Italian National Agency for New Technologies,
Energy and Sustainable Economic Development

A feasibility analysis of D-based fusion reactions based on classical thermodynamics

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Summary

Introduction: classical thermodynamic and kinetic analysis of processes/reactions

Nuclear processes feasibility analysis: the role of entropy

Analysis of D-based fusion reactions: “thermodynamics vs. kinetics”

Conclusions

Introduction

The comparison of fission and fusion development would suggest an “intrinsic” difference among them

Fission is very spontaneous: after the discovery, the power plants were built in a few years

Fusion seems difficult to realize, very challenging under both physical and technological standpoints

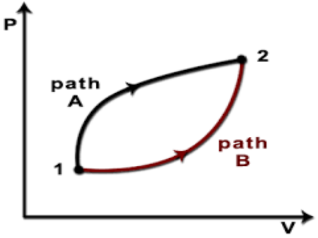
Is it reasonable to apply the “classical” thermodynamic approach to study nuclear reactions? Can thermodynamics explain the different “spontaneity level” of fusion and fission?

Thermodynamic analysis of processes/reactions

Classical thermodynamic analysis is a powerful tool to assess, at equilibrium, the spontaneity of a reaction/process

In a thermodynamic analysis is useful to rely on the assessment of state functions (U, H, S, G, … and their linear combinations)

Once an initial and final state of the reaction/process have been defined, a thermodynamic analysis is uniquely determined => the change of the state functions between the initial and final states does not depend on the intermediate states or the reaction path followed



Work (L) and heat transfer (Q) are path functions (i.e. depends on the path)
Internal energy ($U = Q - L$) is a state function

The relationship between G (the Gibbs free energy) and H (the enthalpy) and S (the entropy) is:

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

The change of *G* *at constant temperature and pressure* can be calcualted from:

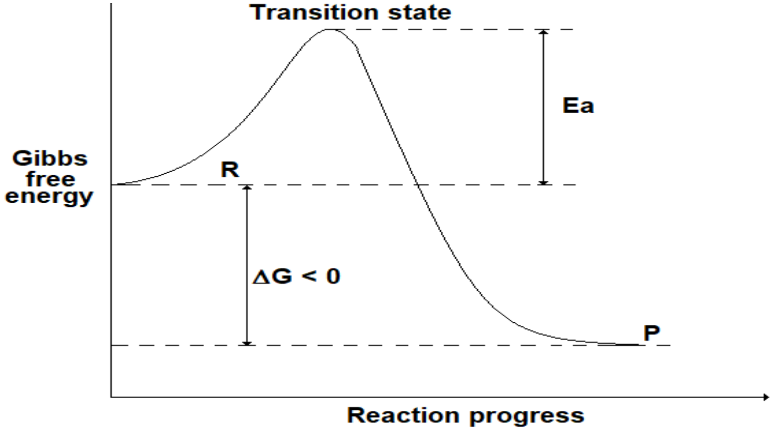
$$\boxed{\mathbf{\Delta G = \Delta H - T\,\Delta S}}$$

A reaction occurs spontaneously when **$\Delta G < 0$**, i.e. the amount of energy made available to produce work ($-\Delta G$) corresponds to the energy released ($-\Delta H = Q_{value}$) net of the entropic contribution ($T\,\Delta S$)

Kinetic analysis of processes/reactions

The thermodynamic assessment provides us no info about the reaction kinetics, i.e. the speed at which the reaction occurs. For instance, in some cases it can be verified experimentally that a spontaneous reaction ($\Delta G < 0$) proceeds very slowly making unfeasible the process studied.

To explain the kinetics of a chemical reaction, it is introduced the presence of an energy barrier (Ea, activation energy) that corresponds to a "transition state" due to the formation of intermediate compounds. The higher the energy barrier, the slower the reaction.



The reaction rate (moles of reactants that react per volume and time unit) is defined as the product of the rate constant by the concentrations of the reactants.

The rate constant (arbitrary units) can be written:

$$k = A\, e^{-\frac{Ea}{R\,T}}$$

Nuclear processes

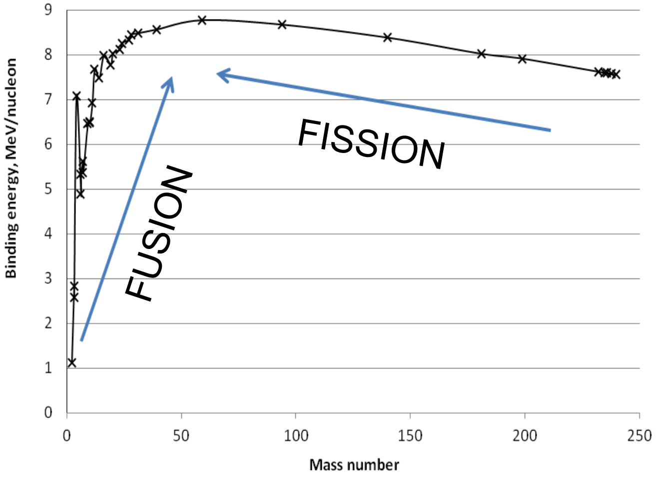
Present approach (in nuclear physics) for establishing the feasibility of a nuclear reaction/process relies on the assessment of:

- – the Q-value (in practice, a *thermodynamic* parameter related to change of enthalpy)
- – the reaction rate (a *kinetic* parameter)

Nuclear processes: thermodynamics

Exothermic nuclear reactions take place when the final products have a total mass larger than that of the reagent ones. The Q-value is calculated through the Einstein's equation relating the mass defect with the energy released by nuclear reactions:

$$E = \Delta m\ c^2$$



The "average binding energy per nucleon" vs. "mass number" exhibits a maximum at around A = 56 then identifying two regions: i) light atoms (with A < 56) merge to form a heavier nucleus (i.e. fusion reactions take place), and ii) heavy nuclei (with A > 56) split into smaller fragments (i.e. fission reactions occur).

Nuclear processes: kinetics

The reaction rate (the number of reactions per unit time and per unit volume) is proportional to the cross section that has the dimension of an area and is a measure of the probability that a nuclear reaction will occur.

In particular, in the case of a nuclear fusion reaction, two positively charged nuclei must come into contact by winning the repulsive Coulomb force. The Gamow's theory through the cross section links the probability of fusion to the tunneling of the Coulomb barrier:

$$\sigma(\varepsilon) = \frac{S(\varepsilon)}{\varepsilon}\, e^{\left(-\sqrt{\frac{\varepsilon_G}{\varepsilon}}\right)}$$

The Gamow energy (ε_G) in practice acts as an energy barrier (this formula is similar to the expression of the rate constant of chemical reactions).

Feasibility analysis of nuclear processes

This introduction allows us to conceive a series of questions:

Q1) Under the thermodynamic point of view, do the feasibility analyses of nuclear reactions miss anything?

Q2) If so, what is the rationale around the approach so far adopted?

Q3) How the entropic contribution can affect the thermodynamic analysis of fusion reactions?

Nuclear processes analysis: anything missing?

Q1) Under the thermodynamic point of view, does the feasibility analysis of nuclear reactions miss anything?

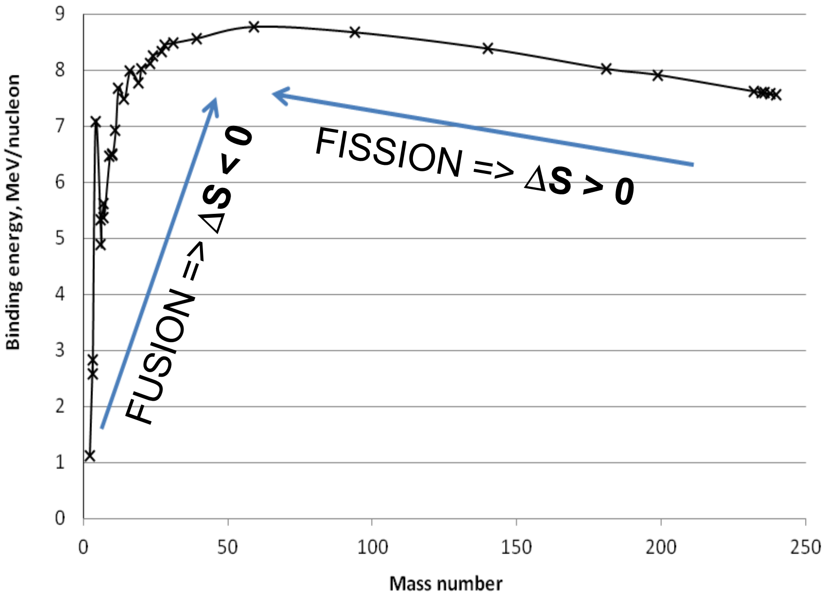
Under the thermodynamic proint of view, the feasibility analyses so far carried out have valuated only the Q-value of the nuclear reactions that corresponds to the change of enthalpy:

$$\text{Q-value} = -\Delta H$$

In other words, the entropic contribution ($T\ \Delta S$) to the change in Gibbs energy has been neglected:

$$\Delta G = \Delta H + (???)$$

Nuclear processes analysis



Fusion: light atoms merge to form a heavier nucleus => **ΔS < 0**

Fission: heavy nuclei split into smaller fragments => **ΔS > 0**

Nuclear processes analysis: the role of entropy

Q2) If so, what is the rationale around the approach so far adopted?

Nuclear reactions are characterized by releases of energy (about 1 MeV per particle) much higher than those of chemical reactions (about 1 eV per particle) and therefore they exhibit very negative ΔH:

$$|\Delta H_{nucl}| >> |\Delta H_{chim}|$$

The Gibbs energy variation values for nuclear reactions are represented in the deep (negative) part of the graph “Energy vs. T”

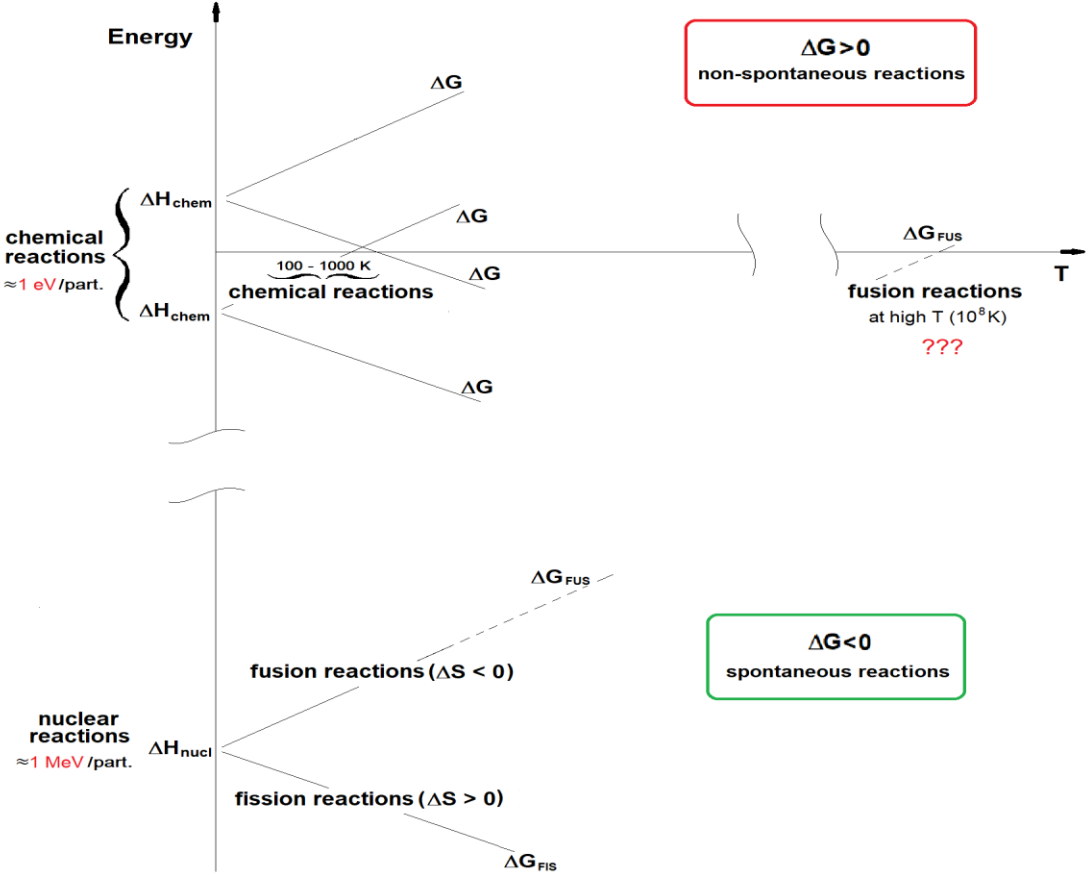
Fission reactions are expected to exhibit positive change of entropy (heavy nuclei split into smaller fragments) and the resulting ΔG is the sum of two negative terms and, therefore, is always negative:

$$\Delta H_{FIS} < 0,\ \Delta S_{FIS} > 0 \Rightarrow \Delta G_{FIS} = \Delta H - T\Delta S < 0$$

Fusion reactions exhibit negative change of entropy (light atoms merge to form a heavier nucleus) and are non-spontaneous when the term $T\Delta S$ overcomes the Q-value:

$$\Delta G_{FUS} > 0 \text{ when } |T\,\Delta S_{FUS}| > |\Delta H_{FUS}|$$

Nuclear processes analysis: the role of entropy



Nuclear processes analysis: the thermodynamic critical T*

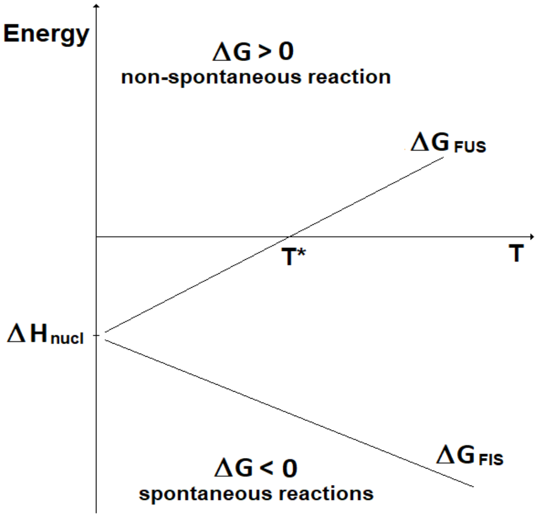
Q3) How the entropic contribution can affect the thermodynamic analysis of fusion reactions?

In fusion reactions, $\Delta S < 0$ and then a share of the energy released ($- T\,\Delta S$) is spent to make the system more ordered then reducing the level of spontaneity.

At very high temperature, the entropic term may achieve very huge values and, possibly, balances or overcomes the energy released => the temperature acts as a very powerful amplifier of the entropic term ($- T\,\Delta S$) that can balance all the enormous energy released (Q_{value}).

In a first approximation (constant P and T), the feasibility of fusion could be established by introducing a temperature T* calculated for the condition $\Delta G_{FUS} = 0$:

$$T^* = \Delta H / \Delta S \quad \text{or} \quad T^* = Q\text{-value} / |\Delta S|$$



Analysis of D-based fusion reactions

The D-based fusion reactions of interest for application in magnetic confined plasmas (tokamak) take place at around 1.5 ×10^8 K (13 keV):

DT reaction => 4He + n $^2_1H + ^3_1H = ^4_2He + ^1_0n$

with a Q-value of 17.586 MeV, maximum cross section of 5.0 barn at 64 keV

DD reaction => T + p $^2_1H + ^2_1H = ^3_1H + ^1_1p$

with a Q-value of 3.267 MeV, maximum cross section of 0.096 barn at 1250 keV

DD reaction => 3He + n $^2_1H + ^2_1H = ^3_2He + ^1_0n$

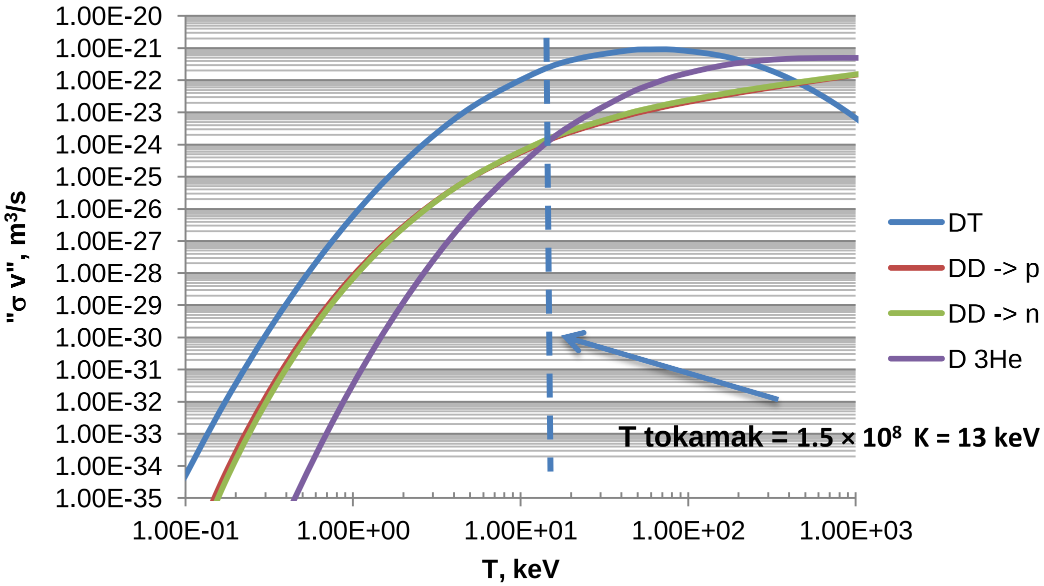
with a Q-value of 4.032 MeV, maximum cross section of 0.11 barn at 1750 keV

D 3He reaction => 4He + p $^2_1H + ^3_2He = ^4_2He + ^1_1p$

with Q-value of 18.351 MeV, a maximum cross section of 0.9 barn at 250 keV

Analysis of D-based fusion reactions: the kinetics

The reaction DT exhibits the highest reactivity at the tokamaks temperature (1.5×10^8 K, ≈ 13 keV). It is the main process considered in the designs of future fusion power plants where the tritium needed is produced by a Li-based breeding blanket surrounding the plasma chamber.



Maxwell-averaged *reactivities of D-based reactions* calculated from literature [Hively L.M., 1977, 1983]

Analysis of D-based fusion reactions: the thermodynamics

Entropy assessment via statistical thermodynamics

Sackur-Tetrode equation

$$S = n \cdot R \cdot \left[ln\left(\frac{M^{\frac{3}{2}} \cdot T^{\frac{5}{2}}}{P} \right) - 1.16 \right]$$

Such an equation can be applied to particles in form of atoms/molecules at low pressure (namely perfect gas) while its use for nucleons (neutrons, protons, etc.) could be questionable.

The **initial and final states** of the D-based reactions considered have to be selected among **those in which only particles in the form of atoms are present**.

Analysis of D-based fusion reactions: the thermodynamics

$$D + T = {}^{4}\mathrm{He} + 17.586\ \mathrm{MeV}$$

$$D + D = \mathrm{T} + 3.267\ \mathrm{MeV}$$

$$D + D = {}^{3}\mathrm{He} + 4.032\ \mathrm{MeV}$$

$$D + {}^{3}\mathrm{He} = {}^{4}\mathrm{He} + 18.351\ \mathrm{MeV}$$

The final state is specifically chosen in correspondence of the condition in which all the subatomic particles (i.e. neutrons and protons) present in the second term of D-based reactions are disappeared and their energy has been transferred to the surrounding system. In this way, the products of these reactions consist only of mono-atomic particles (^{4}He, tritium, ^{3}He) plus an amount of heat corresponding to the Q-value.

⇩

Such an assumption complies with the architecture of the tokamak machines presently studied where the energy carried by the neutrons is changed into heat at the level of the shielding and/or blanket systems.

Analysis of D-based fusion reactions: the thermodynamics

Initial state: plasma at temperature T and pressure 5 × 10^{-5} atm (≈ 5 Pa)

Final state: He or tritium atoms at 700 K (blanket/shieldings) and low pressure (1 atm)

Main hypotheses:

- the reacting particles, at plasma state, behave as a perfect gas,
- negligible effect of pressure in the assessment of entropy,
- the change in enthalpy is assumed to be constant and equal to the Q-value,
- according to the initial and final states defined for the D-based fusion reactions, **there is no contribution of nucleons** (neutrons, protons) and other sub-atomic particles **to the assessment of the thermodynamic functions**.

The relationship among the state functions “G = H – T S” is integrated between the iniatial and final states:

$$\Delta G = \Delta H - \Delta(T\ S) = -\ \text{Q-value} - [T_{fin}\ S_{fin}] + [T_{in}\ S_{in}]$$

T_{fin} = 700 K while the temperature T* (at which $\Delta G = 0$) is calculated by:

$$\text{Q-value} = [T\ S]_{T^*} - [T\ S]_{700\ K}$$

Analysis of D-based fusion reactions

Calculations of Entropy via Sackur-Tetrode:

- same entropy values for DT and D3He and for the two branches of DD,

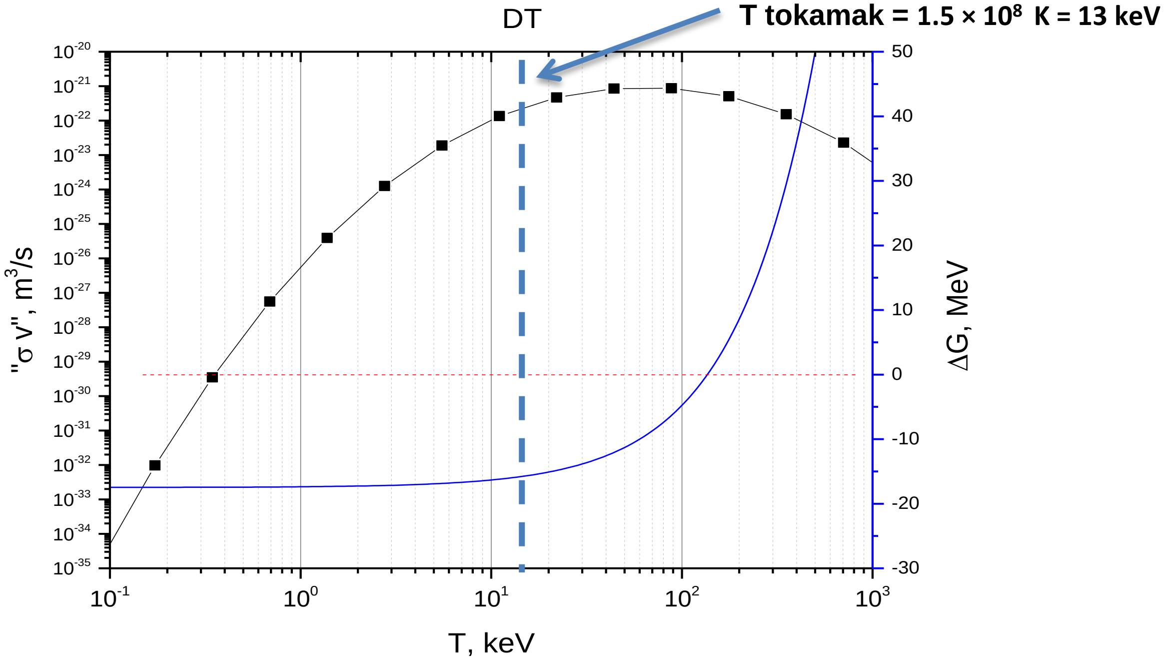
- modest effect of pressure.

The ΔG of “DT and D3He” reactions , as well as that of the “two branches of DD”, differ only for the enthalpic contribution (Q-value) that in both cases is about 0.8 MeV.

	T* **keV (K)**	**ΔG at 13 keV (1.5 ×10⁸ K)** **MeV**	**<σv> at 13 keV (1.5 ×10⁸ K)** **m³/s**	**T of σ_{max}** **keV (K)**	**ΔG (at T of σ_{max})** **MeV**
DT	1.32×10^{2} (1.58×10^{9})	- 16.0	1.91×10^{-22}	64 (7.42×10^{8})	- 9.51
DD-> ^{3}He	2.67×10^{1} (3.10×10^{8})	- 1.77	$\approx 1 \times 10^{-24}$	1750 (2.03×10^{10})	2.43×10^{2}
DD-> T	3.34×10^{1} (3.88×10^{8})	- 2.53	$\approx 1 \times 10^{-24}$	1250 (1.45×10^{10})	1.70×10^{2}
D ^{3}He	1.42×10^{2} (1.65×10^{9})	- 16.8	7.40×10^{-25}	250 (2.90×10^{9})	9.81

Analysis of D-based fusion reactions

thermodynamics ⇔ kinetics

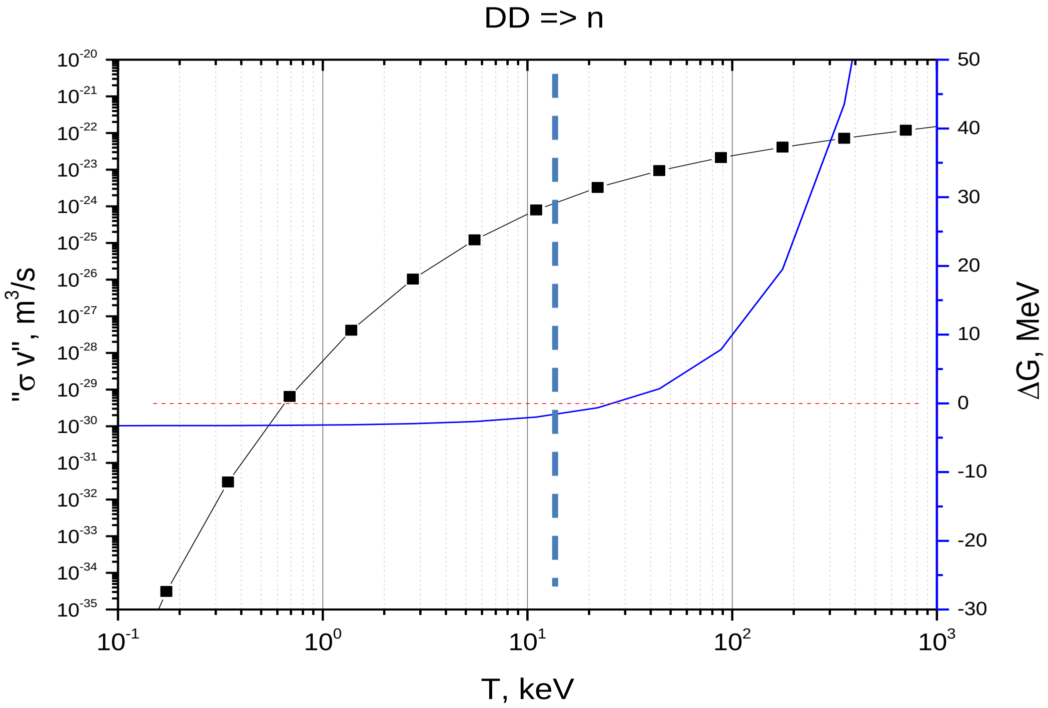


T tokamak = 1.5×10^8 K = 13 keV

The reaction DT exhibits a sound spontaneity with a value $\Delta G = -16.0$ MeV at $1.5\ 10^8$ K, a temperature that is close to its reactivity maximum (around 10^{-22} m^3/s)

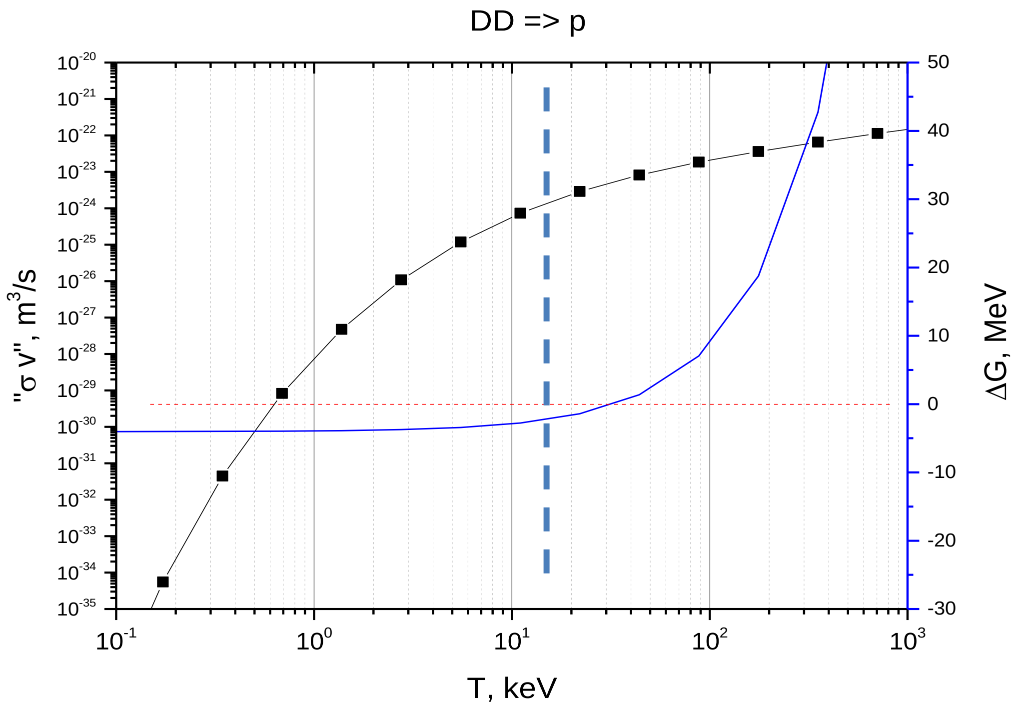
Analysis of D-based fusion reactions

thermodynamics ⇔ kinetics



Analysis of D-based fusion reactions

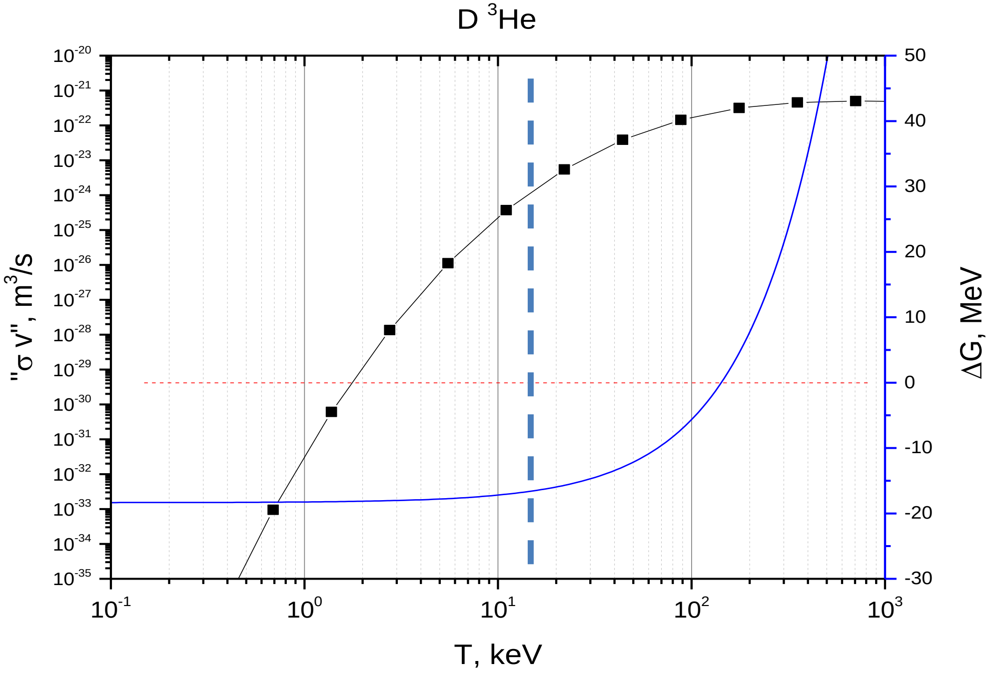
thermodynamics ⬄ kinetics



The two branches of the DD reaction exhibit poor performance in terms of both thermodynamic spontaneity and reactivity (ΔG around - 2.0 MeV and reactivity 10^{-24} m^3/s).

Analysis of D-based fusion reactions

thermodynamics ⇔ kinetics



The D^{3}He reaction exhibits at 1.5 10^8 K a ΔG similar to that of DT reaction while the reaction kinetics is near that of the DD reactions (around 10^{-24} m^3/s). An increase of the temperature (1.0 10^9 K) could improve the reactivity (up to 10^{-22} m^3/s) and keep the ΔG negative.

Conclusions 1/2

- From a thermodynamic point view, this analysis provides evidence that for the hot plasmas the operation at a very high temperature acts to reduce the feasibility of the fusion processes. In fact, the higher the temperature, the higher the share of the energy released by the fusion reaction ($Q_{value} = - \Delta H$) that is absorbed by the entropic term ($T\Delta S$). For the DT, moving from 1.5×10^9 to 3.0×10^9 K the ΔG increases (i.e. the energy released reduces) by about 1.5 MeV.

- The reaction DT is the most promising for exploiting the fusion energy in tokamaks

- The two branches of the DD reaction exhibit poor performance in terms of both thermodynamic spontaneity and reactivity (ΔG around - 2.0 MeV and reactivity 10^{-24} m^3/s). Any change of the temperature is ineffective to improve the reaction feasibility (the increase of the temperature improves the reaction kinetics but reduces the reaction conversion, and vice versa)

- The D^3He reaction could be appealing since uses a non-radioactive fuel (3He instead of tritium) and allows to directly convert a part of the plasma energy into electricity. At 1.5 10^8 K, ΔG is similar to that of DT reaction while the reaction kinetics is near that of the DD reactions (around 10^{-24} m^3/s). An increase of the temperature (1.0 10^9 K) could improve the reactivity (up to 10^{-22} m^3/s) and keep the ΔG negative but would introduce several complications (the need of a much higher plasma confinement and plasma pressure, never demonstrated experimentally).

Conclusions 2/2

Future perspectives:

- Assessment of S for neutrons, protons and other subatomic particles ….
- Plasma heating: can the thermodynamic analysis help to study the effectiveness of plasma heating? Under the thermodynamic point, how can the different heating systems affect the feasibility of fusion reactions? ….

Other (non magnetically confined) fusion approaches, open questions:

- fusion reactions carried out at low temperature (i.e. lattice confinement fusion) are thermodynamically favored although characterized by slow kinetics that could affect their reproducibility.
- and the inertial fusion?
- for fusion in the stars (*different/complex plasma regimes*) the Sackur-Tetrode cannot be applied (too much high pressures/densities), what is a suitable model for assessing the entropy?

Thank you

Acknowledgments

Luigi Marrelli
Antonino Pietropaolo

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https://www.mdpi.com/2673-4141/3/1/4

Classical Thermodynamic Analysis of D-Based Nuclear Fusion Reactions: The Role of Entropy
https://www.mdpi.com/1996-1073/16/10/3996

Backup slides

Backup slides

Thermodynamic analysis of processes/reactions

The relationship between G (the Gibbs free energy) and H (the enthalpy) and S (the entropy) is:

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

And the change of *G at constant temperature and pressure* can be calcualted from:

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

Reaction spontaneity

A reaction occurs spontaneously when $\Delta G < 0$, i.e. the amount of energy made available to produce work ($-\Delta G$) corresponds to the energy released ($-\Delta H = Q_{value}$) net of the entropic contribution ($T\,\Delta S$)

Preliminary design of units of process/chemical plants

The degree of conversion (share of reactants and products present at equilibrium) expressed by the equilibrium constant K_p can be obtained from the change of Gibbs free energy via the:

$$aA_{(g)} + bB_{(g)} \rightleftharpoons gG_{(g)} + hH_{(g)}$$

$$(\Delta H)\ \Delta G = -\,R\,T \ln K_p$$

$$K_p = \frac{p_G^g\, p_H^h}{p_A^a\, p_B^b}$$

Energy balances

Mass balances

Thermodynamic analysis of processes/reactions

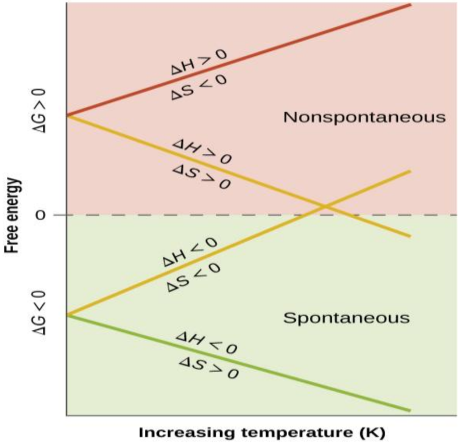
ΔG (negative) corresponds to the max. work that a system can do on the surroundings

ΔH corresponds to the heat exchanged:

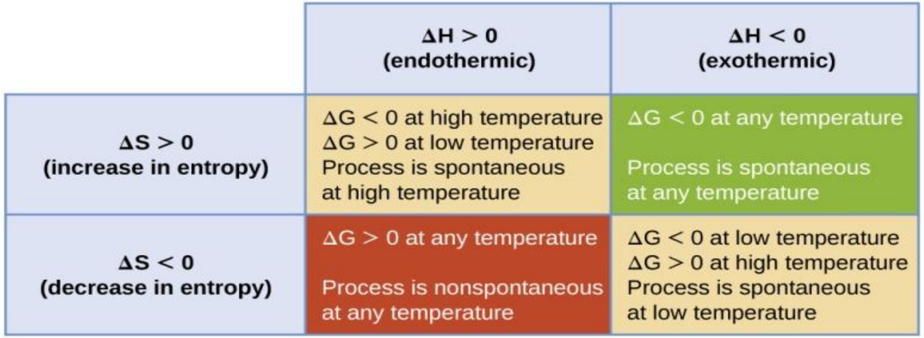
- $\Delta H < 0$ exothermic reaction
- $\Delta H > 0$ endothermic reaction

Meaning of $\Delta G = \Delta H - T\,\Delta S$:

only a part of all the energy released by an exothermic reaction ($\Delta H < 0$) is made available to perform work ($-\Delta G$) since when $\Delta S < 0$ a fraction of this work ($-T\,\Delta S$) is spent to make the system more ordered



Summary of the Four Scenarios for Enthalpy and Entropy Changes



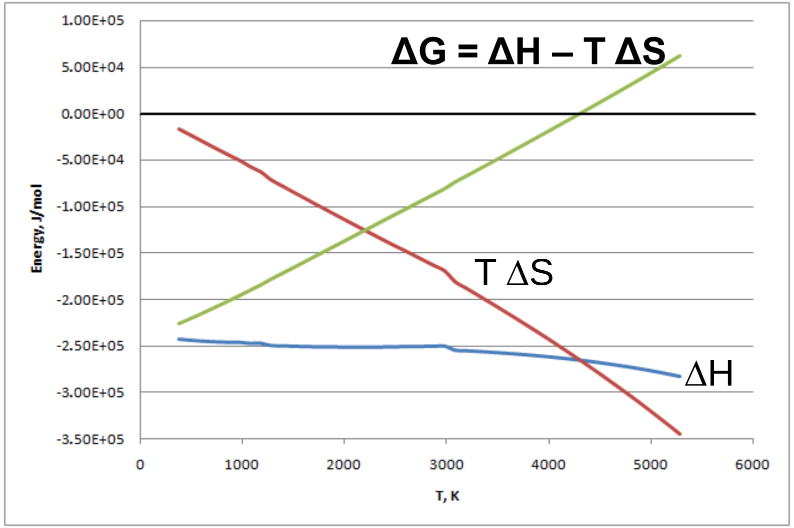
	ΔH > 0 **(endothermic)**	**ΔH < 0** **(exothermic)**
ΔS > 0 **(increase in entropy)**	ΔG < 0 at high temperature ΔG > 0 at low temperature Process is spontaneous at high temperature	ΔG < 0 at any temperature Process is spontaneous at any temperature
ΔS < 0 **(decrease in entropy)**	ΔG > 0 at any temperature Process is nonspontaneous at any temperature	ΔG < 0 at low temperature ΔG > 0 at high temperature Process is spontaneous at low temperature

Thermodynamic analysis of processes/reactions

Example. The reaction between hydrogen and oxygen to form water (e.g. the oxyhydrogen torch):

$$H_2 + 0.5\ O_2 = H_2O$$

This reaction is strongly exothermic ($\Delta H \approx -250$ kJ/mol) and occurs with a reduction of the moles number and then with a negative change of entropy ($\Delta S \approx -55$ J/mol)



The entropic term ($-T\Delta S$) increases with temperature: about 55 kJ/mol every 1000 K

⇩

At about 4500 K, all the energy released ($\Delta H \approx -250$ kJ/mol) is spent for making the system more ordered and $\Delta G = 0$ (the reaction is non-spontaneous)

The higher the temperature the more difficult and the more expensive is to make order

Analysis of D-based fusion reactions: the thermodynamics