $\Delta n_{\text{gas}} = n_{\text{gas}}(\text{products}) - n_{\text{gas}}(\text{reactants})$.

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Enthalpy

EXAMPLE QUESTION

Q: For the reaction:



Calculate ΔU .

A: $\Delta H = \Delta U + \Delta n_{\text{gas}} RT$, and $\Delta n_{\text{gas}} = 1 - 0 = +1$

$$\text{so } \Delta U = \Delta H - \Delta n_{\text{gas}} RT$$

$$= 178,000 \text{ J mol}^{-1} - 1 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

$$= \text{J mol}^{-1}$$

$$= \text{J mol}^{-1} = \text{kJ mol}^{-1}$$

Standard States

The values of thermodynamic state functions such as ΔU and ΔH for any process depend on the temperature, pressure and composition of the system involved in the process.

To tabulate values, a set of standard reference conditions is needed:

Standard conditions (or **standard state**) are defined as:

pressure = 1.0 bar (= $1.0 \times 10^5 \text{ Pa} \approx 1 \text{ atm}$)

compounds = pure (unmixed) substances at 1.0 bar and specified T

solutes = a concentration of 1.0 mol L⁻¹ for all species in solution

The **temperature** is not part of the specification of standard conditions and must be specified separately.

The enthalpy change for a process where all substances (reactants and products) are at standard conditions is denoted ΔH° or ΔH^\ominus (similarly for ΔU° or ΔU^\ominus etc.).

Standard Enthalpy Changes

Tables almost of ΔH° for generic physical or chemical processes always list **standard molar enthalpy changes** (the word *molar* is often dropped).

The particular process is indicated by a subscript after the Δ , e.g. $\Delta_{\text{vap}}H$ (in older books or on the web you might see ΔH_{vap}).

Phase transitions:

- solid \rightarrow liquid ΔH° = standard enthalpy of **fusion** or **melting** = $\Delta_{\text{fus}}H^\circ$
liquid \rightarrow gas ΔH° = standard enthalpy of **vaporisation** = $\Delta_{\text{vap}}H^\circ$
solid \rightarrow gas ΔH° = standard enthalpy of **sublimation** = $\Delta_{\text{sub}}H^\circ$

Because enthalpy is a state function: $\Delta_{\text{sub}}H^\circ = \Delta_{\text{fus}}H^\circ + \Delta_{\text{vap}}H^\circ$

A small part of a typical ‘*short*’ compendium ...

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TABLE 6. Enthalpies of vaporization of organic compounds, 1880–2002—Continued

Molecular formula	Compound (Temperature range/K)	$\Delta_{\text{vap}}H_m$ (kJ mol ⁻¹)	Mean temperature (T_m /K)	Method	CAS registry number Reference
CF ₄ O ₄ S	trifluoromethylperoxyfluorosulfonate (233–286)	27.7	(259)		[60/15]
CF ₄ O ₅ S ₂	fluorosulfonic acid trifluoromethane sulfonic acid anhydride (308–338)	32.9	(323)	A	[21595-44-8] [87/5][99/16]
CF ₄ O ₆ S ₂	trifluoromethyl fluorodisulfate (292–351)	34.4	(321)		[60/15]
CF ₅ NO	pentafluoromethoxyamine (167–210)	18.5	(195)	A	[4217-93-0] [87/5][65/19]
CF ₅ OPS	phosphorothionic difluoride, S-trifluoromethyl ester (293–353)	23.1	(323)		[52752-66-6] [99/16]
CF ₅ OPS	trifluoromethylthiophosphoryl difluoride	23.0			[74/38]
CF ₅ O ₃ P	trifluoromethoxyphosphoryl difluoride (225–264)	27.4	(245)		[73/37]
CF ₅ O ₃ P	difluoroperoxyphosphoric acid trifluoromethyl ester (241–280)	32.0	(265)	A	[39125-42-3] [87/5][73/37]
CF ₅ PS	trifluoromethyl thioldifluorophosphine	24.3			
CF ₆ N ₂ O ₂ S ₂	N,N'-(difluoromethylene)bisimidosulfuryl fluoride (283–308)	36.0	(295)		[20094-83-1] [68/21]
CF ₆ N ₂ S ₂	difluoromethane bis(S,S-difluorosulfilimine) (230–313)	36.0	(245)	A	[17686-45-2] [87/5][99/16]
CF ₆ PS	difluoro(trifluoromethylthio)phosphine (293–353)	22.3	(323)		[52752-65-5] [99/16]
CF ₈ OS	pentafluoro(trifluoromethoxy) sulfur (217–262)	24.4	(247)	A	[1873-23-0] [87/5][64/18]
CF ₈ S	trifluoro(pentafluorothio)methane (223–252)	20.2	(253)	I	[373-80-8] [01/22]
CF ₉ NOS	tetrafluoro(difluoroamino)(trifluoromethoxy) sulfur (257–298)	28.7	(247)	A	[87/5][99/16]
CF ₁₀ O ₅ S ₂	[μ -(carbonodiperoxato)]decafluoro disulfur 291				[27/5164-10-1]

And on & on & on it goes...

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TABLE 6. Enthalpies of vaporization of organic compounds, 1880–2002—Continued

Molecular formula	Compound (Temperature range/K)	$\Delta_{\text{vap}}H_m$ (kJ mol ⁻¹)	Mean temperature (T_m /K)	Method	CAS registry number Reference
$\text{C}_{52}\text{H}_{104}$	(566–864) 1-dopentaccontene	149.1	(581)	A, EST	[99/16] [66575-85-7]
	(563–857)	149.8	(578)		[99/16]
$\text{C}_{52}\text{H}_{104}$	hexatetracontylcyclohexane	148.5	(580)	EST	[66575-86-8]
	(565–865)				[99/16]
$\text{C}_{52}\text{H}_{106}$	dopentaccontane			A, EST	[7719-79-1]
	(611–861)	152.0	(626)		[87/5][66/8]
$\text{C}_{52}\text{H}_{106}$	2-methylpentaccontane			EST	[66575-87-9]
	(563–854)	151.2	(578)		[99/16]
$\text{C}_{52}\text{H}_{106}\text{S}$	1-dopentaccontanethiol			EST	[66575-88-0]
	(575–873)	152.6	(590)		[99/16]
$\text{C}_{53}\text{H}_{100}$	heptatetracontylbenzene			EST	[66575-89-1]
	(569–868)	150.1	(584)		[99/16]
$\text{C}_{53}\text{H}_{106}$	heptatetracontylcyclohexane			A, EST	[66563-49-3]
	(568–869)	149.6	(583)		[99/16]
$\text{C}_{53}\text{H}_{106}$	1-tripentaccontene			EST	[66577-50-2]
	(566–861)	150.9	(581)		[99/16]
$\text{C}_{53}\text{H}_{108}$	tripentaccontane			A, EST	[7719-80-4]
	(615–866)	153.4	(630)		[87/5][66/8]
$\text{C}_{53}\text{H}_{108}$	2-methylpentaccontane			EST	[66575-90-4]
	(566–858)	152.3	(581)		[99/16]
$\text{C}_{53}\text{H}_{108}\text{S}$	1-tripentaccontanethiol			EST	[66575-91-5]
	(578–877)	153.7	(593)		[99/16]
$\text{C}_{54}\text{H}_{102}$	octatetracontylbenzene			A, EST	[66575-92-6]
	(572–873)	151.1	(587)		[99/16]
$\text{C}_{54}\text{H}_{108}$	octatetracontylcyclohexane			EST	[66575-93-7]
	(571–873)	150.6	(586)		[99/16]
$\text{C}_{54}\text{H}_{110}$	1-tetrapentaccontene			A, EST	[66575-94-8]
	(569–865)	151.9	(584)		[99/16]
$\text{C}_{54}\text{H}_{110}$	tetrapentaccontane			EST	[66575-95-9]
	(618–870)	155.0	(633)		[99/16]

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And then Table 7 starts...

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TABLE 7. Enthalpies of vaporization of select organo-metallic and inorganic compounds, 1880–2002—Continued

Molecular formula	Compound (Temperature range/K)	$\Delta_{\text{vap}}H_m$ (kJ mol ⁻¹)	Mean temperature (T_m /K)	Method	CAS registry number Reference
$\text{C}_4\text{H}_{10}\text{Zn}$	(248–318) diethyl zinc	29.9	(283)	BG	[46/13] [557-20-0]
		37.9	(298)		[83/1]
$\text{C}_6\text{H}_{14}\text{Zn}$		40.2±2.1		BG	[49/21][82/15]
	(250–391)	39.9	(265)		[47/5]
$\text{C}_6\text{H}_{14}\text{Zn}$	dipropyl zinc	40.2		BG	[46/13]
		43±2			[628-91-1]
$\text{C}_6\text{H}_{14}\text{Zn}$			(341)	BG	[02/43]
	(313–370)	42.1±0.4			[84/34]
$\text{C}_6\text{H}_{14}\text{Zn}$		45.6±2.5		BG	[49/21][82/15]
		39.5			[49/25]
$\text{C}_6\text{H}_{14}\text{Zn}$		40.3		BG	[46/13]
	diisopropyl zinc				[625-81-0]
$\text{C}_8\text{H}_{18}\text{Zn}$	(303–345) dibutyl zinc	41.8±0.5	(324)	BG	[84/34]
	(310–338)	47.4	(324)		[46/4]
$\text{C}_8\text{H}_{18}\text{Zn}$		50.7±0.3	(342)	BG	[1119-90-0]
	(305–379)	54.4±3.3			[84/13]
$\text{C}_8\text{H}_{18}\text{Zn}$		45.3		BG	[49/21][82/15]
		42.9			[49/25]
$\text{C}_8\text{H}_{18}\text{Zn}$	di-sec-butyl zinc			BG	[46/13]
	(287–372)	40.9±0.2	(330)		[7446-94-8]
$\text{C}_8\text{H}_{18}\text{Zn}$	diisobutyl zinc			BG	[84/13]
	(288–372)	44.6±0.2	(330)		[7446-94-8]
$\text{C}_8\text{H}_{18}\text{Zn}$	di-tert-butyl zinc			BG	[84/13]
	(300–322)	49.3±0.8	(311)		[14402-93-8]
$\text{C}_{10}\text{H}_{22}\text{Zn}$	dipentyl zinc	48.6			[49/25]
$\text{C}_{12}\text{H}_{26}\text{Zn}$	dihexyl zinc				

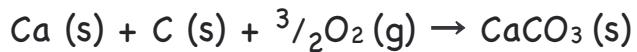
J. Phys. Chem. Ref. Data, Vol. 32, No. 2, 2003

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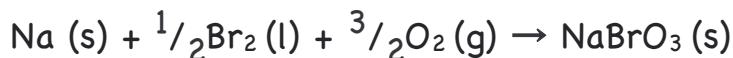
Enthalpy of formation

The standard **enthalpy of formation** ($\Delta_f H^\circ$) of a compound is ΔH° for the process of forming one mole of the compound from elements in their reference states:

elements in reference states at 1 bar → compound at 1 bar : $\Delta H^\circ = \Delta_f H^\circ$



$$\Delta H^\circ = \Delta_f H^\circ (\text{CaCO}_3(\text{s})) = -1207 \text{ kJ mol}^{-1}$$



$$\Delta H^\circ = \Delta_f H^\circ (\text{NaBrO}_3(\text{s})) = -334 \text{ kJ mol}^{-1}$$



The enthalpy of formation of an element in its reference state is zero (because this is a 'null' reaction).

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Hess's Law

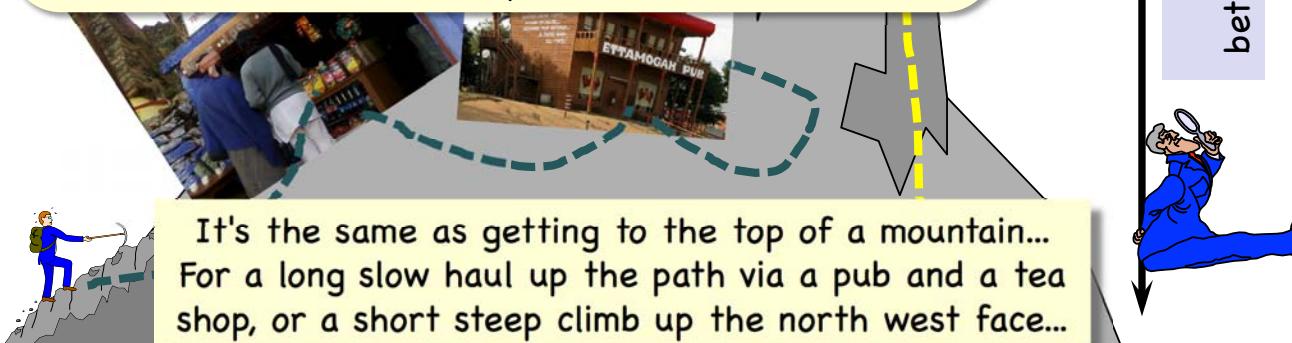
... and the top is always the same



Hess's law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps

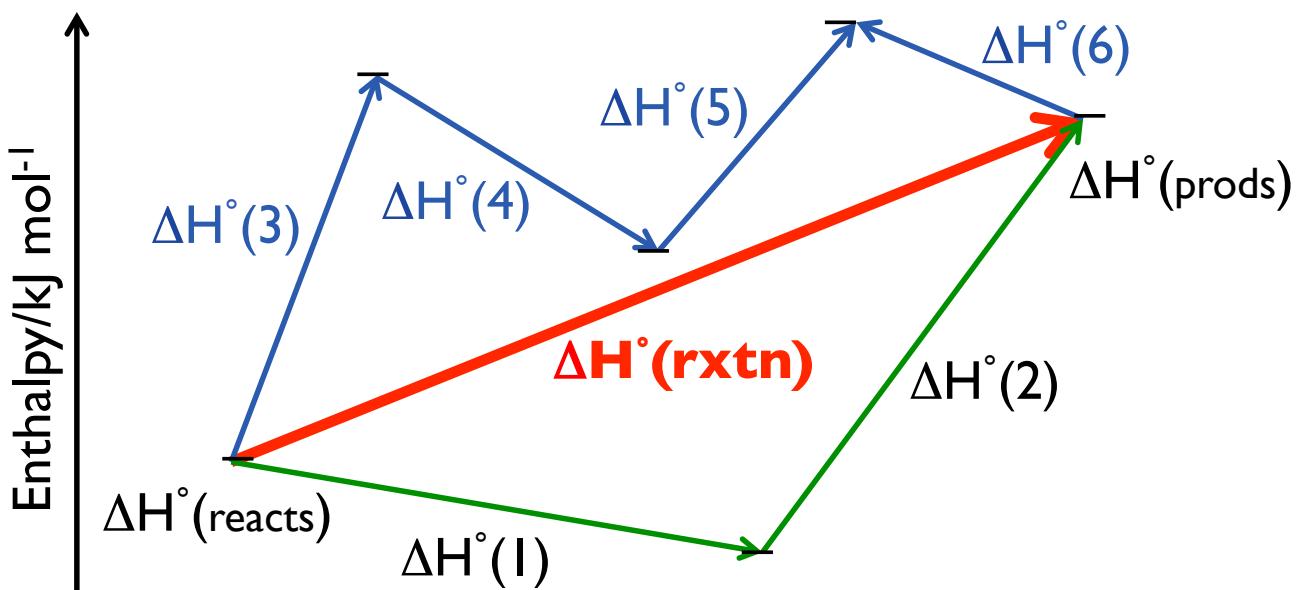
This is another consequence of the 1st Law

...the distance between the bottom...



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Hess's Law



$$\begin{aligned}\Delta H^\circ(\text{rxtn}) &= \Delta H^\circ(\text{products}) - \Delta H^\circ(\text{reactants}) \\ &= \Delta H^\circ(1) + \Delta H^\circ(2) \\ &= \Delta H^\circ(3) + \Delta H^\circ(4) + \Delta H^\circ(5) - \Delta H^\circ(6)\end{aligned}$$

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Enthalpy of reaction

The enthalpy change accompanying a chemical reaction is $\Delta_r H$
(or $\Delta_r H^\circ$ if the reaction is carried out under standard conditions)
or more often written just as ΔH .

apply Hess's Law:

$$\Delta_r H^\circ = \sum_{\text{all products } i} m_i \Delta_f H^\circ_{\text{product } i} - \sum_{\text{all reactants } j} m_j \Delta_f H^\circ_{\text{reactant } j}$$

this means – the enthalpy change for a reaction equals the enthalpy change to form the products from elements minus the enthalpy change to form the reactants from elements (m_i, m_j = stoichiometric no's in the balanced reaction equation)

Enthalpy of reaction

EXAMPLE

Q: Calculate ΔH° (298 K) for: $2\text{ZnS} (\text{s}) + 3\text{O}_2 (\text{g}) \rightarrow 2\text{ZnO} (\text{s}) + 2\text{SO}_2 (\text{g})$

using these enthalpies of formation (at 298K):

$$\Delta_f H^\circ (\text{ZnS}) = -206 \text{ kJ mol}^{-1},$$

$$\Delta_f H^\circ (\text{ZnO}) = -350 \text{ kJ mol}^{-1},$$

$$\Delta_f H^\circ (\text{SO}_2) = -297 \text{ kJ mol}^{-1}$$

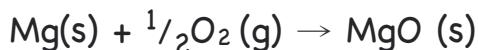
A:
$$\begin{aligned}\Delta_r H^\circ &= \sum m_i \Delta_f H^\circ_{\text{product } i} - \sum m_j \Delta_f H^\circ_{\text{reactant } j} \\ &= 2 \times \Delta_f H^\circ (\text{ZnO}) + 2 \times \Delta_f H^\circ (\text{SO}_2) - \{2 \times \Delta_f H^\circ (\text{ZnS}) + 3 \times \Delta_f H^\circ (\text{O}_2)\} \\ &= 2 \times -350 + 2 \times -297 - \{2 \times -206 + 3 \times 0\} = \quad \text{kJ mol}^{-1}\end{aligned}$$

Note: enthalpy of formation of $\text{O}_2 (\text{g}) = 0$ (element in its standard state).

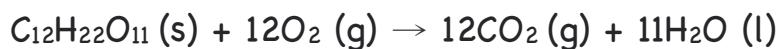
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Enthalpy of combustion

The standard **enthalpy of combustion** ($\Delta_c H^\circ$) is the standard enthalpy change for the reaction of **one mole of a substance with oxygen** to form an oxide* or (for organic compounds) $\text{CO}_2 (\text{g})$, $\text{H}_2\text{O} (\text{l})$, and $\text{N}_2 (\text{g})$.



$$\Delta_c H^\circ = -602 \text{ kJ mol}^{-1}$$



$$\Delta_c H^\circ = -5637 \text{ kJ mol}^{-1}$$

* the stable oxide with the highest oxidation state

Enthalpy of combustion

EXAMPLE QUESTION

Q: Calculate $\Delta_f H^\circ$ for acetylene (C_2H_2) given its $\Delta_c H^\circ = -1301 \text{ kJ mol}^{-1}$ plus $\Delta_f H^\circ(CO_2(g)) = -394 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(H_2O(l)) = -286 \text{ kJ mol}^{-1}$.

A: ΔH° for the combustion reaction is given, use it and the other $\Delta_f H^\circ$ to calculate the unknown $\Delta_f H^\circ (C_2H_2)$.



$$\Delta_r H^\circ = \sum m_i \Delta_f H^\circ_{\text{product } i} - \sum m_j \Delta_f H^\circ_{\text{reactant } j}$$

$$-1301 = 2 \Delta_f H^\circ (CO_2(g)) + \Delta_f H^\circ (H_2O(l)) - \{\Delta_f H^\circ (C_2H_2) + \frac{5}{2} \Delta_f H^\circ (O_2)\}$$

$$-1301 = 2 \times -394 + -286 - \{\Delta_f H^\circ (C_2H_2) + 5/2 \times 0\}$$

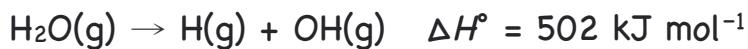
$$\text{rearrange and solve gives } \Delta_f H^\circ (C_2H_2) = \quad \text{kJ mol}^{-1}$$

Bond Enthalpies

The standard enthalpy change for breaking one mole of a particular type of chemical bond (with all reactants and products being gaseous) is called the **bond dissociation energy** or **bond enthalpy**.



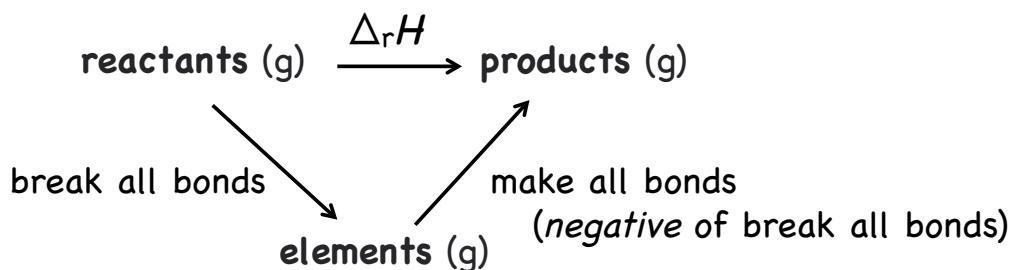
The value of a particular bond enthalpy will depend on what other bonds are present in the molecule, e.g.



Average bond enthalpies are calculated from the dissociation enthalpies of compounds which have bond types in common.

Using Bond Enthalpies

The enthalpy change for a gas-phase reaction:



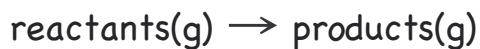
$$\Delta_r H = \sum_{\text{all bonds}}^{} \text{reactant bond enthalpies} - \sum_{\text{all bonds}}^{} \text{product bond enthalpies}$$

Common mistake:

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Using Bond Enthalpies

The enthalpy change for a gas-phase reaction:



$$\Delta_r H = \sum_{\text{all bonds}}^{} \text{reactant bond enthalpies} - \sum_{\text{all bonds}}^{} \text{product bond enthalpies}$$

EXAMPLE QUESTION

Q: Calculate $\Delta_r H^\circ$ from bond enthalpies for: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$

A: $\Delta_r H = \sum \text{reactant bond enthalpies} - \sum \text{product bond enthalpies}$

$$\begin{aligned} &= (2 \times \text{HH bond enthalpy} + \text{OO bond enthalpy}) - 4 \times \text{OH bond enthalpy} \\ &= (2 \times 436 + 498) - 4 \times 463 \text{ kJ mol}^{-1} = -482 \text{ kJ mol}^{-1} \end{aligned}$$

(c.f. -484 kJ mol^{-1} using $\Delta_f H^\circ$ values: why the difference?)

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Other Standard Enthalpy Changes

Enthalpy of atomisation is the standard enthalpy of formation of a gaseous monatomic element (*i.e.* per mole of gaseous atoms formed).



If the standard reference state of the element is a diatomic gas, then the enthalpy of atomisation is easily calculated from the bond enthalpy. For O₂ the enthalpy of atomisation = 1/2 bond enthalpy.

Ionization enthalpy is defined as the enthalpy change for forming gas-phase cation from a gas-phase molecule, atom, or ion. The first ionization enthalpy for an atom is the enthalpy change for:

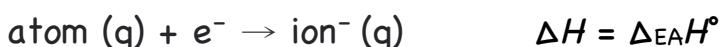


The second ionisation enthalpy is the least energy required to remove an electron from a +1 ion:

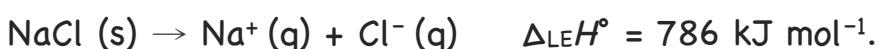


Other Standard Enthalpy Changes... 2

Electron affinities are defined as the enthalpy change for forming gas-phase anions from gas-phase atoms:



Lattice enthalpy is ΔH for forming gas-phase ions from an ionic solid, *e.g.*



Smaller ions and larger charges give larger lattice enthalpies.

For example: $\Delta_{\text{LE}}H^\circ(\text{LiF}) = 1050 \text{ kJ mol}^{-1}$ (smaller ions than NaCl)

$\Delta_{\text{LE}}H^\circ(\text{MgO}) = 3923 \text{ kJ mol}^{-1}$ (similar size ions to NaCl, but larger charges).

Entropy & the Second Law



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Spontaneous Processes

Spontaneous processes occur without involvement of outside factors

Spontaneous processes:

- a gas expands to fill its container
- heat flows from a hotter to a colder object
- nitrogen and hydrogen react to form ammonia, but not completely

Non-spontaneous processes:

- a gas contracts into a portion of its container
- heat flows from a colder to hotter object
- nitrogen and hydrogen convert completely into ammonia
- a tennis ball at rest gets colder and starts to bounce

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Spontaneous Reactions

- ◆ Reactions and processes usually have a preferred direction
 - gases and miscible solutions **spontaneously** mix
 - chemical reactions always go **spontaneously** to equilibrium
- ◆ The reaction that does occur under the given conditions is known as the **spontaneous reaction**
- ◆ Mixtures do not spontaneously un-mix even when there is no energy change involved (ie. OK by 1st Law)

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Spontaneous vs Quick

It may not always be obvious what the spontaneous reaction is, if it is very slow.

However there appears to be a common aspect of spontaneous reactions

....

Do note that spontaneous is not the same as me suddenly bursting into song & dance during this lecture!

Spontaneous reactions may be very slow because of kinetic considerations.



Warning: may spontaneously burst into song & dance done VERY BADLY

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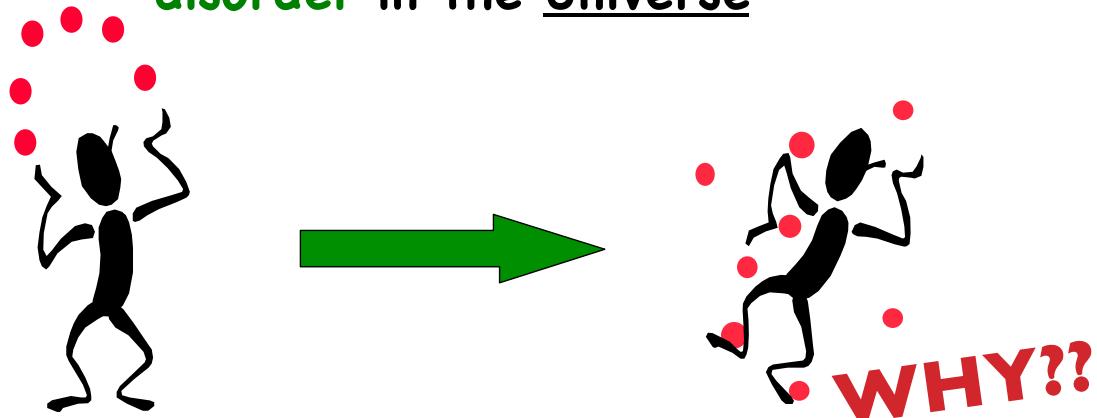
Why Spontaneous ?

Although many *exothermic* reactions appear spontaneous, so are many *endothermic* processes; e.g.

NH_4NO_3 is readily soluble in water, which gets colder (endothermic).

How come ?? The answer is that:

Spontaneous is anything that increases the net disorder in the Universe



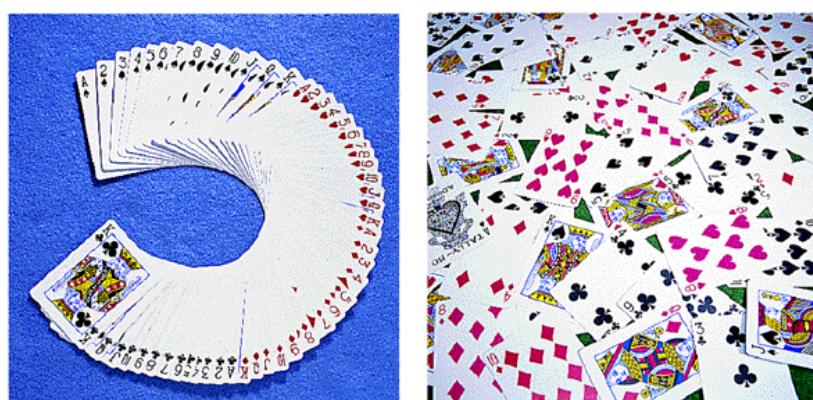
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Spontaneous reactions

... lead to the most probable outcome

Disordered systems are more likely than ordered ones...

...because, simply, there are more ways of creating disorder



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Entropy (S, units = J K⁻¹ mol⁻¹)

Entropy is a measure of the **disorder** of a system, and can be determined for all substances (unlike H and U).

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$



disorder increases

Entropy is another state function



The entropy change for a process is

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

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2nd Law: if spontaneous, entropy of *universe* increases

ice-block



spontaneous
 ΔS increase

*at Sydney's
ambient p & T*

non-spontaneous
 ΔS decrease

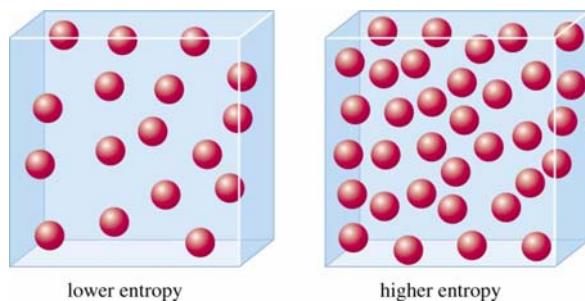
puddle of
water

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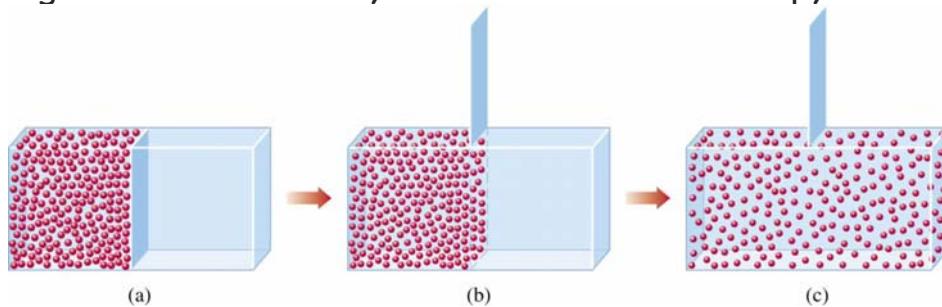
Entropy: the molecular view

[Blackman 8.5]

- ❖ Increasing the **number of particles** in a system increases its entropy.



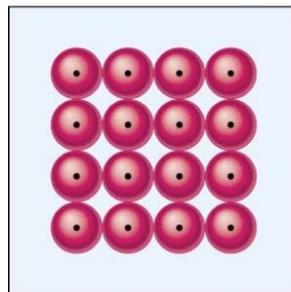
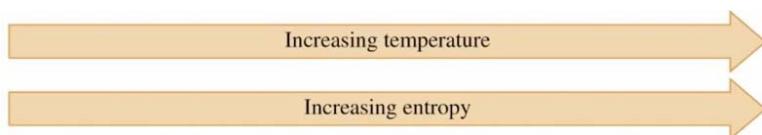
- ❖ Increasing the **volume** of a system increases its entropy



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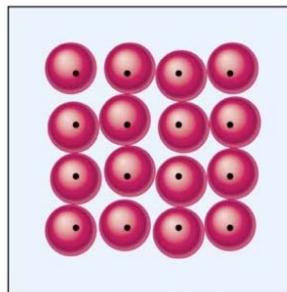
Entropy: the molecular view

- ❖ Increasing the energy (**temperature**) of a system increases its entropy



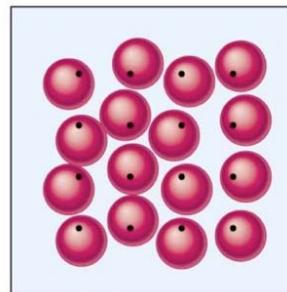
At close to absolute zero, the atoms, represented by coloured spheres, rest at their equilibrium lattice positions, represented by black dots. There is perfect order and minimum entropy.

(a)



At a higher temperature, the particles vibrate about their equilibrium positions. In this 'frozen' view of a moment in time, we see that there is greater disorder than at absolute zero.

(b)

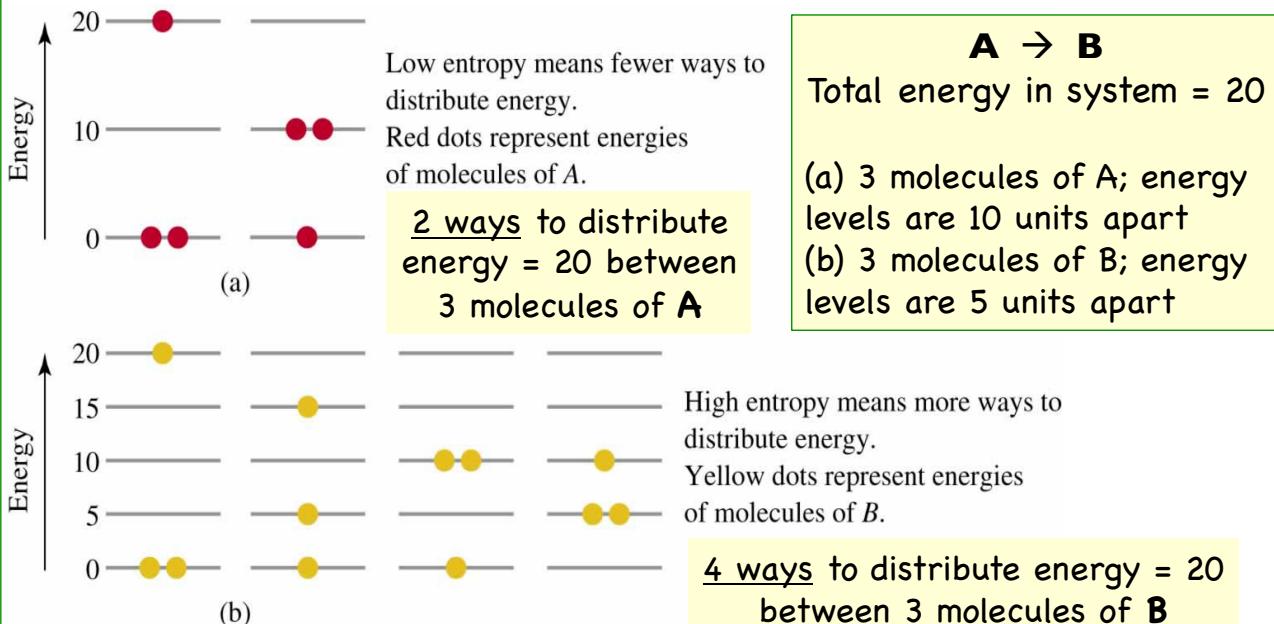


At a still higher temperature, vibration is more violent and at any instant the particles are found in even more disordered arrangements.

(c)

Entropy: the molecular view

- Increasing the number of ways the total energy of the system can be distributed amongst the particles making up the system increases its entropy (**energy distribution**)



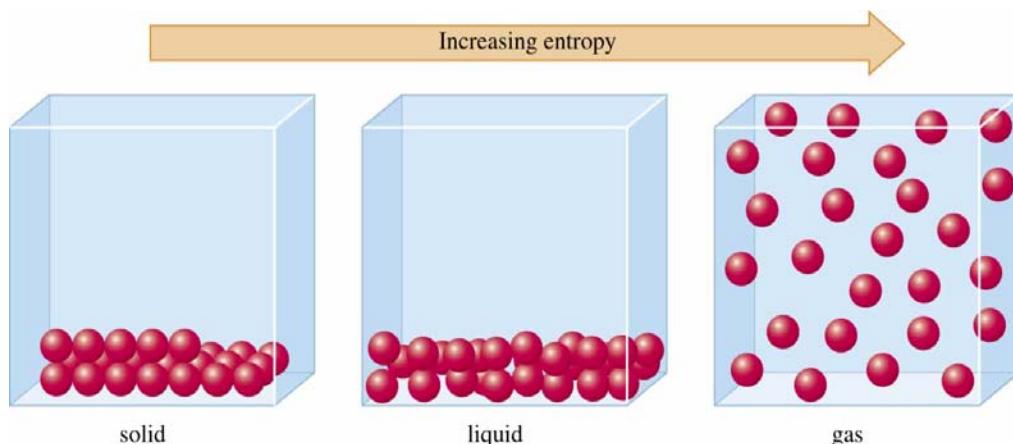
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Entropy: the molecular view

- The **state of matter** of a substance

The distribution (or range) of energies particles have in a solid is narrower than in a liquid, and in a gas the particles have the widest distribution of energies

For a given substance: $S(\text{solid}) < S(\text{liquid}) < S(\text{gas})$



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Entropy: the molecular view

- ❖ Any **reaction** that **overall produces gas** molecules will have a positive ΔS

EXAMPLE QUESTION

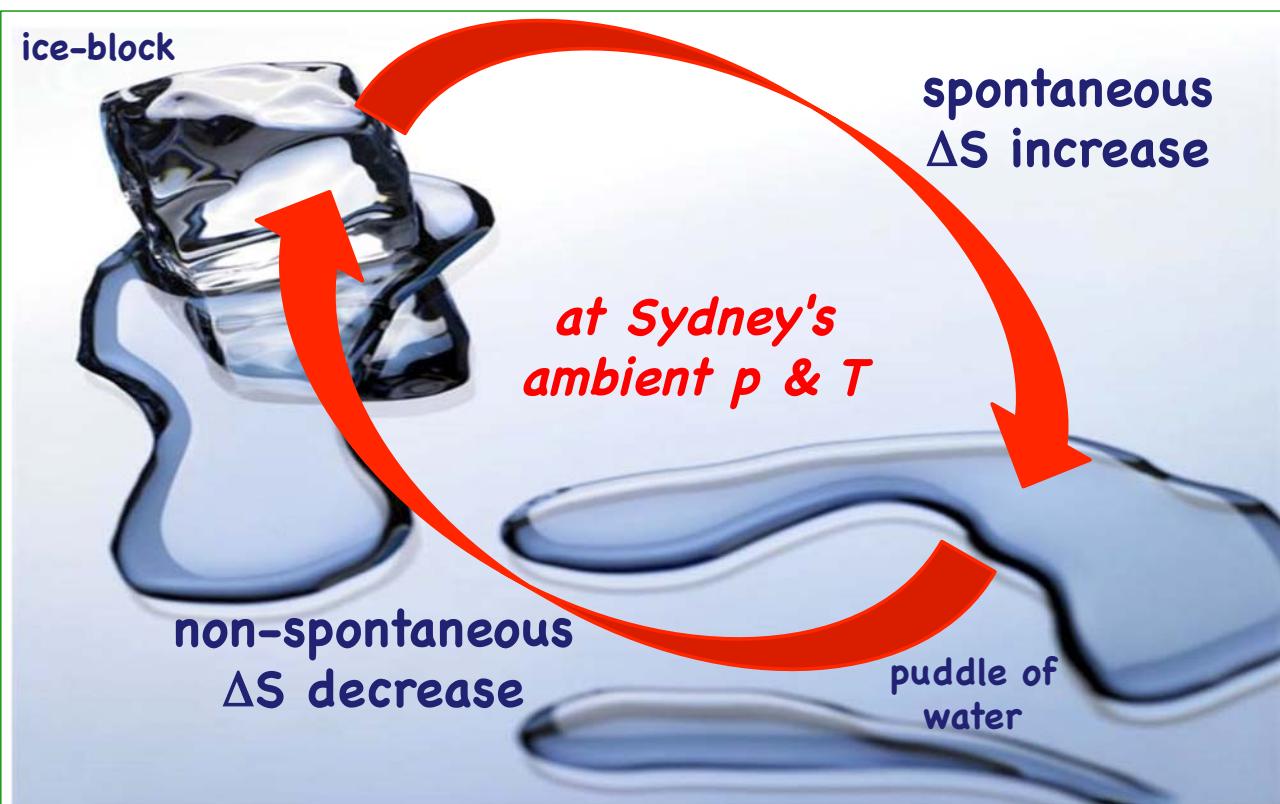
Q: For the following reactions, is the change in entropy zero or positive or negative ?

A:



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2nd Law: if spontaneous, entropy of *universe* increases



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3rd Law (define entropy S = 0 at T = 0 K)

1. The third law says that the entropy of all pure crystalline solids tends to a constant value at 0 K.
2. We call this value $S = 0$, so we can calculate the entropy of any system at a temperature > 0 K.
3. Knowing S for the reactants and products of a reaction allows us to calculate ΔS :

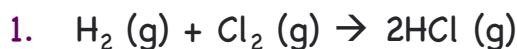
$$\Delta_r S^\circ = \sum m_i S^\circ_{\text{product } i} - \sum m_j S^\circ_{\text{reactant } j}$$

but note that above 0 K, no S° is zero (even for elements in their standard reference states)

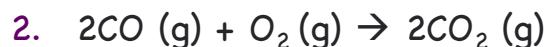
Calculating Entropy

EXAMPLE QUESTION

- Q. Using tables of standard entropy values at 298 K, calculate the entropy change for the following reactions:



A. $\Delta S^\circ = 2 \times 187 - (131 + 223)$
= $J\ K^{-1}\ mol^{-1}$



A. $\Delta S^\circ = 2 \times 214 - (2 \times 198 + 205)$
= $- J\ K^{-1}\ mol^{-1}$



A. $\Delta S^\circ = 192 + 3 \times 131 - 2 \times 193$
= $J\ K^{-1}\ mol^{-1}$

	$S^\circ / J\ K^{-1}\ mol^{-1}$
$CO_2(g)$	214
$CO(g)$	198
$O_2(g)$	205
$H_2(g)$	131
$N_2(g)$	192
$NH_3(g)$	192
$Cl_2(g)$	223
$HCl(g)$	187

Entropy: heat and temperature

[Blackman 8.7]

For a reversible process, the entropy change for a system can be calculated from the heat associated with the process and the absolute temperature of the system:

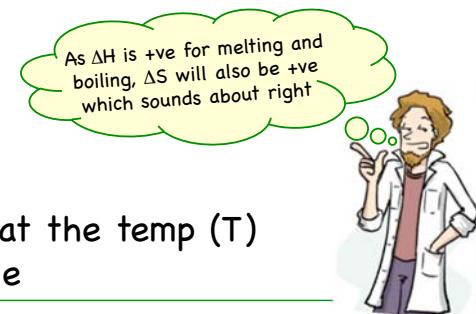
$$dS = \frac{dq_{rev}}{T}$$

where q_{rev} is the heat change for the reversible process

This allows the entropy change of a phase transition when heating a substance to be calculated:

$$\Delta S = \frac{\Delta H}{T}$$

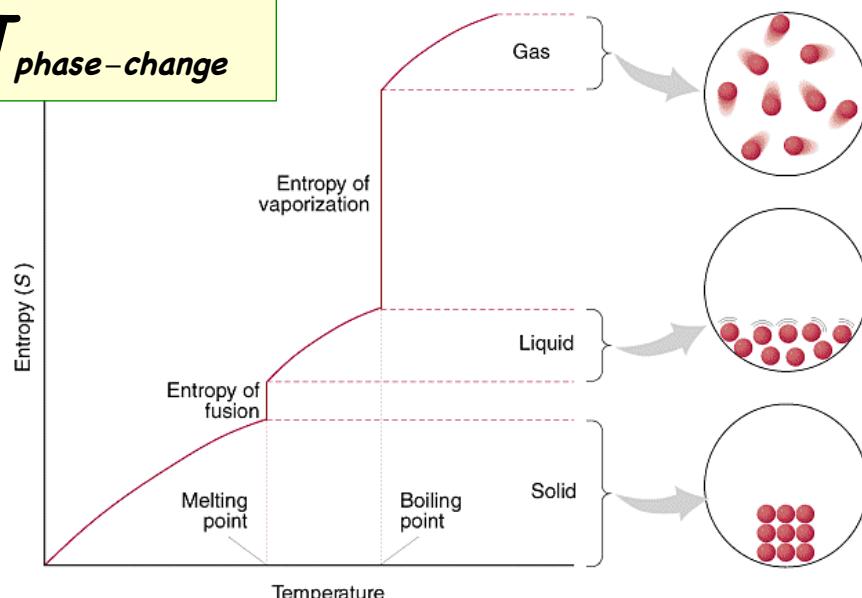
where ΔH is the enthalpy change at the temp (T) of the phase change



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Solid → Liquid → Gas

$$\Delta S = \frac{\Delta H_{\text{phase-change}}}{T_{\text{phase-change}}}$$



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Entropy Change in the Universe

[Blackman 8.6]

- ◆ **2nd Law:** In any spontaneous process, the entropy of the universe increases.

The Universe = System (the bit we are interested in; your reaction) + Surroundings (all the rest)

so: $\Delta S_{\text{Universe}} = \Delta S_{\text{System}} + \Delta S_{\text{surroundings}}$

- ◆ Entropy change of the surroundings comes from the heat from or absorbed by the *reaction*:

so $\Delta S_{\text{surroundings}} = q_{\text{surroundings}} / T$
 $= -\Delta H_{\text{system}} / T$ (at constant P)

- ◆ Entropy change of the system is calculated using:

$$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}} \quad (\text{see previous slides})$$

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Entropy Change in the Universe... cont'd

- Therefore...

$$\begin{aligned}\Delta S_{\text{Universe}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= \Delta S_{\text{system}} - \Delta H_{\text{system}} / T\end{aligned}$$

- Rearranging (x both sides by $-T$):

so $-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$

- ◆ OK: we're chemists and interested in the system (a reaction), not the universe. So we define:

Gibbs Free Energy (G : units kJ mol^{-1}): $\Delta G = -T\Delta S_{\text{universe}}$

which is:

$$\boxed{\Delta G = \Delta H_{\text{system}} - T\Delta S_{\text{system}}}$$

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Gibbs Free Energy (kJ mol^{-1})

for a **spontaneous process**

$$\Delta G = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

$$< 0$$

... because $\Delta G = -T\Delta S_{\text{universe}}$ and $\Delta S_{\text{universe}} > 0$

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Gibbs Energy (G , units: kJ mol^{-1})

$$\Delta G = \Delta H - T\Delta S$$

< 0 for a spontaneous process

Spontaneous for...

		ΔH	
		$+ve$	$-ve$
ΔS	$+ve$	if $T\Delta S > \Delta H$	Always
	$-ve$	Never	if $\Delta H > T\Delta S$

Gibbs Energy is another state function



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Gibbs Energy (G , units: kJ mol^{-1})

ΔG equals the maximum energy which can be converted to non-expansion (e.g. electrical) work in a constant pressure and temperature process, so is sometimes referred to as the *free* (i.e. 'available') *energy*.

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Standard Gibbs Energy (kJ mol^{-1})

$\Delta_r G^\circ$ for a chemical reaction can be calculated from the $\Delta_f G^\circ$ for the reactants and products or from $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for the reaction.

For a reaction:

$$\begin{aligned}\Delta_r G^\circ &= \sum_{\text{products}} m_i \Delta_f G^\circ_{\text{product } i} - \sum_{\text{reactants}} m_j \Delta_f G^\circ_{\text{reactant } j} \\ &= \Delta_r H^\circ - T \Delta_r S^\circ\end{aligned}$$

$\Delta G^\circ_{\text{reaction}}$ ($\Delta_r G^\circ$) is the *free energy change when 1 mol reactants is changed into 1 mol products under standard conditions*

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Important !

$$\Delta G \neq \Delta G^\circ$$



Gibbs energy and
standard Gibbs energy
are completely different

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Gibbs Energy Change for Reactions

EXAMPLE QUESTION

Q: Calculate $\Delta_r G^\circ$ for $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ from (i) the Gibbs energies of formation and (ii) $\Delta_r H^\circ$ and $\Delta_r S^\circ$. Is the reaction spontaneous under standard conditions at 298 K?

A: (i)
$$\begin{aligned}\Delta_r G^\circ &= \sum m_i \Delta_f G^\circ_{\text{product } i} - \sum m_j \Delta_f G^\circ_{\text{reactant } j} \\ &= \Delta_f G^\circ(\text{CaO}(\text{s})) + \Delta_f G^\circ(\text{CO}_2(\text{g})) - \Delta_f G^\circ(\text{CaCO}_3(\text{s})) \\ &= \underline{\hspace{10em}} \text{kJ mol}^{-1}\end{aligned}$$

(ii)
$$\begin{aligned}\Delta_r H^\circ &= \sum m_i \Delta_f H^\circ_{\text{product } i} - \sum m_j \Delta_f H^\circ_{\text{reactant } j} \\ &= \Delta_f H^\circ(\text{CaO}(\text{s})) + \Delta_f H^\circ(\text{CO}_2(\text{g})) - \Delta_f H^\circ(\text{CaCO}_3(\text{s})) \\ &= \underline{\hspace{10em}} \text{kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r S^\circ &= \sum m_i S^\circ_{\text{product } i} - \sum m_j S^\circ_{\text{reactant } j} \\ &= S^\circ(\text{CaO}(\text{s})) + S^\circ(\text{CO}_2(\text{g})) - S^\circ(\text{CaCO}_3(\text{s})) \\ &= \underline{\hspace{10em}} \text{J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{so } \Delta_r G^\circ &= \Delta_r H^\circ - T\Delta_r S^\circ = 178 \times 10^3 \text{ J mol}^{-1} - 298 \text{ K} \times 159 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= \underline{\hspace{10em}} \text{kJ mol}^{-1}\end{aligned}$$

... $\Delta_r G^\circ$ therefore the reaction is at 298K

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Gibbs Energy and Spontaneous Processes

$\Delta_r G < 0 \Rightarrow$ Process is Spontaneous

$\Delta_r G > 0 \Rightarrow$ Process is Non-spontaneous
(= spontaneous in the opposite direction!)

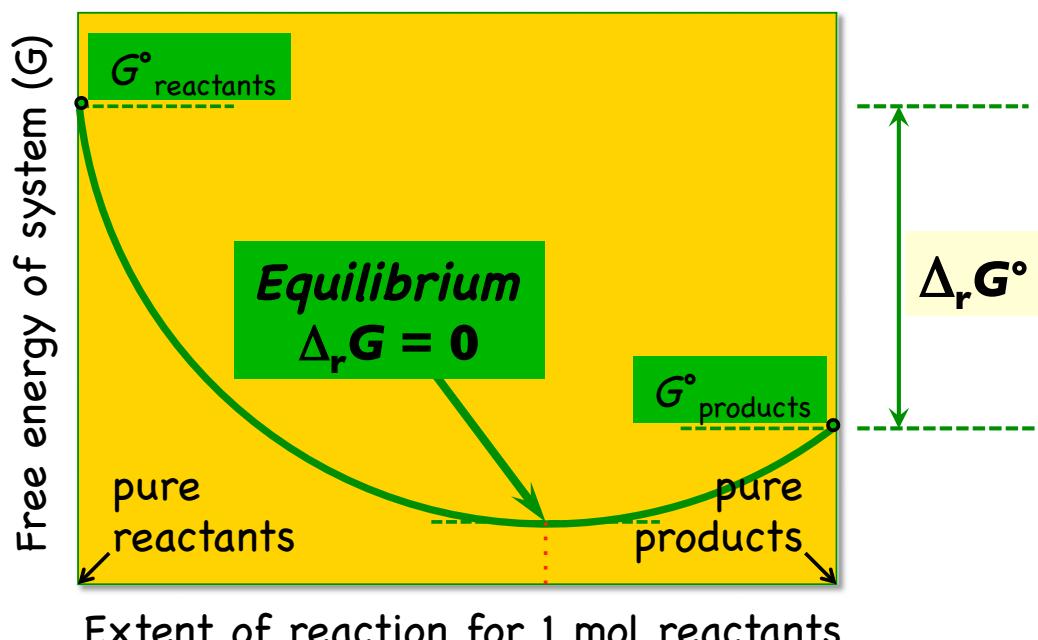
So what about ...

$\Delta_r G = 0 ?? \Rightarrow$

(corresponds to a minimum in the free energy of the system: e.g. plot of G versus extent of reaction; on the next slide)

Equilibrium

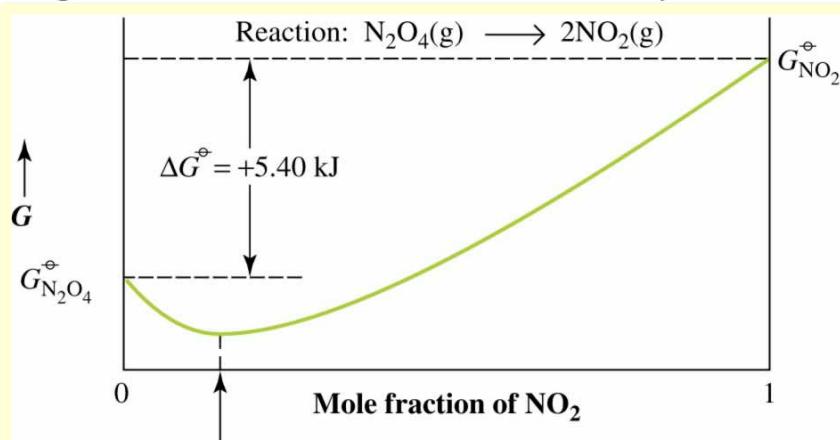
- ◆ At equilibrium: G is at a minimum, $\Delta_r G = 0$
- ◆ (Rate of forward reaction = rate of reverse reaction)



Gibbs Energy and Equilibrium

[Blackman 9.3]

- ◆ A graph of G for a chemical reaction from pure reactants to pure products has a minimum at the composition of the system at equilibrium.
- ◆ Starting from pure reactants, the only spontaneous change is for the system to move to equilibrium as any further change would increase G and according to the Second Law would not be spontaneous.



Equilibrium occurs here at a total pressure of $1.013 \times 10^5 \text{ Pa}$ with about 16.6% of the N_2O_4 decomposed.

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Equilibrium constant

- ◆ The composition of the system at equilibrium can be determined from $\Delta_r G^\ominus$:

$$\Delta_r G^\ominus = -RT \ln K$$

- ◆ If $\Delta_r G^\ominus > 0$ (+ve), then $\ln K$ is -ve and $K < 1$ (reactants are favoured)

If $\Delta_r G^\ominus < 0$ (-ve), then $\ln K$ is +ve and $K > 1$ (products are favoured)

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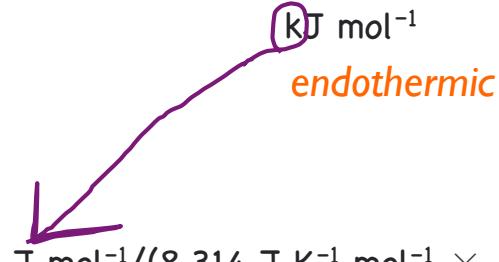
Gibbs Energy and Equilibrium

EXAMPLE QUESTION

Q: Calculate $\Delta_r G^\circ$ and K for the reaction $2CO_2(g) \rightarrow 2CO(g) + O_2(g)$ at 298 K starting from standard free energies of formation.

A:
$$\begin{aligned}\Delta_r G^\circ &= \sum m_i \Delta_f G^\circ_{\text{product } i} - \sum m_j \Delta_f G^\circ_{\text{reactant } j} \\ &= 2 \times \Delta_f G^\circ(CO(g)) + \Delta_f G^\circ(O_2(g)) - 2 \times \Delta_f G^\circ(CO_2(g)) \\ &= \end{aligned}$$

(values from SICD)



Rearranging $\Delta_r G^\circ = -RT \ln K$ gives

$$\ln K = \Delta_r G^\circ / RT =$$

= $J \text{ mol}^{-1} / (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \text{K})$

So $K =$ (standard state 1 bar).

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Changes in K with T

◆ Assuming $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are independent of T

$$\text{then } \Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -RT \ln K$$

$$\text{so } \ln K = -(\Delta_r H^\circ / RT) + (\Delta_r S^\circ / R)$$

◆ Therefore: the sign of ΔH° determines if K increases or decreases with changes in temperature.

If $\Delta_r H^\circ > 0$ (endothermic), increasing T causes K to increase (more products are formed).

If $\Delta_r H^\circ < 0$ (exothermic), increasing T causes K to decrease (more reactants are formed).

These results are in accord with Le Châtelier's principle: e.g. for endothermic reactions, increasing the temperature increases the amount of products (and vice versa for exothermic reactions).

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Calculating changes in K with T

- ◆ Assuming $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are independent of T

then $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -RT \ln K$

and $\ln K = -(\Delta_r H^\circ / RT) + (\Delta_r S^\circ / R)$

- ◆ So, the equilibrium constant for a reaction at temperature T_2 is related to the equilibrium constant at temperature T_1 by the **van't Hoff equation**:

$$\ln(K_{T_2}) - \ln(K_{T_1}) = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

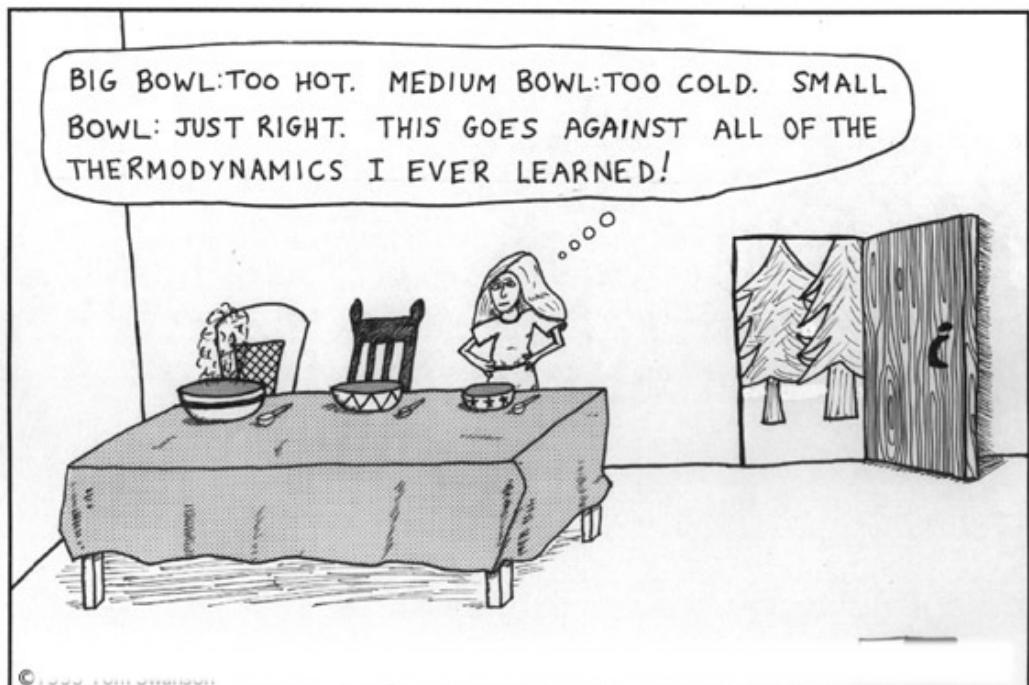
Don't bother to learn this equation

you'll always be given this equation,
so just know how to plug in the numbers



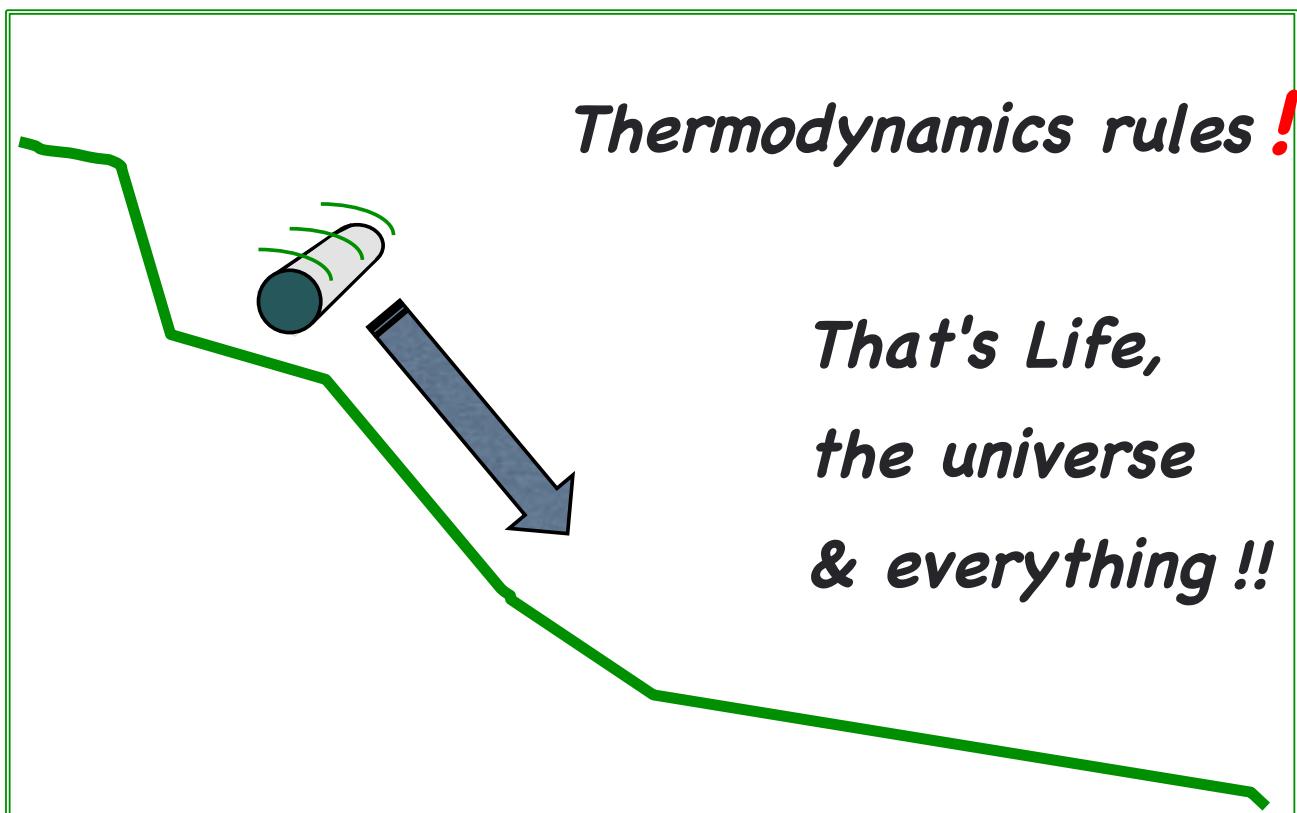
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Still confused... so was - - -



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Chemical Thermodynamics & Life



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How should I study for this topic?

THINK CRITICALLY!!

Ask yourself: **Do I understand** everything presented? Can I do all the problems... from lectures, worksheets & tutes?

Try to **understand** the material...
(use the syllabus & lectures as a guide)

Attend **lectures**, do **worksheets**...

Read **lecture notes** & **textbook** ...

Do some more problems ...
(from **tutorials**, **textbook** & **sample exams**)

Do some more problems ...



**repeat till you
understand it all!!**

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