

Recall:

Overview of Part II [Energy] Material

Split into three related sections

✓ 5. Basic Physics of Energy (~4/5 lectures)

- Sources & consumption of energy
- Forms of energy, units etc
- Basic balance calculations

Here →
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6. Basics of Energy Transfer (~6/7 lectures)

- Thermodynamics
- More sophisticated balance calculations etc.

7. Basics of Biological Energetics (~4 lectures)

- How do animals, cells etc store & use energy

Lectures 10/11

TOPICS

spontaneous processes

decreasing energy principles for
non-isolated systems

energy potentials & max work

6.7

Calorimetry

what you
should be
able to
do

det. if a given process is
spontaneous or not

calc. changes in Gibbs free energy
& enthalpy

do calorimetry (energy
measurement) calculations
such as determining heat
capacity of subst.

Examples

- o Calculate the energy released if you oxidised the entire glucose content of a 65g Moro bar. Assume the glucose content of the Moro bar is 70g per 100g. Gibbs free energy of glucose is -2870 kJ/mol. The molecular weight of glucose is 180.16 g/mol.
- o A typical lead acid battery undergoes the following chemical reaction to produce energy:
- $$\text{Pb (s)} + \text{PbO}_2 \text{ (s)} + 2\text{H}_2\text{SO}_4^{2-} \text{ (l)} \rightarrow 2\text{PbSO}_4 \text{ (s)} + 2\text{H}_2\text{O (l)}$$
- Given the values for Gibbs free energy of formation in the table above, determine the electrochemical work produced at 298 K.
- o Calculate the heat of reaction (or enthalpy of reaction), ΔH_f , for the chemical reaction of the lead acid battery above. Describe whether this reaction is endothermic or exothermic. Compare the Gibbs free energy value with the heat of reaction. What does this mean in terms of heat to/from the environment?
- o Calculate ΔH if a piece of metal with a specific heat of $0.98 \text{ kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ and a mass of 2 kg is heated from 22°C to 28°C .
- o A 1 g sample of octane is burned in a bomb calorimeter containing 1200 g of water at an initial temperature of 25°C . After the reaction the final temperature of the water is 33.2°C . The heat capacity of the calorimeter (known as the calorimeter constant) is 837 J/ $^\circ\text{C}$. The specific heat of water is $4.184 \text{ J/g}^\circ\text{C}$. Calculate the heat of combustion of octane in kJ/mol.

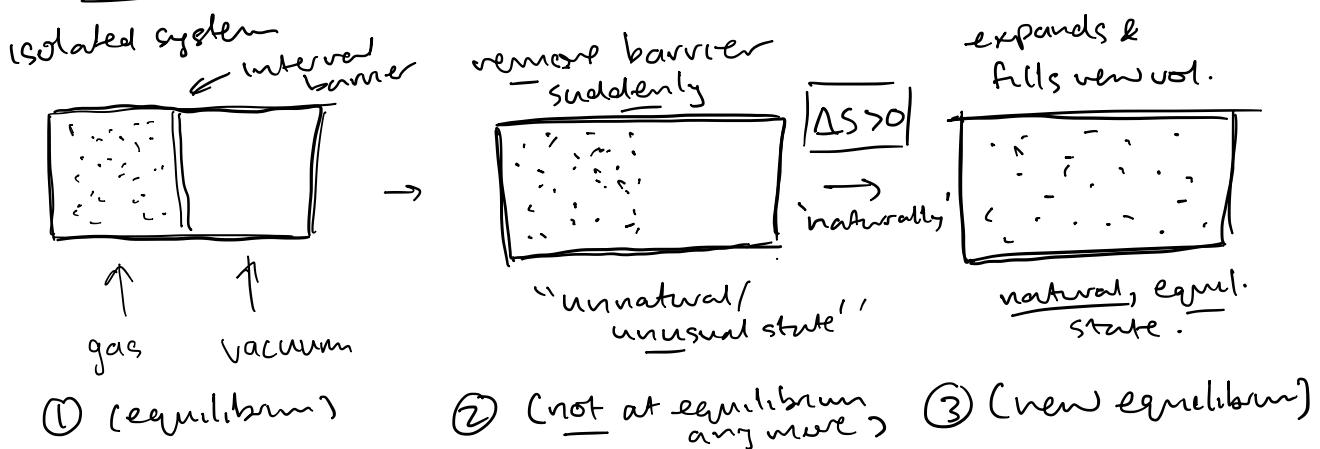
Spontaneous processes (first: in isolated systems)

We have seen (briefly) that in isolated systems, spontaneous processes are associated with an increase in entropy, $\Delta S > 0$

Spontaneous process?

- 'Natural' / likely to occur without needing energy input
- 'Driven' by changes in entropy
- "Entropic" process, driven by "entropic" forces

Example: Free expansion of a gas



Note: → No energy input/output for ② → ③ process
$$\boxed{W=Q=0, \Delta U=0 \quad \Delta S > 0}$$

→ A purely entropic process of 'microscopic rearrangements' etc.

→ re-establishes equilibrium after disturbance or 'unusual' starting conditions
↳ source of asymmetry!

Spontaneous processes for non-isolated systems?

Q: What kinds of process are 'natural' for non-isolated systems?

First, isolated:

'natural' coord (state equation)*

$$S = S(N, V, U) \quad |$$

↑ ↗ ↗
number vol. internal
molecules energy

Natural principle

$$\Delta S > 0, \text{ until maximum}$$

(maximum entropy)
for $S_W = S_Q = 0$

(* natural coord: those that will be held fixed for spontaneous)

Idea: maximising entropy
in isolated (fixed energy & no work/heat)
system is equivalent to
minimising energy when
entropy (& vol) is fixed.

$$\Delta S > 0$$

} entropy increases

} energy decreases
 $\Delta E < 0$

(stated without proof!)

natural coord $| U = U(N, V, S) \quad |$

Other 'energies' (for non-isolated systems)

- Instead of U for fixed entropy & or volume we can 'change coord' to give other natural energies for given system
- These coord changes are called 'Legendre transformations' & 'swap' two state variables in natural coord by subtracting their product ... p.m.s!
- These new 'energies' have physical interp. in terms of maximum available work under given conditions
- Spontaneous processes minimise these energies, i.e. $\Delta E < 0$ until minimum
- An energy/potential is most convenient to use when its natural state vars' will be held fixed

Potentials (energies)

to minimise

$-TS$ (swap T & S)

Internal Energy

$$U = U(N, V, S)$$

Helmoltz Free Energy

$$F = F(N, V, T) \quad \text{coord}$$

$$F = U - TS \quad \text{def.}$$

+ PV

swap PV .

Enthalpy

$$H = H(N, P, S)$$

$$H = U + PV$$

Gibbs Free energy

$$G = G(N, P, T)$$

$$G = U - TS + PV$$

$\hookrightarrow \Delta \text{Energy} < 0 \Rightarrow \text{spontaneous}$

Helmholtz free energy

$$\boxed{F = U - TS} \quad | \quad \text{def" .}$$

$$\boxed{\text{Transforms: } U(V, S) \rightarrow F(V, T)} \quad |$$

convenient
for
constant vol,
constant temp.

not as
useful for
therm. &
biol. as
Gibbs (E
enthalpy)

- o Physical interpretation:
maximum work under constant
vol, constant temperature

$$\text{First law: } \Delta U = Q - W^{\text{by}}$$

$$\text{ideal: } Q = T \Delta S$$

$$W^{\text{by}} = W^{\text{by max}}$$

} first & const.
law temp

$$\Rightarrow \boxed{W^{\text{by max}} = \Delta U - T \Delta S} \\ = \Delta F !$$

$$\boxed{T \Delta F < 0} \quad | \quad \begin{array}{l} \text{for spontaneous} \\ \text{constant vol,} \\ \text{constant temp} \\ \text{processes} \end{array}$$

\rightarrow Gibbs free energy \neq

$$G = U - TS + PV \quad (-(-PV))$$

Transforms:

$$U(V, S) \rightarrow G(P, T)$$

convenient for
constant pressure,
constant temp.

often
good
approx
for
chem
&
biol.

Physical interpretation:

\rightarrow maximum chemical work under
constant pressure & temp
reactions!

\rightarrow max chemical work (not incl.
 $P\Delta V$)

First law

$$\Delta U = Q - W^{\text{by}}$$

(ideal) $Q = T \Delta S$

$$W^{\text{by}} = P \Delta V - n \Delta N \quad \begin{matrix} \text{? include chemical work here!} \\ (\text{max: } -n \Delta N) \end{matrix}$$

$$\Rightarrow \Delta U = T \Delta S - P \Delta V + n \Delta N$$

$$\Rightarrow \Delta U + P \Delta V - T \Delta S = \boxed{\Delta G = n \cdot \Delta N}$$

chemical potential

(chemical 'pressure' or 'force')

= max chemical work 'on' or 'inside'
systems!

Also: $\boxed{\Delta G < 0} \rightarrow$ spontaneous reaction

$\Delta G < 0$	exergonic
$\Delta G > 0$	endergonic
$\Delta G = 0$	equil.

Enthalpy

$$\boxed{H = U + PV}$$

Transforms:

$$\boxed{(U(V,S) \rightarrow H(P,S)}$$

convenient for
constant pressure, &
then applic. const
entropy

• Physical interpretation:

- maximum amount of 'thermal energy' extractable,
- i.e. maximum 'thermal work'
or 'heat of reaction'
(heat absorbed, $\underline{Q^{(m) \text{ pos}}}$)

First law

$$\Delta U = Q - W^{\text{by}}$$

$$\text{ideal } Q = T \Delta S$$

$$W^{\text{by}} = P \Delta V$$

$$\Rightarrow \boxed{\Delta U + P \Delta V = Q}$$

(maximum)
"Heat of reaction"

\Rightarrow measuring thermal energy /
heat given off during
reaction:

Calorimetry

\rightarrow see later.

Terminology

(Energy / Gibbs free energy)

for
constant P, T

Exergonic — positive energy from system to surroundings $\rightarrow \Delta G < 0$

Endergonic — negative energy from system to surroundings $\rightarrow \Delta G > 0$

(Heat / Enthalpy)

for
constant pressure

Exothermic — release of heat $\rightarrow \Delta H < 0$

Endothermic — absorption of heat $\rightarrow \Delta H > 0$

Multiple processes or steps ?

Δ Energy (free energy, enthalpy)

etc is additive for multiple processes or steps:

$$\left. \begin{aligned} \Delta G^{(\text{net})} &= \Delta G^{(1)} + \Delta G^{(2)} + \dots \\ \Delta H^{(\text{net})} &= \Delta H^{(1)} + \Delta H^{(2)} + \dots \end{aligned} \right\}$$

etc -

For reactions 1: reactants \rightarrow products, use:

$$(\Delta \text{Energy} = \Delta \text{Energy}_{\text{products}} - \Delta \text{Energy}_{\text{reactants}})$$

Examples!

Gibbs free energy

- Calculate the energy released if you oxidised the entire glucose content of a 65g Moro bar. Assume the glucose content of the Moro bar is 70g per 100g. Gibbs free energy of glucose is -2870 kJ/mol. The molecular weight of glucose is 180.16 g/mol.

$$\rightarrow 65 \text{ g of bar} \times \frac{70 \text{ g of glucose}}{100 \text{ g of bar}} \times \frac{1 \text{ mol}}{180.16 \text{ g}} = 65 \times 0.7 \times \frac{1}{180.16} \text{ mol of glucose}$$

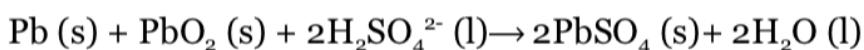
$$\Delta G = (0.7 \times 65 \text{ g}) \times \left(\frac{1}{180.16} \frac{\text{mol}}{\text{g}} \right) \times (-2870 \frac{\text{kJ}}{\text{mol}}) \approx -725 \text{ kJ}$$

Table 5: Examples of standard Gibbs free energy of formation, which is the Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard state (at 298 K and 1 atm).

Substance	Phase	Chemical Formula	ΔG_f° (kJ.mol ⁻¹)
Water	liquid	H ₂ O	-237.14
Water	gas	H ₂ O	-228.61
Oxygen	gas	O ₂	0
Hydrogen	gas	H ₂	0
Carbon dioxide	gas	CO ₂	-394.39
Lead	solid	Pb	0
Lead sulfate	solid	PbSO ₄	-813.2
Lead oxide	solid	PbO ₂	-215.48
Sulfuric acid	liquid	H ₂ SO ₄	-744.63

= product
= reactant

A typical lead acid battery undergoes the following chemical reaction to produce energy:



Given the values for Gibbs free energy of formation in the table above, determine the electrochemical work produced at 298 K.

$$\begin{aligned} \Delta G &= \Delta G^{\text{products}} - \Delta G^{\text{reactants}} \\ &= [2 \times (-813.2) + 2 \times (-237.14)] \\ &\quad - [0 + (-215.48) + 2 \times (-744.63)] \\ &\approx \underline{-396.02 \text{ kJ}} \quad (\Delta G < 0 \\ &\quad \Rightarrow \text{spontaneous}) \\ &= \underline{\text{chemical work}} \quad (\text{Ans}) \end{aligned}$$

Examples!

Enthalpy

Table 6: Example enthalpy of formation values at 298 K and 1 atm.

Substance	Phase	Chemical Formula	ΔH_f° (kJ.mol ⁻¹)
Water	liquid	H ₂ O	-285.83
Water	gas	H ₂ O	-241.8
Oxygen	gas	O ₂	0
Hydrogen	gas	H ₂	0
Carbon dioxide	gas	CO ₂	-393.5
Lead	solid	Pb	0
Lead sulfate	solid	PbSO ₄	-919.94
Lead oxide	solid	PbO ₂	-274.47
Sulfuric acid	liquid	H ₂ SO ₄	-909.27

= reactant
= product

(A)

Calculate the heat of reaction (or enthalpy of reaction), ΔH_f for the chemical reaction of the lead acid battery above. Describe whether this reaction is endothermic or exothermic. Compare the Gibbs free energy value with the heat of reaction. What does this mean in terms of heat to/from the environment?

$$\rightarrow (A) \Delta H = \Delta H^{\text{product}} - \Delta H^{\text{reactant}}$$

$$= [2 \times (-285.83) + 2 \times (-919.94)] - [0 + (-274.47) + 2 \times (-909.27)] \quad \left. \right\} \text{most important.}$$

$$\approx -319 \text{ kJ} \quad (\Delta H = Q^m, \text{ (mark)} \\ \qquad \qquad \qquad \Rightarrow \text{Heat expelled} \\ \qquad \qquad \qquad \Rightarrow \text{exothermic reaction})$$

(B) (More subtle/difficult)

$$w = \Delta G; \Delta H = \Delta U + P\Delta V^\circ - T\Delta S$$

$$\& \Delta U = w + Q; \text{ don't assume } \Delta H = Q$$

$$\Delta H = \Delta G + Q \Rightarrow Q^m = \Delta H - \Delta G > 0$$

actual system has absorbed / used extra heat ?!

as thus battery uses extra heat, not just reaction. $\left. \right\} \begin{array}{l} \text{reaction} \\ Q = \Delta H \& \\ \text{is exothermic. But} \\ \text{overall battery syst.} \\ \text{is endothermic.} \end{array}$

\Rightarrow another source of energy rev.

\rightarrow 0 Calculate ΔH if a piece of metal with a specific heat of 0.98 kJ·kg⁻¹·K⁻¹ and a mass of 2 kg is heated from 22°C to 28°C.

$$\text{use/assume } \Delta H = Q = c_p m \Delta T; \\ = 0.98 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \times 2 \text{ kg} \times 6 \text{ K} \\ \approx 11.8 \text{ kJ}$$

Note

$$\Rightarrow T(\text{°C}) = T(\text{°C}) + 273.15$$

$$\Rightarrow \Delta T(\text{K}) = \Delta T(\text{°C})$$

(273 cancels)

\rightarrow just a ref.

Calorimetry

Where do table values come from?)

- Science of measuring changes in state vers to determine the heat transfer associated with a given chemical, physical etc process (e.g. combustion/burning a substance)

- Hence determine the 'energy content' available via the process & substance

- Basic device : "Bomb Calorimeter"
 \Rightarrow changes in temperature
 $\text{to measure heat capacity}$

\Rightarrow Recall :

$$\& \left. \begin{array}{l} dQ = C_v dT \\ dQ = m C_v dT \end{array} \right\}$$

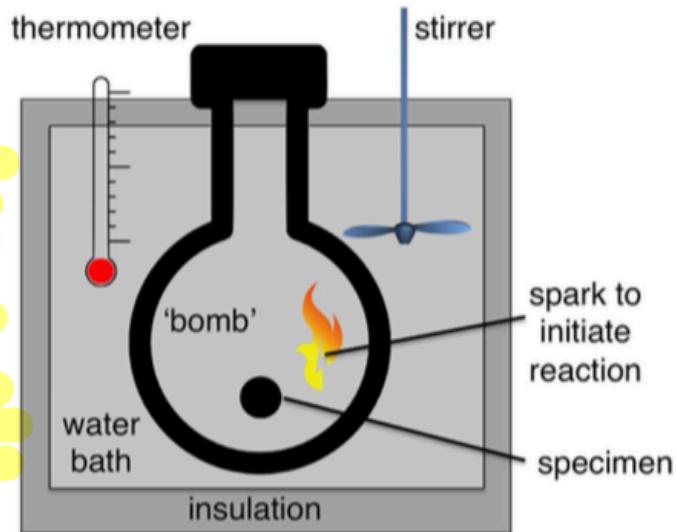
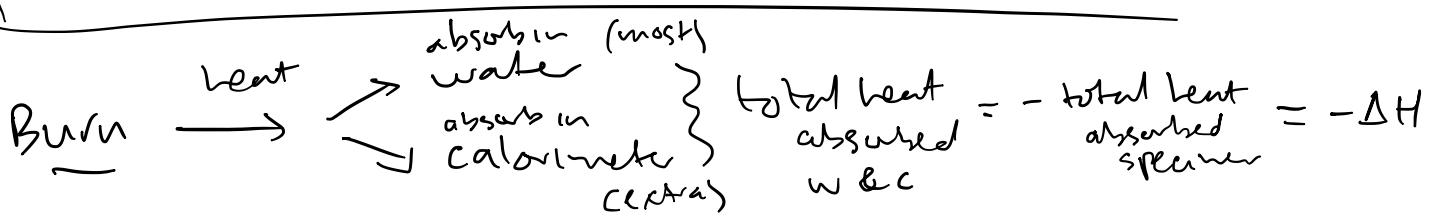


Figure 20: The 'bomb' calorimeter. A specimen is placed in a reaction chamber, which is filled with O₂ at high pressure (>20 atm) to ensure the reaction is fast and complete. The increase in temperature in the surrounding water is recorded and converted to an energy increase. Insulation helps to prevent the heat escaping into the surrounds.



Example



A 1 g sample of octane is burned in a bomb calorimeter containing 1200 g of water at an initial temperature of 25°C. After the reaction the final temperature of the water is 33.2°C. The heat capacity of the calorimeter (known as the calorimeter constant) is 837 J/g°C. The specific heat of water is 4.184 J/g°C. Calculate the heat of combustion of octane in kJ/mol.

First, total heat transfers

$$\Delta T = 8.2^\circ\text{C}$$

1. Heat absorbed by water

$$q_w = C_{wm} \Delta T = 4.184 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}} \times 1200 \text{g} \times 8.2^\circ\text{C} \approx 41.2 \text{ kJ}$$

2. Heat absorbed by calorimeter (extra, not absorbed by water)

$$q_c = C_c \Delta T = 837 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}} \times 8.2^\circ\text{C} \approx 6.86 \text{ kJ}$$

3. Total heat absorbed w&c.

$$q = q_w + q_c = 41.2 + 6.86 = 48.1 \text{ kJ}$$

\rightarrow Total heat released by w&c = $-q = -48.1 \text{ kJ}$

(Total heat absorbed by specimen)

ΔH in kJ/mol; octane molar mass: 114 g/mol

$\Delta H = \text{heat absorbed by specimen (ideal)} = \text{heat released (w&c)}$

$$= \frac{-48.1 \text{ kJ}}{1 \text{ g burned}} \times \frac{114 \text{ g}}{\text{mol}}$$

$$\approx -5483 \text{ kJ/mol}$$

(exothermic)