2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 18

Room 3-442
Friday, April 12, 11:00am - 1:00pm

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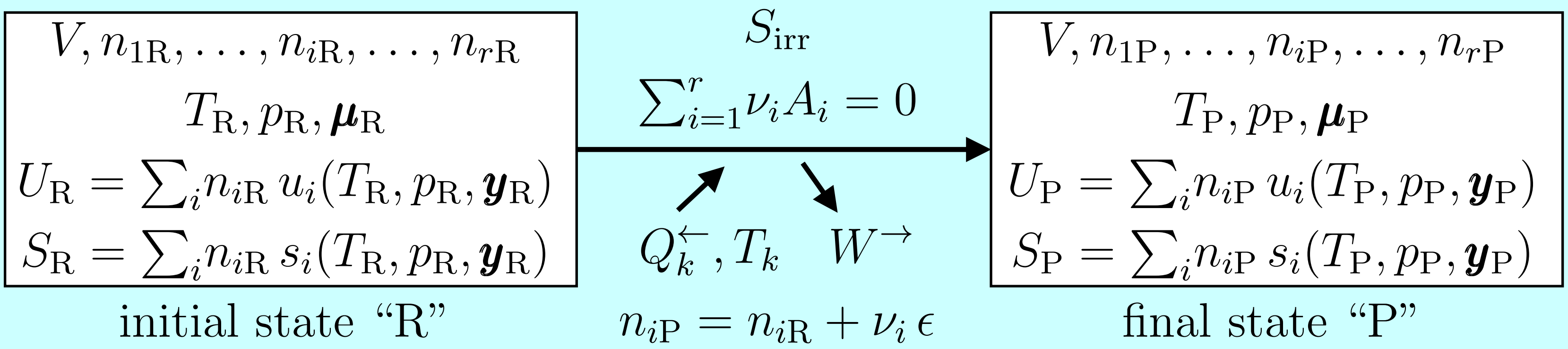
Systems with chemical reactions

energy and entropy balances
notation and stoichiometry
properties of reaction
properties of formation

Energy and entropy balances for closed and open
systems with chemical reactions



$$V, n_{1\mathrm{R}}, \ldots, n_{i\mathrm{R}}, \ldots, n_{r\mathrm{R}}$$
$$T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{\mu}_\mathrm{R}$$
$$U_\mathrm{R} = \sum_i n_{i\mathrm{R}}\, u_i(T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{y}_\mathrm{R})$$
$$S_\mathrm{R} = \sum_i n_{i\mathrm{R}}\, s_i(T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{y}_\mathrm{R})$$

initial state “R”

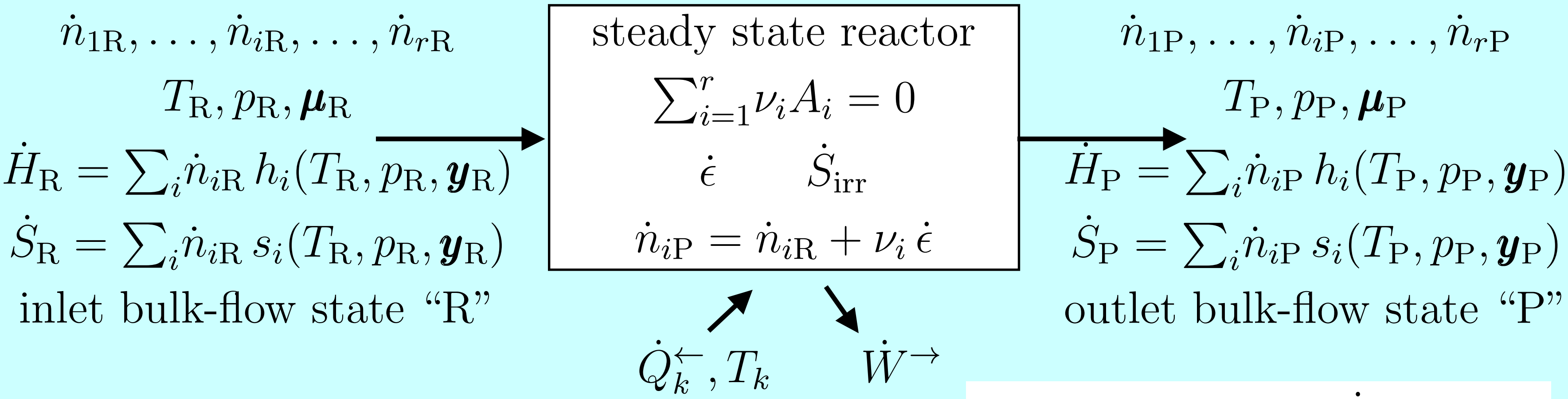
$$S_\mathrm{irr}$$
$$\sum_{i=1}^r \nu_i A_i = 0$$
$$Q_k^\leftarrow, T_k \qquad W^\rightarrow$$
$$n_{i\mathrm{P}} = n_{i\mathrm{R}} + \nu_i\, \epsilon$$

$$V, n_{1\mathrm{P}}, \ldots, n_{i\mathrm{P}}, \ldots, n_{r\mathrm{P}}$$
$$T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{\mu}_\mathrm{P}$$
$$U_\mathrm{P} = \sum_i n_{i\mathrm{P}}\, u_i(T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{y}_\mathrm{P})$$
$$S_\mathrm{P} = \sum_i n_{i\mathrm{P}}\, s_i(T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{y}_\mathrm{P})$$

final state “P”

$$U_\mathrm{P} - U_\mathrm{R} = \sum_k Q_k^\leftarrow - W^\rightarrow$$

$$S_\mathrm{P} - S_\mathrm{R} = \sum_k \frac{Q_k^\leftarrow}{T_k} + S_\mathrm{irr}$$



$$\dot n_{1\mathrm{R}}, \ldots, \dot n_{i\mathrm{R}}, \ldots, \dot n_{r\mathrm{R}}$$
$$T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{\mu}_\mathrm{R}$$
$$\dot H_\mathrm{R} = \sum_i \dot n_{i\mathrm{R}}\, h_i(T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{y}_\mathrm{R})$$
$$\dot S_\mathrm{R} = \sum_i \dot n_{i\mathrm{R}}\, s_i(T_\mathrm{R}, p_\mathrm{R}, \boldsymbol{y}_\mathrm{R})$$

inlet bulk-flow state “R”

steady state reactor

$$\sum_{i=1}^r \nu_i A_i = 0$$
$$\dot\epsilon \qquad \dot S_\mathrm{irr}$$
$$\dot n_{i\mathrm{P}} = \dot n_{i\mathrm{R}} + \nu_i\, \dot\epsilon$$

$$\dot Q_k^\leftarrow, T_k \qquad \dot W^\rightarrow$$

$$\dot n_{1\mathrm{P}}, \ldots, \dot n_{i\mathrm{P}}, \ldots, \dot n_{r\mathrm{P}}$$
$$T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{\mu}_\mathrm{P}$$
$$\dot H_\mathrm{P} = \sum_i \dot n_{i\mathrm{P}}\, h_i(T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{y}_\mathrm{P})$$
$$\dot S_\mathrm{P} = \sum_i \dot n_{i\mathrm{P}}\, s_i(T_\mathrm{P}, p_\mathrm{P}, \boldsymbol{y}_\mathrm{P})$$

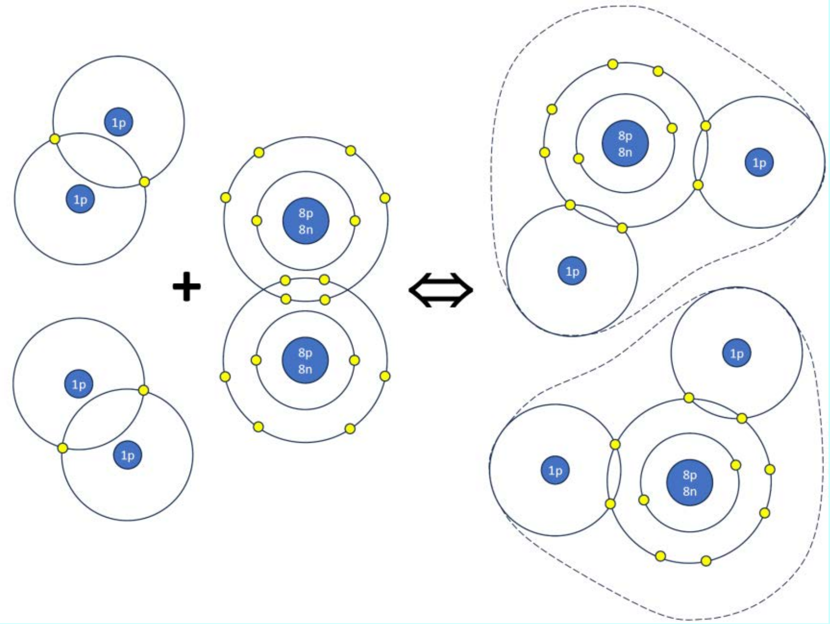
outlet bulk-flow state “P”

$$0 = \dot H_\mathrm{R} - \dot H_\mathrm{P} + \sum_k \dot Q_k^\leftarrow - \dot W^\rightarrow$$

$$0 = \dot S_\mathrm{R} - \dot S_\mathrm{P} + \sum_k \frac{\dot Q_k^\leftarrow}{T_k} + \dot S_\mathrm{irr}$$

Notation and stoichiometry:

proportionality relations, reaction coordinates



chemical reaction mechanism

$$2H_2 + O_2 = 2H_2O \quad \text{or} \quad -2H_2 - O_2 + 2H_2O = 0$$

composition: $n_{H_2},\ n_{O_2},\ n_{H_2O}$

changes in composition: $\Delta n_{H_2},\ \Delta n_{O_2},\ \Delta n_{H_2O}$

proportionality relations

$$\frac{\Delta n_{H_2}}{-2} = \frac{\Delta n_{O_2}}{-1} = \frac{\Delta n_{H_2O}}{2} = \Delta\epsilon$$

$\epsilon =$ reaction coordinate

chemical symbols

$$A_1 = H_2,\ A_2 = O_2,\ A_3 = H_2O$$

stoichiometric coefficients

$$\nu_1 = -2,\ \nu_2 = -1,\ \nu_3 = 2$$

rewrite the mechanism as

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 = 0$$

$$\boxed{\textstyle\sum_i \nu_i A_i = 0}$$

proportionality relations

$$\frac{\Delta n_1}{\nu_1} = \frac{\Delta n_2}{\nu_2} = \frac{\Delta n_3}{\nu_3} = \Delta\epsilon$$

$$\Delta n_i = \nu_i\,\Delta\epsilon \quad \forall i$$

$$\boxed{n_{i\mathrm{P}} = n_{i\mathrm{R}} + \nu_i\,\epsilon}$$

where $\epsilon = \epsilon_\mathrm{P} - \epsilon_\mathrm{R}$

$$\dot n_i = \nu_i \dot\epsilon \quad \forall i$$

$$\boxed{\dot n_{i\mathrm{P}} = \dot n_{i\mathrm{R}} + \nu_i\,\dot\epsilon}$$

Properties of reaction

The balance equations require these differences: $U_\mathrm{P}-U_\mathrm{R}$, $S_\mathrm{P}-S_\mathrm{R}$, $\dot H_\mathrm{P}-\dot H_\mathrm{R}$, $\dot S_\mathrm{P}-\dot S_\mathrm{R}$. For example,

$$U_\mathrm{P}-U_\mathrm{R} = \textstyle\sum_i n_{i\mathrm{P}}\, u_i(T_\mathrm{P},p_\mathrm{P},y_{i\mathrm{P}}) - \sum_i n_{i\mathrm{R}}\, u_i(T_\mathrm{R},p_\mathrm{R},y_{i\mathrm{R}}) = \quad \text{add and subtract } u_{ii}(T,p_o)$$

$$= \sum_i n_{i\mathrm{P}} \underbrace{\left[u_i(T_\mathrm{P},p_\mathrm{P},y_{i\mathrm{P}}) - u_{ii}(T,p_o)\right]}_{\substack{\Delta u_i^\mathrm{mix}|_{T_\mathrm{P},p_\mathrm{P}}+ \\ +u_{ii}(T_\mathrm{P},p_\mathrm{P})-u_{ii}(T,p_o)}} - \sum_i n_{i\mathrm{R}} \underbrace{\left[u_i(T_\mathrm{R},p_\mathrm{R},y_{i\mathrm{R}}) - u_{ii}(T,p_o)\right]}_{\substack{\Delta u_i^\mathrm{mix}|_{T_\mathrm{R},p_\mathrm{R}}+ \\ +u_{ii}(T_\mathrm{R},p_\mathrm{R})-u_{ii}(T,p_o)}} + \underbrace{\sum_i \underbrace{(n_{i\mathrm{P}}-n_{i\mathrm{R}})}_{\nu_i\,\epsilon}\, u_{ii}(T,p_o)}_{\epsilon\sum_i \nu_i\, u_{ii}(T,p_o) = \epsilon\,\Delta u^o(T)}$$

$$\dot H_\mathrm{P}-\dot H_\mathrm{R} = \textstyle\sum_i \dot n_{i\mathrm{P}}\, h_i(T_\mathrm{P},p_\mathrm{P},y_{i\mathrm{P}}) - \sum_i \dot n_{i\mathrm{R}}\, h_i(T_\mathrm{R},p_\mathrm{R},y_{i\mathrm{R}}) = \quad \text{add and subtract } h_{ii}(T,p_o)$$

$$= \sum_i \dot n_{i\mathrm{P}} \underbrace{\left[h_i(T_\mathrm{P},p_\mathrm{P},y_{i\mathrm{P}}) - h_{ii}(T,p_o)\right]}_{\substack{\Delta h_i^\mathrm{mix}|_{T_\mathrm{P},p_\mathrm{P}}+ \\ +h_{ii}(T_\mathrm{P},p_\mathrm{P})-h_{ii}(T,p_o)}} - \sum_i \dot n_{i\mathrm{R}} \underbrace{\left[h_i(T_\mathrm{R},p_\mathrm{R},y_{i\mathrm{R}}) - h_{ii}(T,p_o)\right]}_{\substack{\Delta h_i^\mathrm{mix}|_{T_\mathrm{R},p_\mathrm{R}}+ \\ +h_{ii}(T_\mathrm{R},p_\mathrm{R})-h_{ii}(T,p_o)}} + \underbrace{\sum_i \underbrace{(\dot n_{i\mathrm{P}}-\dot n_{i\mathrm{R}})}_{\nu_i\,\dot\epsilon}\, h_{ii}(T,p_o)}_{\dot\epsilon\sum_i \nu_i\, h_{ii}(T,p_o) = \dot\epsilon\,\Delta h^o(T)}$$

So, we defined the properties of reaction

at T and standard pressure $p_o = 1\,\mathrm{atm}$:

$$\Delta u^o(T) = \textstyle\sum_i \nu_i\, u_{ii}(T,p_o)$$
$$\Delta s^o(T) = \textstyle\sum_i \nu_i\, s_{ii}(T,p_o)$$
$$\Delta h^o(T) = \textstyle\sum_i \nu_i\, h_{ii}(T,p_o)$$
$$\Delta g^o(T) = \textstyle\sum_i \nu_i\, g_{ii}(T,p_o)$$
$$\Delta g^o(T) = \Delta h^o(T) - T\,\Delta s^o(T)$$
$$\Delta v^o(T) = \textstyle\sum_i \nu_i\, v_{ii}(T,p_o)$$
$$\Delta h^o(T) = \Delta u^o(T) + p_o\,\Delta v^o(T)$$

at STP: $T_o = 298.15\,\mathrm{K}$ and $p_o = 1\,\mathrm{atm}$:

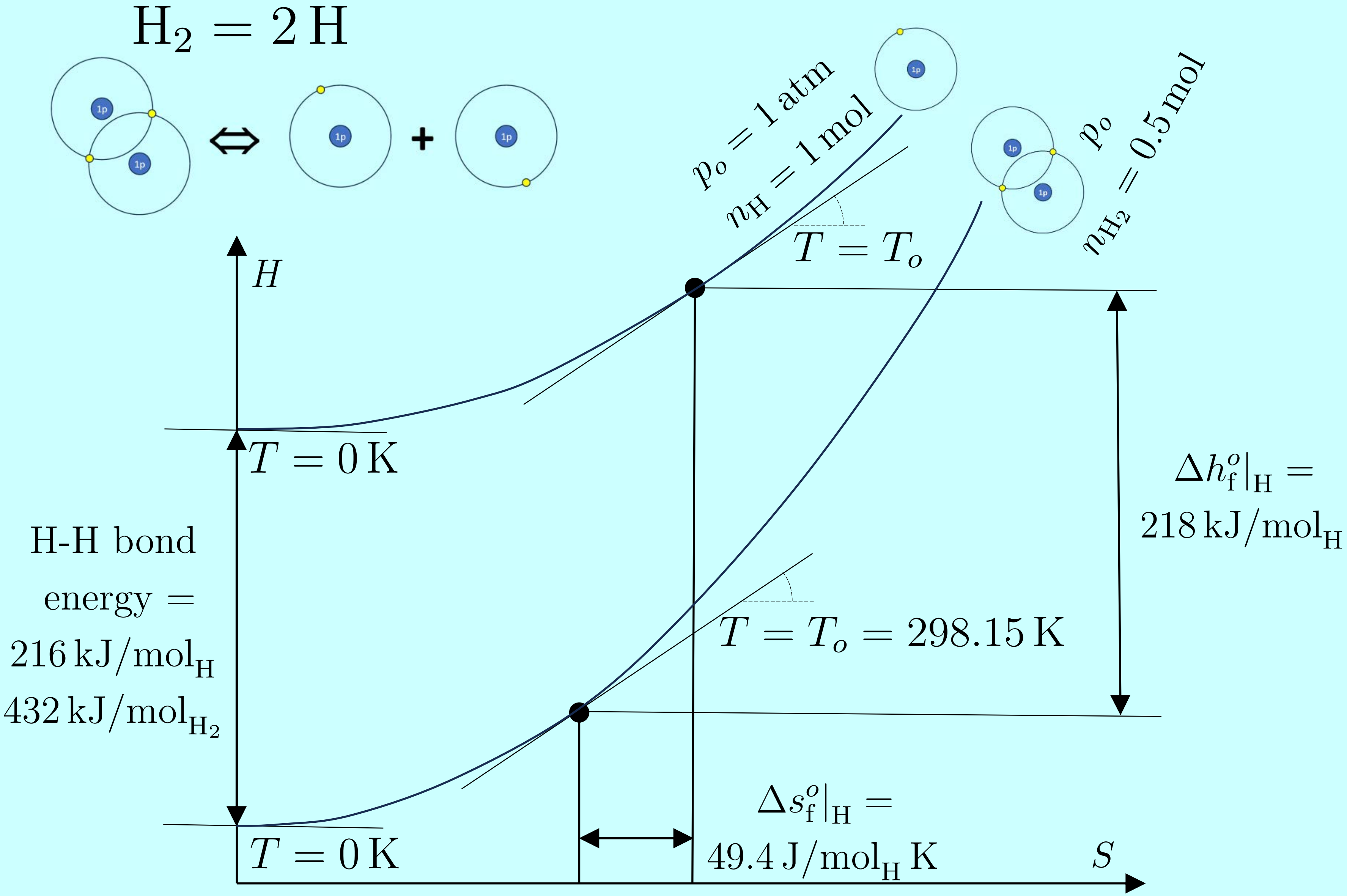
$$\Delta u^o = \textstyle\sum_i \nu_i\, u_{ii}(T_o,p_o)$$
$$\Delta s^o = \textstyle\sum_i \nu_i\, s_{ii}(T_o,p_o)$$
$$\Delta h^o = \textstyle\sum_i \nu_i\, h_{ii}(T_o,p_o)$$
$$\Delta g^o = \textstyle\sum_i \nu_i\, g_{ii}(T_o,p_o)$$
$$\Delta g^o = \Delta h^o - T_o\,\Delta s^o$$
$$\Delta v^o = \textstyle\sum_i \nu_i\, v_{ii}(T_o,p_o)$$
$$\Delta h^o = \Delta u^o + p_o\,\Delta v^o$$

using the Hess relation and the properties of formation at STP:

$$\Delta u^o = \textstyle\sum_i \nu_i\, \Delta u_\mathrm{f}^o|_i$$
$$\Delta s^o = \textstyle\sum_i \nu_i\, \Delta s_\mathrm{f}^o|_i$$
$$\Delta h^o = \textstyle\sum_i \nu_i\, \Delta h_\mathrm{f}^o|_i$$
$$\Delta g^o = \textstyle\sum_i \nu_i\, \Delta g_\mathrm{f}^o|_i$$
$$\Delta v^o = \textstyle\sum_i \nu_i\, \Delta v_\mathrm{f}^o|_i$$

Enthalpy of formation of H and H-H bond energy

$$H_2 = 2\,H$$



H-H bond energy $=$

$216\,\text{kJ/mol}_H$

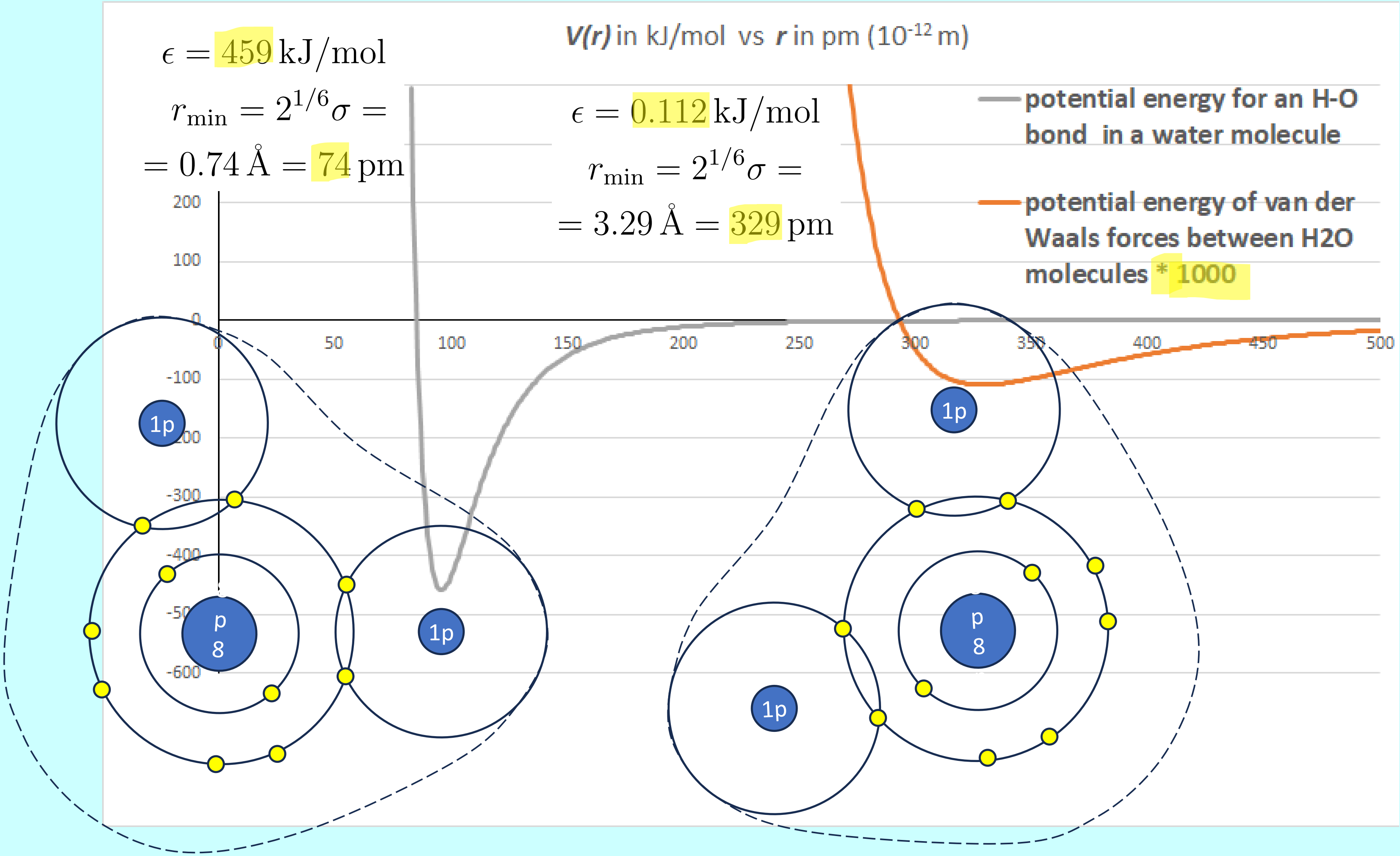
$432\,\text{kJ/mol}_{H_2}$

$\Delta h_f^o|_H =$ $218\,\text{kJ/mol}_H$

$\Delta s_f^o|_H =$ $49.4\,\text{J/mol}_H\,\text{K}$

van der Waals forces vs covalent bonds

van der Waals forces have a significant impact on the physical properties of substances, such as boiling points, melting points, and solubility. But they are very weak compared to ionic or covalent bonds.



$$\epsilon = 459\,\mathrm{kJ/mol}$$

$$r_{\min} = 2^{1/6}\sigma =$$

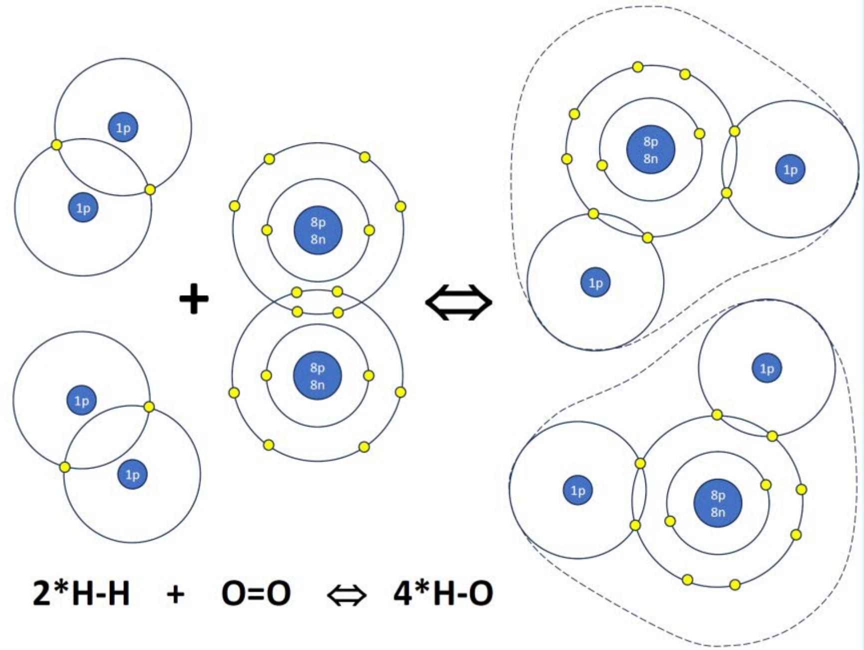
$$= 0.74\,\text{Å} = 74\,\mathrm{pm}$$

$$\epsilon = 0.112\,\mathrm{kJ/mol}$$

$$r_{\min} = 2^{1/6}\sigma =$$

$$= 3.29\,\text{Å} = 329\,\mathrm{pm}$$

Enthalpy of formation and bond energies



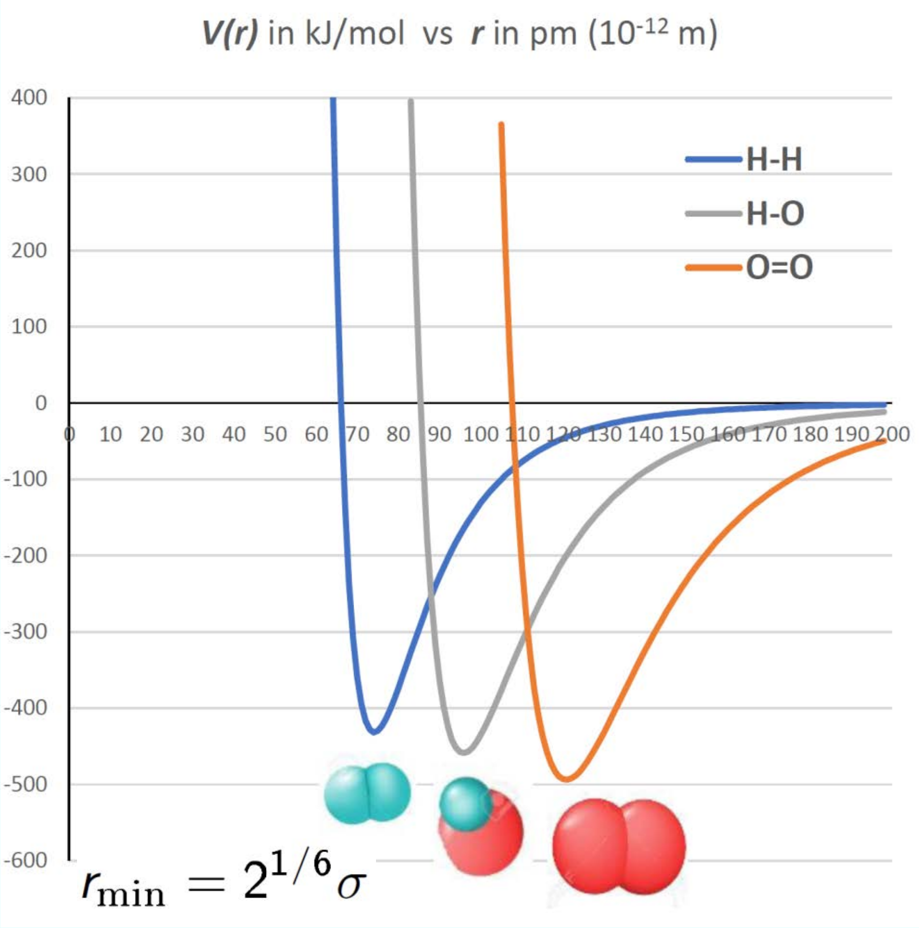
2*H-H + O=O ⇔ 4*H-O

Bond parameters	Lennard Jones		H-H	O=O	H-O
Strength	**ε**	kJ/mol	**432**	**494**	**459**
Length	**r_min**	10^{-12} m	**74.1**	**120.8**	**95.8**

2*ε(H-H) + ε(O=O) - 4*ε(H-O)	**-478**
Enthalpy of formation of 2 moles of water	**-484**

$$V_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$= \epsilon\left[\left(\frac{r_{\min}}{r}\right)^{12} - 2\left(\frac{r_{\min}}{r}\right)^{6}\right]$$


V(r) in kJ/mol vs *r* in pm (10^{-12} m)

$$r_{\min} = 2^{1/6}\sigma$$

Properties of formation and Hess relation

Define a complete set of independent elemental constituents A_j^{e}:

Completeness: for every molecule A_i there must be a reaction of formation from the A_j^{e}'s:

$$\textstyle\sum_j \alpha_{ij} A_j^{\mathrm{e}} = A_i \qquad \text{or in our notation} \qquad -\sum_j \alpha_{ij} A_j^{\mathrm{e}} + A_i = 0 \qquad \text{or also} \qquad A_i = \sum_j \alpha_{ij} A_j^{\mathrm{e}}$$

Independence: the A_j^{e}'s cannot be transformed into one another:

$$\textstyle\sum_j \beta_j A_j^{\mathrm{e}} = 0 \quad \Rightarrow \quad \beta_j = 0 \ \forall j$$

Practical choice: $\{A_j^{\mathrm{e}}\}$ = the species with nuclei of only one type that are most stable at STP, one for each atomic number Z_j^{e} in the periodic table (isotopes are chemically equivalent).

Property of formation at STP of a generic chemical species A_i:

$$\textstyle\Delta u_{\mathrm{f}}^o|_i = -\sum_j \alpha_{ij} u_{jj}^{\mathrm{e}}(T_o, p_o) + u_{ii}(T_o, p_o)$$

We can safely select $u_{jj}^{\mathrm{e}}(T_o, p_o) = 0$: in fact, for any mechanism $\sum_i \nu_i A_i = 0$ we can write:

$$\textstyle\sum_i \nu_i A_i = \sum_i \nu_i \sum_j \alpha_{ij} A_j^{\mathrm{e}} = \sum_j \left(\sum_i \nu_i \alpha_{ij}\right) A_j^{\mathrm{e}} = 0 \qquad \Rightarrow \qquad \sum_i \nu_i \alpha_{ij} = 0 \ \forall j$$

$$\textstyle\Delta u^o = \sum_i \nu_i u_{ii}(T_o, p_o) = \sum_i \nu_i \left[\Delta u_{\mathrm{f}}^o|_i + \sum_j \alpha_{ij} u_{jj}^{\mathrm{e}}(T_o, p_o)\right] = \sum_i \nu_i \Delta u_{\mathrm{f}}^o|_i + \sum_j \overbrace{\sum_i \nu_i \alpha_{ij}}\, u_{jj}^{\mathrm{e}}(T_o, p_o)$$

Therefore, we conventionally choose these references:

$$u_{jj}^{\mathrm{e}}(T_o, p_o) = 0 \qquad \text{for the } A_j^{\mathrm{e}}\text{'s and}$$

$$u_{ii}(T_o, p_o) = \Delta u_{\mathrm{f}}^o|_i \qquad \text{for all other species}$$

and use the **Hess relation**

$$\textstyle\Delta u^o = \sum_i \nu_i \Delta u_{\mathrm{f}}^o|_i$$

Careful! Properties of formation at STP are listed for the **fictitious ideal gas state** by extrapolating the ideal-gas correlations for $c_{p,ii}(T)$ from the T, p range where they hold, down to T_o, p_o:

$$h_{ii}(T_o, p_o) = h_{ii}(T, p_o) - \int_{T_o}^{T} c_{p,ii}(T')\, \mathrm{d}T' \qquad s_{ii}(T_o, p_o) = s_{ii}(T, p_o) - \int_{T_o}^{T} \frac{c_{p,ii}(T')}{T'}\, \mathrm{d}T' - R \ln \frac{p_o}{p}$$

Properties of formation and Hess relation

Hess relation $\Delta h^o = \sum_i \nu_i \, \Delta h^o_{\rm f}|_i$

For the reaction $CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$ $\qquad M_{CH_4} = 16\,\text{kg/kmol}$

$$-1(-74.9) - 2(0) + 1(-393.8) + 2(-242) = -802.9\,\text{MJ/kmol}_{CH_4} = -50.2\,\text{MJ/kg}_{CH_4}$$

For the reaction $C_8H_{18} + 12.5\,O_2 = 8\,CO_2 + 9\,H_2O$ $\qquad M_{C_8H_{18}} = 114\,\text{kg/kmol}$

$$-1(-224.3) - 12.5(0) + 8(-393.8) + 9(-242) = -5120\,\text{MJ/kmol}_{C_8H_{18}} = -44.9\,\text{MJ/kg}_{C_8H_{18}}$$

Substance	Formula	Δh^o_f MJ/kmol	Δg^o_f MJ/kmol	Δs^o_f kJ/kmol K
Acetic acid	$C_2H_4O_2$	−336.5	−286.3	−168.4
Acetone	CH_3COCH_3	−217.7	−153.2	−216.5
Acetylene	C_2H_2	226.9	209.3	58.8
Ammonia	NH_3	−45.7	−16.2	−99.1
Argon	Ar	0	0	0
Benzene	C_6H_6	83.0	129.7	−156.9
Carbon	C	0	0	0
Carbon dioxide	CO_2	−393.8	−394.6	2.9
Carbon monoxide	CO	−110.6	−137.4	89.7
Chlorine	Cl_2	0	0	0
Chloroform	$CHCl_3$	−101.3	−68.6	−109.8
Ethane	C_2H_6	−84.7	−33.0	−173.7
Ethanol	C_2H_5OH	−235.0	−168.4	−223.3
Ethylene	C_2H_4	52.3	68.2	−53.1
Fluorine	F_2	0	0	0
Freon 12	CCl_2F_2	−481.5	−442.5	−130.6
Freon 13	$CClF_3$	−695.0	−654.4	−136.2
Freon 21	$CHCl_2F$	−298.9	−268.4	−102.5
Freon 22	$CHClF_2$	−502.0	−470.9	−104.3

Substance	Formula	Δh^o_f MJ/kmol	Δg^o_f MJ/kmol	Δs^o_f kJ/kmol K
Hydrogen	H_2	0	0	0
Hydrogen (atomic)	H	218.0	203.3	49.4
Hydrogen chloride	HCl	−92.4	−95.3	10.0
Hydroxyl	OH	39.5	34.3	17.4
Isooctane	C_8H_{18}	−224.3	13.7	−798.6
Methane	CH_4	−74.9	−50.9	−80.6
Methanol	CH_3OH	−201.3	−162.6	−129.8
Methylene chloride	CH_2Cl_2	−95.5	−68.9	−89.0
Naphthalene	$C_{10}H_8$	151.1	223.7	−243.8
Nitric oxide	NO	90.4	86.8	12.4
Nitrogen	N_2	0	0	0
Nitrogen (atomic)	N	472.8	455.6	57.6
Nitrogen dioxide	NO_2	33.9	52.0	−60.8
Nitrous oxide	N_2O	81.6	103.7	−74.1
n-Octane	C_8H_{18}	−208.6	16.4	−754.6
Oxygen	O_2	0	0	0
Oxygen (atomic)	O	249.2	231.8	58.3
Ozone	O_3	142.8	162.9	−67.5
Propane	C_3H_8	−103.9	−23.5	−269.8
Propylene	CH_2CHCH_3	20.4	62.8	−142.0
Water	H_2O	−242.0	−228.8	−44.4

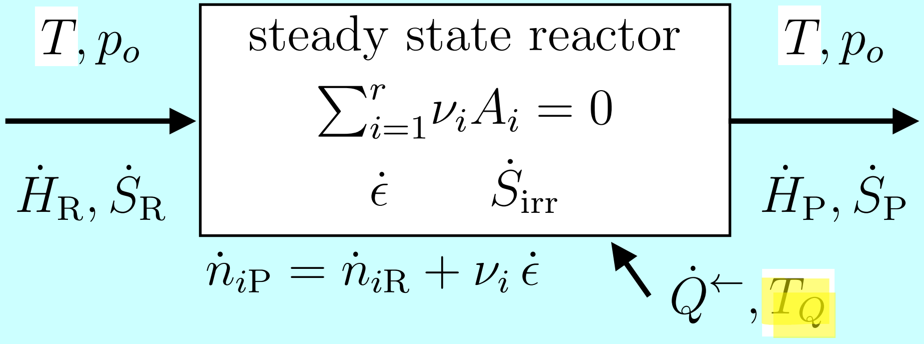
Adapted from Table 29.4 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Systems with chemical reactions

what determines the direction
of spontanueos reaction
and
how temperature affects it

Exergy
Maximum work obtainable
Minimum work required

When is an isothermobaric reaction product- or reactant-favored?



T, p_o

steady state reactor

$\sum_{i=1}^{r} \nu_i A_i = 0$

$\dot{\epsilon}$ $\dot{S}_{\rm irr}$

T, p_o

$\dot{H}_{\rm R}, \dot{S}_{\rm R}$

$\dot{H}_{\rm P}, \dot{S}_{\rm P}$

$\dot{n}_{i\rm P} = \dot{n}_{i\rm R} + \nu_i\, \dot{\epsilon}$

$\dot{Q}^{\leftarrow}, T_Q$

Assume:

- steady-state
- heat interaction at T_Q maintains inlet and outlet temperatures at T
- in and out streams are either pure component or ideal GD mixtures
- neglect mixing terms in the entropies

$$0 = \dot{H}_R(T) - \dot{H}_P(T) + \dot{Q}^{\leftarrow}$$

$$0 = \dot{S}_R(T) - \dot{S}_P(T) + \frac{\dot{Q}^{\leftarrow}}{T_Q} + \dot{S}_{\rm irr}$$

$$T_Q \dot{S}_{\rm irr} = -\dot{\epsilon}\, \underbrace{[\Delta h^o(T) - T_Q\, \Delta s^o(T)]}_{\substack{\text{this must be negative}\\ \text{for the reaction to be}\\ \text{product-favored}}} \geq 0$$

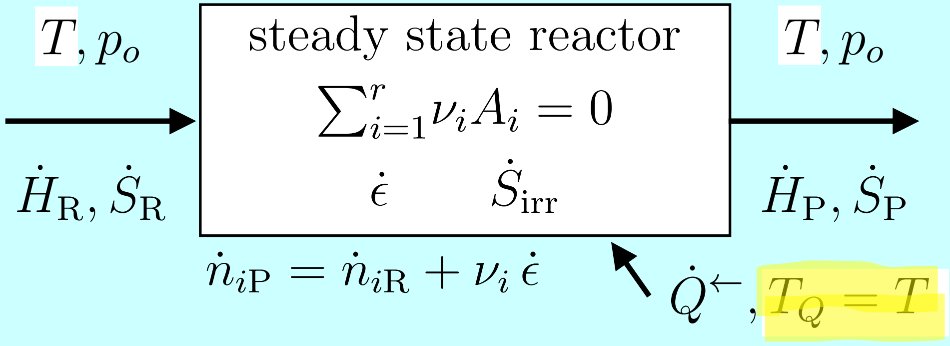
$$\dot{H}_P(T) - \dot{H}_R(T) = \dot{\epsilon}\, \Delta h^o(T)$$

$$\dot{S}_P(T) - \dot{S}_R(T) = \dot{\epsilon}\, \Delta s^o(T)$$

$$\frac{\dot{S}_{\rm irr}}{R\, \dot{\epsilon}} = -\frac{\Delta h^o(T) - T_Q\, \Delta s^o(T)}{R\, T_Q}$$

$\Delta h^o(T)$	$\Delta s^o(T)$	$\dot{\epsilon}$
< 0 (exothermic)	> 0	> 0 (at any temperature)
> 0 (endothermic)	< 0	< 0 (at any temperature)
< 0 (exothermic)	< 0	> 0 (if $-\Delta s^o(T) < -\Delta h^o(T)/T_Q$)
> 0 (endothermic)	> 0	< 0 (if $\Delta s^o(T) < \Delta h^o(T)/T_Q$)

When is an isothermobaric reaction product- or reactant-favored?



Assume:

- steady-state
- heat interaction at T_Q maintains inlet and outlet temperatures at T
- in and out streams are either pure component or ideal GD mixtures
- neglect mixing terms in the entropies

$$0 = \dot{H}_R(T) - \dot{H}_P(T) + \dot{Q}^{\leftarrow}$$

$$0 = \dot{S}_R(T) - \dot{S}_P(T) + \frac{\dot{Q}^{\leftarrow}}{T} + \dot{S}_{\rm irr}$$

$$T_Q \dot{S}_{\rm irr} = -\dot{\epsilon}\, [\Delta h^o(T) - T\, \Delta s^o(T)] = -\dot{\epsilon}\, \Delta g^o(T) \geq 0$$

$\Delta g^o(T)$ must be negative for the reaction to be product-favored

$$\dot{H}_P(T) - \dot{H}_R(T) = \dot{\epsilon}\, \Delta h^o(T)$$

$$\dot{S}_P(T) - \dot{S}_R(T) = \dot{\epsilon}\, \Delta s^o(T)$$

$$\frac{\dot{S}_{\rm irr}}{R\, \dot{\epsilon}} = -\frac{\Delta g^o(T)}{R\, T}$$

$$\frac{\rm d}{{\rm d}T} \frac{\dot{S}_{\rm irr}}{R\, \dot{\epsilon}} = -\frac{\rm d}{{\rm d}T} \frac{\Delta g^o(T)}{R\, T} = \frac{\Delta h^o(T)}{R\, T^2}$$

$\Delta h^o(T)$	$\Delta g^o(T)$	$\dot{\epsilon}$
< 0 (exothermic)	< 0	> 0 (but can go negative for lower T)
> 0 (endothermic)	< 0	> 0 (but can go negative for higher T)
< 0 (exothermic)	> 0	< 0 (but can go positive for higher T)
> 0 (endothermic)	> 0	< 0 (but can go positive for lower T)

When is an **isothermal** reaction product- or reactant-favored?

Recall $g_{ii} = \mu_{ii}$ and $h_{ii} = \left(\dfrac{\partial(\mu_{ii}/T)}{\partial(1/T)}\right)_p$

$$\frac{\mathrm{d}}{\mathrm{d}(1/T)}\frac{\Delta g^o(T)}{RT} = \frac{\mathrm{d}}{\mathrm{d}(1/T)}\frac{\sum_i \nu_i\, \mu_{ii}(T,p_o)}{RT}$$

$$= \sum_i \nu_i \frac{\mathrm{d}}{\mathrm{d}(1/T)}\frac{\mu_{ii}(T,p_o)}{RT}$$

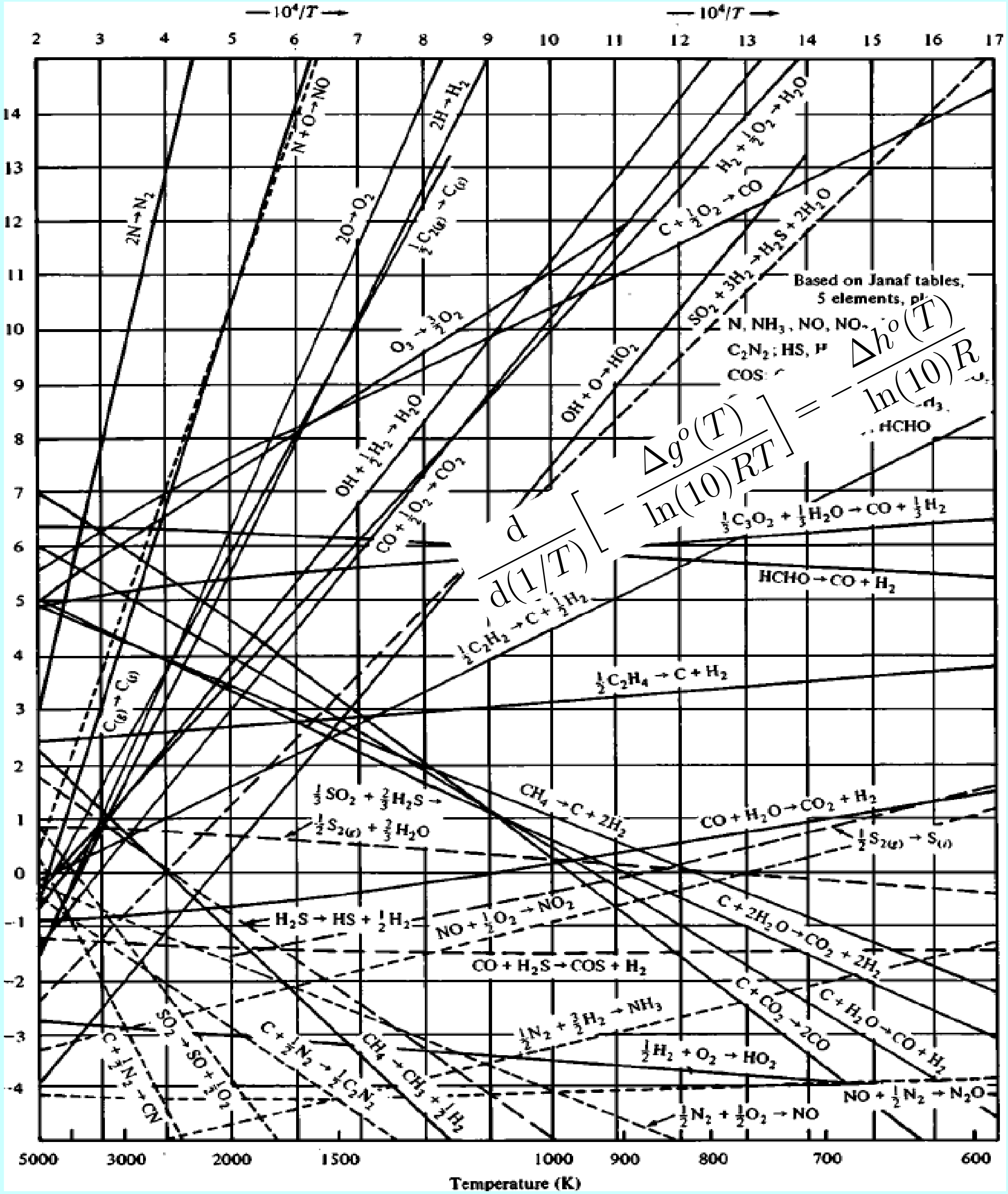
$$= \sum_i \nu_i \frac{h_{ii}(T,p_o)}{R} = \frac{\Delta h^o(T)}{R}$$

$$\frac{\dot{S}_{\mathrm{irr}}}{\ln(10)R\dot{\varepsilon}} = -\frac{\Delta g^o(T)}{\ln(10)RT}$$

product-favored

For $T = T_Q$,

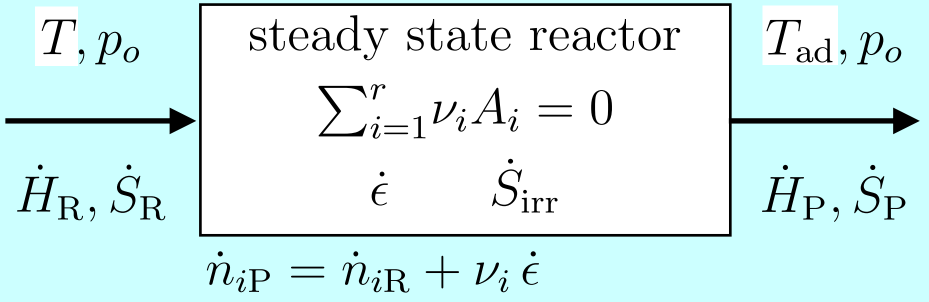
reactant-favored



$$\frac{\mathrm{d}}{\mathrm{d}(1/T)}\left[-\frac{\Delta g^o(T)}{\ln(10)RT}\right] = -\frac{\Delta h^o(T)}{\ln(10)R}$$

Adapted from Figure 30.1 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

When is an **adiabatic** reaction product- or reactant-favored?



T, p_o

steady state reactor

$\sum_{i=1}^{r} \nu_i A_i = 0$

$\dot\epsilon \qquad \dot S_{\rm irr}$

$T_{\rm ad}, p_o$

$\dot H_{\rm R}, \dot S_{\rm R}$

$\dot H_{\rm P}, \dot S_{\rm P}$

$\dot n_{i\rm P} = \dot n_{i\rm R} + \nu_i\, \dot\epsilon$

Assume:

- steady-state
- adiabatic, no heat interactions
- in and out streams are either pure component or ideal GD mixtures
- neglect mixing terms in the entropies

$$0 = \dot H_R(T) - \dot H_P(T_{\rm ad}) \quad \Rightarrow \quad \text{solve for } T_{\rm ad}$$

$$0 = \dot S_R(T) - \dot S_P(T_{\rm ad}) + \dot S_{\rm irr}$$

$$T\, \dot S_{\rm irr} = -\dot\epsilon\, \Delta g^o(T) - \dot E{\rm x}_P(T_{\rm ad}) \geq 0$$

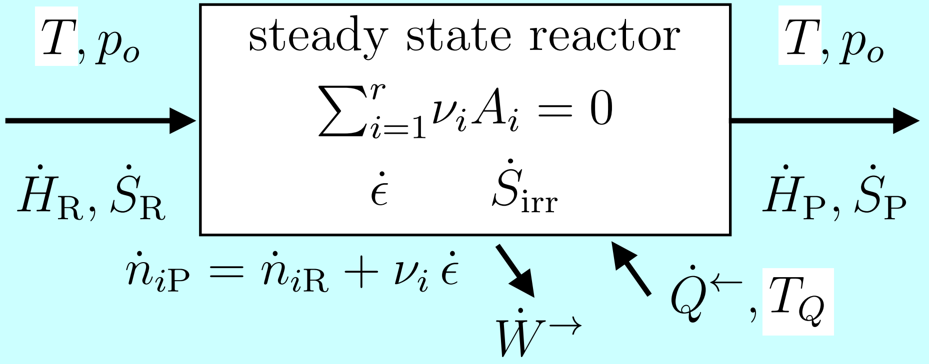
For $\dot\epsilon > 0$, $\Delta g^o(T)$ must be negative enough that $-\dot\epsilon\, \Delta g^o(T)$ is greater than the exergy* needed to heat/cool the products from enviromental T to $T_{\rm ad}$

$$\dot H_P(T) - \dot H_R(T) = \dot\epsilon\, \Delta h^o(T)$$

$$\dot S_P(T) - \dot S_R(T) = \dot\epsilon\, \Delta s^o(T)$$

$$\dot E{\rm x}_{\rm P}(T_{\rm ad}) = \dot H_P(T_{\rm ad}) - \dot H_P(T) - T\left[\dot S_P(T_{\rm ad}) - \dot S_P(T)\right]$$

Exergy / Maximum work obtainable / Minimum work required



T, p_o

steady state reactor

$\sum_{i=1}^{r} \nu_i A_i = 0$

$\dot\epsilon \qquad \dot S_{\text{irr}}$

T, p_o

$\dot H_{\text{R}}, \dot S_{\text{R}}$

$\dot H_{\text{P}}, \dot S_{\text{P}}$

$\dot n_{i\text{P}} = \dot n_{i\text{R}} + \nu_i\, \dot\epsilon$

$\dot W^{\rightarrow}$

$\dot Q^{\leftarrow}, T_Q$

Assume:

- steady-state, with a work interaction
- heat interaction at T_Q maintains inlet and outlet temperatures at T
- in and out streams are either pure component or ideal GD mixtures
- neglect mixing terms in the entropies

$$0 = \dot H_R(T) - \dot H_P(T) + \dot Q^{\leftarrow} - \dot W^{\rightarrow}$$

$$0 = \dot S_R(T) - \dot S_P(T) + \frac{\dot Q^{\leftarrow}}{T_Q} + \dot S_{\text{irr}}$$

$$\dot H_P(T) - \dot H_R(T) = \dot\epsilon\, \Delta h^o(T)$$

$$\dot S_P(T) - \dot S_R(T) = \dot\epsilon\, \Delta s^o(T)$$

$$\dot W^{\rightarrow} = -\dot\epsilon\, \underbrace{\left[\Delta h^o(T) - T_Q\, \Delta s^o(T)\right]} - T_Q \dot S_{\text{irr}}$$

this must be negative
for $\dot\epsilon > 0$ and $\dot W^{\rightarrow} > 0$

$$\dot W^{\rightarrow}_{\text{max}} = -\dot\epsilon\, [\Delta h^o(T) - T_Q\, \Delta s^o(T)]$$

Equivalently,

$$\dot W^{\leftarrow} = \dot\epsilon\, \underbrace{\left[\Delta h^o(T) - T_Q\, \Delta s^o(T)\right]} + T_Q \dot S_{\text{irr}}$$

if this is positive
$\dot\epsilon > 0$ requires $\dot W^{\leftarrow} > 0$

$$\dot W^{\leftarrow}_{\text{min}} = \dot\epsilon\, [\Delta h^o(T) - T_Q\, \Delta s^o(T)]$$

Systems with chemical reactions

Oxidation of hydrocarbons
Heating values of fuels
Exergy of a fuel
Adiabatic flame temperature

Oxidation of hydrocarbons

Overall basic reaction mechanism, assuming full oxidation

$$\boxed{C_kH_\ell + \left(k + \frac{\ell}{4}\right) O_2 = k\, CO_2 + \frac{\ell}{2} H_2O}$$

If oxygen is taken from dry air with mole fraction $y_{O_2} = 0.2095$, 1 mol of O_2 requires 4.77 mol of air. From this, the **stoichiometric air-fuel ratio** is defined as

$$\left(\frac{n_{\rm air}}{n_{\rm fuel}}\right)_{\rm s} = 4.77\left(k + \frac{\ell}{4}\right) \qquad \left(\frac{m_{\rm air}}{m_{\rm fuel}}\right)_{\rm s} = 4.77\left(k + \frac{\ell}{4}\right)\frac{28.96}{M_{\rm fuel}}$$

Moreover, in order to increase the probability of having the oxidation of all the molecules, an excess of air is usually used i.e. $n_{air} = (n_{air})_{\rm s} + (n_{air})_{\rm excess}$, so that the **equivalence ratio** is defined

$$\lambda = \frac{n_{\rm air}/n_{\rm fuel}}{(n_{\rm air}/n_{\rm fuel})_{\rm s}} = \frac{m_{\rm air}/m_{\rm fuel}}{(m_{\rm air}/m_{\rm fuel})_{\rm s}} > 1$$

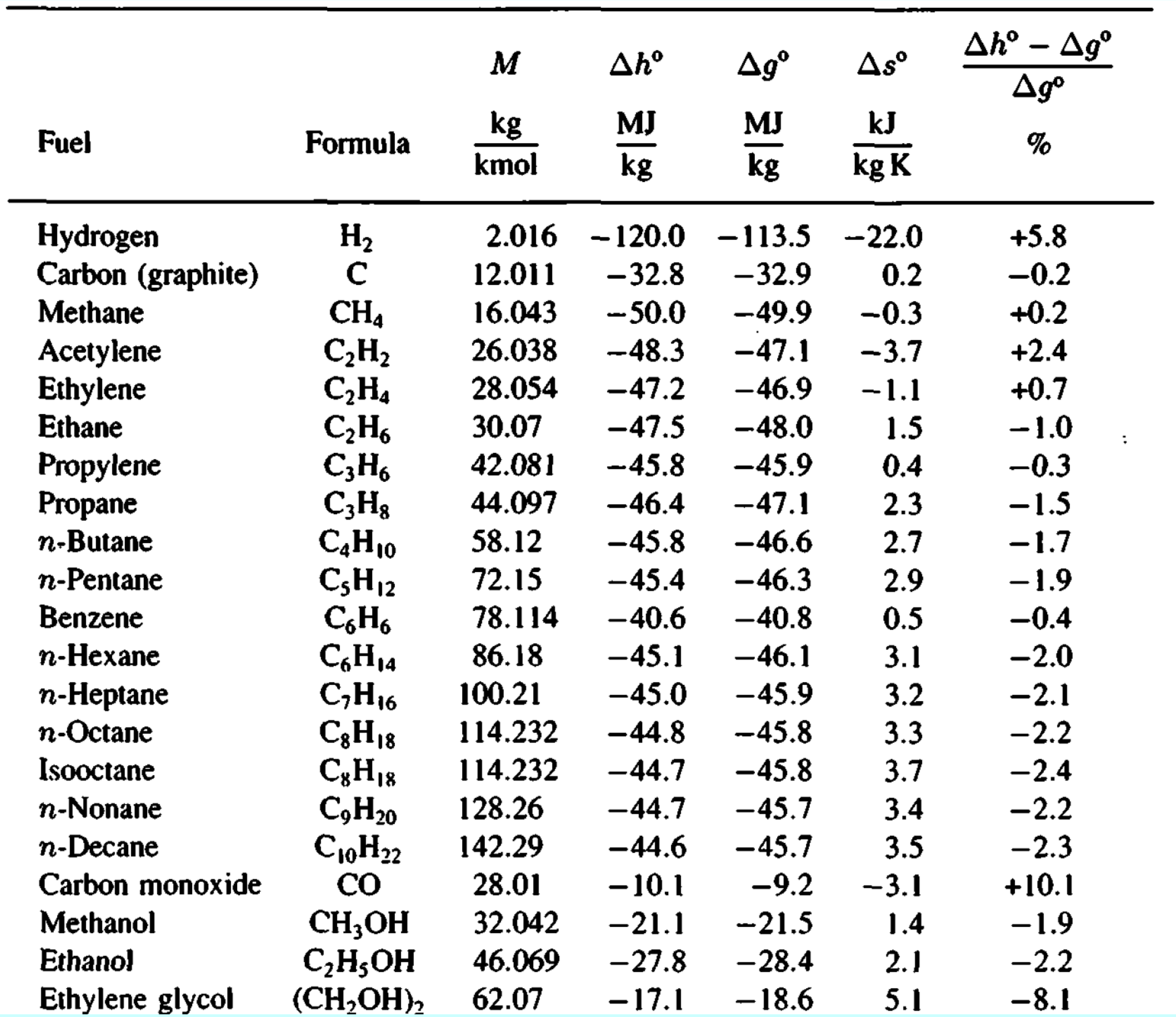
For most hydrocarbons (except H_2)

$$\boxed{-2.4\% < \frac{\Delta h^0 - \Delta g^0}{\Delta g^0} < +2.4\%}$$

and

$$\boxed{40\,\mathrm{MJ/kg} < \mathrm{LHV} = -\Delta h^o < 50\,\mathrm{MJ/kg}}$$

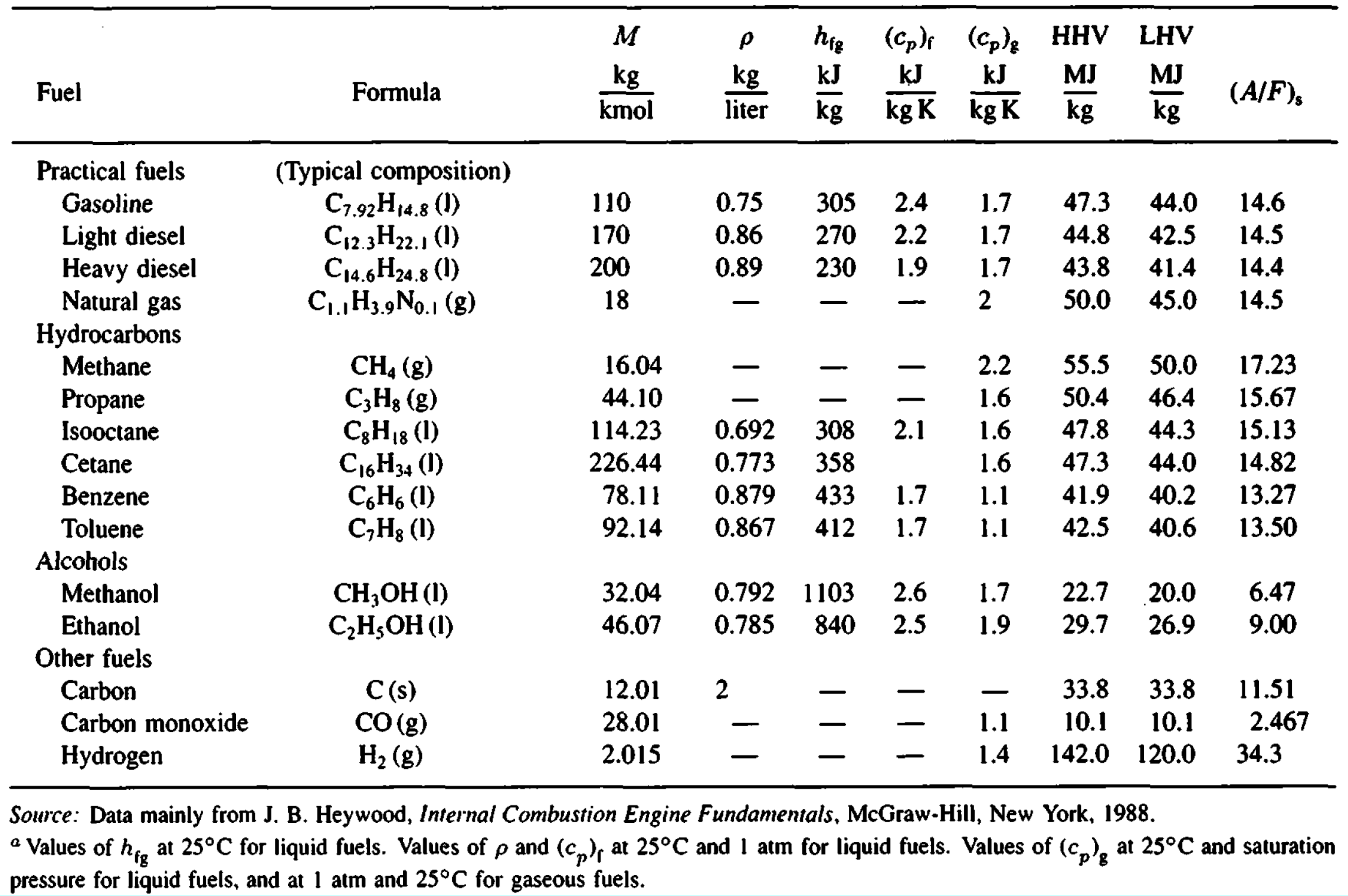
Properties of the reaction of oxidation of hydrocarbons



Fuel	Formula	M $\frac{\text{kg}}{\text{kmol}}$	Δh° $\frac{\text{MJ}}{\text{kg}}$	Δg° $\frac{\text{MJ}}{\text{kg}}$	Δs° $\frac{\text{kJ}}{\text{kg K}}$	$\frac{\Delta h^\circ - \Delta g^\circ}{\Delta g^\circ}$ %
Hydrogen	H_2	2.016	−120.0	−113.5	−22.0	+5.8
Carbon (graphite)	C	12.011	−32.8	−32.9	0.2	−0.2
Methane	CH_4	16.043	−50.0	−49.9	−0.3	+0.2
Acetylene	C_2H_2	26.038	−48.3	−47.1	−3.7	+2.4
Ethylene	C_2H_4	28.054	−47.2	−46.9	−1.1	+0.7
Ethane	C_2H_6	30.07	−47.5	−48.0	1.5	−1.0
Propylene	C_3H_6	42.081	−45.8	−45.9	0.4	−0.3
Propane	C_3H_8	44.097	−46.4	−47.1	2.3	−1.5
n-Butane	C_4H_{10}	58.12	−45.8	−46.6	2.7	−1.7
n-Pentane	C_5H_{12}	72.15	−45.4	−46.3	2.9	−1.9
Benzene	C_6H_6	78.114	−40.6	−40.8	0.5	−0.4
n-Hexane	C_6H_{14}	86.18	−45.1	−46.1	3.1	−2.0
n-Heptane	C_7H_{16}	100.21	−45.0	−45.9	3.2	−2.1
n-Octane	C_8H_{18}	114.232	−44.8	−45.8	3.3	−2.2
Isooctane	C_8H_{18}	114.232	−44.7	−45.8	3.7	−2.4
n-Nonane	C_9H_{20}	128.26	−44.7	−45.7	3.4	−2.2
n-Decane	$C_{10}H_{22}$	142.29	−44.6	−45.7	3.5	−2.3
Carbon monoxide	CO	28.01	−10.1	−9.2	−3.1	+10.1
Methanol	CH_3OH	32.042	−21.1	−21.5	1.4	−1.9
Ethanol	C_2H_5OH	46.069	−27.8	−28.4	2.1	−2.2
Ethylene glycol	$(CH_2OH)_2$	62.07	−17.1	−18.6	5.1	−8.1

Adapted from Figure 31.7 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Heating values of fuels



Fuel	Formula	M $\frac{\text{kg}}{\text{kmol}}$	ρ $\frac{\text{kg}}{\text{liter}}$	h_{fg} $\frac{\text{kJ}}{\text{kg}}$	$(c_p)_f$ $\frac{\text{kJ}}{\text{kg K}}$	$(c_p)_g$ $\frac{\text{kJ}}{\text{kg K}}$	HHV $\frac{\text{MJ}}{\text{kg}}$	LHV $\frac{\text{MJ}}{\text{kg}}$	$(A/F)_s$
Practical fuels	(Typical composition)								
Gasoline	$C_{7.92}H_{14.8}$ (l)	110	0.75	305	2.4	1.7	47.3	44.0	14.6
Light diesel	$C_{12.3}H_{22.1}$ (l)	170	0.86	270	2.2	1.7	44.8	42.5	14.5
Heavy diesel	$C_{14.6}H_{24.8}$ (l)	200	0.89	230	1.9	1.7	43.8	41.4	14.4
Natural gas	$C_{1.1}H_{3.9}N_{0.1}$ (g)	18	—	—	—	2	50.0	45.0	14.5
Hydrocarbons									
Methane	CH_4 (g)	16.04	—	—	—	2.2	55.5	50.0	17.23
Propane	C_3H_8 (g)	44.10	—	—	—	1.6	50.4	46.4	15.67
Isooctane	C_8H_{18} (l)	114.23	0.692	308	2.1	1.6	47.8	44.3	15.13
Cetane	$C_{16}H_{34}$ (l)	226.44	0.773	358		1.6	47.3	44.0	14.82
Benzene	C_6H_6 (l)	78.11	0.879	433	1.7	1.1	41.9	40.2	13.27
Toluene	C_7H_8 (l)	92.14	0.867	412	1.7	1.1	42.5	40.6	13.50
Alcohols									
Methanol	CH_3OH (l)	32.04	0.792	1103	2.6	1.7	22.7	20.0	6.47
Ethanol	C_2H_5OH (l)	46.07	0.785	840	2.5	1.9	29.7	26.9	9.00
Other fuels									
Carbon	C (s)	12.01	2	—	—	—	33.8	33.8	11.51
Carbon monoxide	CO (g)	28.01	—	—	—	1.1	10.1	10.1	2.467
Hydrogen	H_2 (g)	2.015	—	—	—	1.4	142.0	120.0	34.3

Source: Data mainly from J. B. Heywood, *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York, 1988.

[a] Values of h_{fg} at 25°C for liquid fuels. Values of ρ and $(c_p)_f$ at 25°C and 1 atm for liquid fuels. Values of $(c_p)_g$ at 25°C and saturation pressure for liquid fuels, and at 1 atm and 25°C for gaseous fuels.

Adapted from Figure 31.1 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Lower and higher heating values of fuels

In combustion, water is present both in reactants (moist air) and in products, this complicates the stoichiometry. The highest possible mole fraction of water vapor in the gaseous mixture of products of combustion is given by Raoult's law ($1 = \mathrm{H_2O}$)

$$y_{1\mathrm{g}}^{\max} p = p_{\mathrm{sat},11}^{\mathrm{fg}}(T) \quad \text{where } y_{1\mathrm{f}} = 1 \text{ (condensate is pure liquid water)}$$

Let $\phi = y_{1\mathrm{g}}/y_{1\mathrm{g}}^{\max}$ be the relative humidity of the products of combustion in the gaseous phase. Since $p_{\mathrm{sat},11}^{\mathrm{fg}}(25\,^\circ\mathrm{C}) = 3.169\,\mathrm{kPa}$, at STP ($T_o = 25\,^\circ\mathrm{C}$ and $p_o = 1\,\mathrm{atm}$), the maximum amount of vapor is $y_{1\mathrm{g}}^{\max} = 3.169/101.325 = 0.0316$, so that by splitting water vapor and condensate, i.e., $n_{\mathrm{H_2O}} = n_{\mathrm{H_2O,g}} + n_{\mathrm{H_2O,f}}$ we get

$$\left.\begin{aligned}
&\frac{n_{\mathrm{H_2O}}}{n_{\mathrm{C}_k\mathrm{H}_\ell}} = \frac{n_{\mathrm{H_2O,f}}}{n_{\mathrm{C}_k\mathrm{H}_\ell}} + \frac{n_{\mathrm{H_2O,g}}}{n_{\mathrm{C}_k\mathrm{H}_\ell}} = \frac{\ell}{2} \\
&\frac{n_{\mathrm{tot,prod}}}{n_{\mathrm{C}_k\mathrm{H}_\ell}} = \frac{\ell}{4} + 4.77\left(k + \frac{\ell}{4}\right) \\
&\frac{n_{\mathrm{H_2O},g}}{n_{\mathrm{tot,prod}} - n_{\mathrm{H_2O,f}}} = y_{1\mathrm{g}} \le 0.0316
\end{aligned}\right\} \Rightarrow \quad \frac{n_{\mathrm{H_2O,g}}}{n_{\mathrm{C}_k\mathrm{H}_\ell}} \le \frac{0.0316\left[4.77\left(k + \frac{\ell}{4}\right) - \frac{\ell}{4}\right]}{1 - 0.0316} = 0.123\,\ell + 0.156\,k$$

so that when $\ell/2$ exceeds this amount, i.e., when $\ell/k > 0.414$, then part of the water condenses

$$\frac{n_{\mathrm{H_2O,f}}}{n_{\mathrm{C}_k\mathrm{H}_\ell}} = \frac{\frac{\ell}{2} - 0.0316\left[\frac{\ell}{2} + 4.77\left(k + \frac{\ell}{4}\right)\right]}{1 - 0.0316} = 0.469\,\ell - 0.156\,k$$

meaning that the $\dot{Q}_o^{\rightarrow}$ extracted is not only given by $\dot{n}_{\mathrm{C}_k\mathrm{H}_\ell}\Delta h^o$ but also by the condensation enthalpy

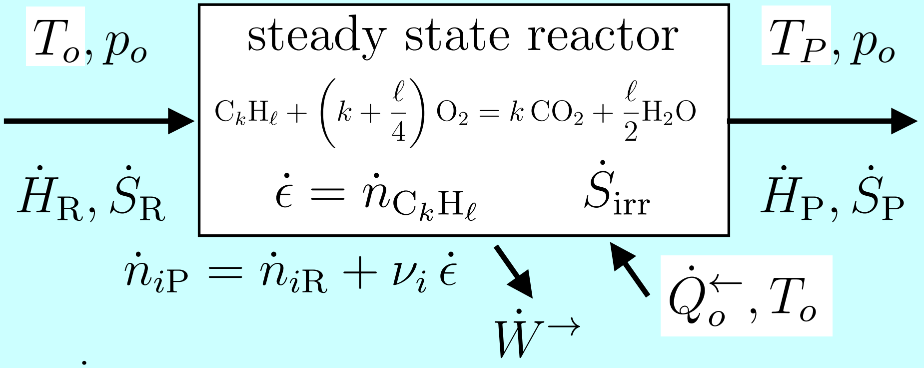
$$\dot{Q}_o^{\rightarrow} = \dot{H}_R^o - \dot{H}_P^o = \dot{n}_{\mathrm{C}_k\mathrm{H}_\ell}\mathrm{HV}_{\mathrm{actual}} \qquad \text{where} \qquad \mathrm{HV}_{\mathrm{actual}} = -\Delta h^o + \frac{\dot{n}_{\mathrm{H_2O,f}}}{\dot{n}_{\mathrm{C}_k\mathrm{H}_\ell}} h_{\mathrm{H_2O,fg}}(T_o)$$

With less details, in the common practice one defines the lower and higher heating values

$$\mathrm{LHV} = -\Delta h^o \qquad \text{and} \qquad \mathrm{HHV} = -\Delta h^o + \frac{\ell}{2} h_{\mathrm{H_2O,fg}}(T_o)$$

For example, for methane, LHV, $\mathrm{HV}_{\mathrm{actual}}$, and HHV are, respectively, 50.1, 54.7, and 55.5 MJ/kg.

Heating value and Exergy of a fuel / Adiabatic flame temperature



T_o, p_o

steady state reactor

$\mathrm{C}_k\mathrm{H}_\ell + \left(k + \frac{\ell}{4}\right) \mathrm{O}_2 = k\,\mathrm{CO}_2 + \frac{\ell}{2}\mathrm{H}_2\mathrm{O}$

$\dot{\epsilon} = \dot{n}_{\mathrm{C}_k\mathrm{H}_\ell}$ $\quad \dot{S}_{\mathrm{irr}}$

T_P, p_o

$\dot{H}_\mathrm{R}, \dot{S}_\mathrm{R}$

$\dot{H}_\mathrm{P}, \dot{S}_\mathrm{P}$

$\dot{n}_{i\mathrm{P}} = \dot{n}_{i\mathrm{R}} + \nu_i\,\dot{\epsilon}$

$\dot{W}^{\rightarrow}$

$\dot{Q}_o^{\leftarrow}, T_o$

Heating value setup: $T_\mathrm{P} = T_o$, $\dot{W}^{\rightarrow} = 0$, $\dot{\epsilon} = \dot{n}_{\mathrm{C}_k\mathrm{H}_\ell}$

$$\dot{Q}_o^{\rightarrow} = \dot{H}_R^o - \dot{H}_P^o = \dot{\epsilon}\,\mathrm{HV}_\mathrm{actual} \quad \text{where} \quad \mathrm{HV}_\mathrm{actual} = -\Delta h^o + \frac{\dot{n}_{\mathrm{H_2O,f}}}{\dot{n}_{\mathrm{C}_k\mathrm{H}_\ell}}\, h_{\mathrm{H_2O,fg}}(T_o)$$

Exergy setup: $T_\mathrm{P} = T_o$, $\dot{W}^{\rightarrow} = \dot{W}^{\rightarrow}_\mathrm{max}$, $\dot{S}_\mathrm{irr} = 0$

$$\dot{W}^{\rightarrow}_\mathrm{max} = \dot{H}_R^o - \dot{H}_P^o - T_o\left(\dot{S}_R^o - \dot{S}_P^o\right) = \dot{\epsilon}\,Ex_{\mathrm{C}_k\mathrm{H}_\ell} \quad \text{where} \quad Ex_{\mathrm{C}_k\mathrm{H}_\ell} = -\Delta h^o + T_o\,\Delta s^o = -\Delta g^o$$

Notice that condensation does not contribute because $h_{\mathrm{H_2O,fg}}(T_o) - T_o\, s_{\mathrm{H_2O,fg}}(T_o) = 0$.

Adiabatic flame temperature setup: $T_\mathrm{P} = T_\mathrm{ad}$, $\dot{Q}_o^{\rightarrow} = 0$, $\dot{W}^{\rightarrow} = 0$, assume ideal GD mix of ideal gases

$$0 = \dot{H}_R^o - \dot{H}_P(T_\mathrm{ad}) = \dot{H}_R^o - \dot{H}_P^o + \dot{H}_P^o - \dot{H}_P(T_\mathrm{ad}) = \dot{\epsilon}\,\mathrm{HV}_\mathrm{actual} - \dot{n}_\mathrm{P}\int_{T_o}^{T_\mathrm{ad}} \sum_i y_{i\mathrm{P}}\, c_{p,ii}(T')\,\mathrm{d}T' \;\Rightarrow\; \begin{array}{c}\text{solve}\\ \text{for } T_\mathrm{ad}\end{array}$$

$$\dot{S}_\mathrm{irr} = \dot{S}_P(T_\mathrm{ad}) - \dot{S}_R^o = \dot{S}_P(T_\mathrm{ad}) - \dot{S}_P^o + \dot{S}_P^o - \dot{S}_R^o = \dot{n}_\mathrm{P}\int_{T_o}^{T_\mathrm{ad}} \frac{\sum_i y_{i\mathrm{P}}\, c_{p,ii}(T')}{T'}\,\mathrm{d}T' + \dot{\epsilon}\,\Delta s^o \approx -0.3\,\dot{\epsilon}\,\frac{\Delta g^o}{T_o}$$

Typical values of $\dfrac{T_o \dot{S}_\mathrm{irr}}{-\dot{\epsilon}\,\Delta g^o}$ are in the range 26% to 30%

Adiabatic flame temperature calculations

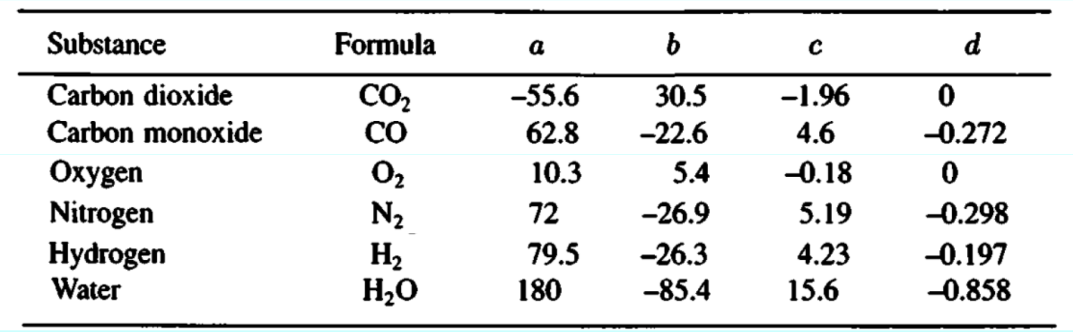
$$c_{p,ii}(T) = a_{ii} + b_{ii}T^{1/4} + c_{ii}T^{1/2} + d_{ii}T^{3/4}$$

$$\sum_i y_{i\mathrm{P}}\, c_{p,ii}(T) = a + b\,T^{1/4} + c\,T^{1/2} + d\,T^{3/4}$$

$$\text{where } a = \sum_i y_{i\mathrm{P}}\, a_{ii} \quad b = \sum_i y_{i\mathrm{P}}\, b_{ii} \quad c = \sum_i y_{i\mathrm{P}}\, c_{ii} \quad d = \sum_i y_{i\mathrm{P}}\, d_{ii}$$

$$\int_{T_o}^{T_{\mathrm{ad}}} \sum_i y_{i\mathrm{P}}\, c_{p,ii}(T')\,\mathrm{d}T' = a\,(T_{\mathrm{ad}} - T_o) + \frac{4}{5}b\,(T_{\mathrm{ad}}^{5/4} - T_o^{5/4}) + \frac{2}{3}c\,(T_{\mathrm{ad}}^{3/2} - T_o^{3/2}) + \frac{4}{7}d\,(T_{\mathrm{ad}}^{7/4} - T_o^{7/4})$$

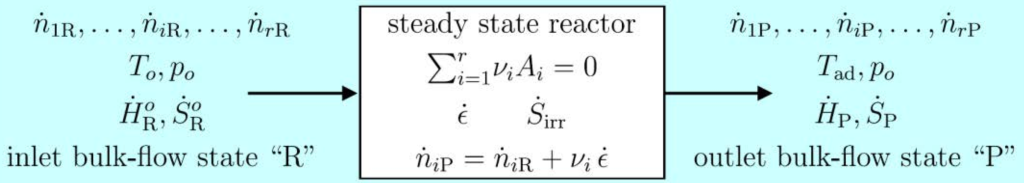
$$\int_{T_o}^{T_{\mathrm{ad}}} \frac{\sum_i y_{i\mathrm{P}}\, c_{p,ii}(T')}{T'}\,\mathrm{d}T' = a\,\ln\frac{T_{\mathrm{ad}}}{T_o} + 4b\,(T_{\mathrm{ad}}^{1/4} - T_o^{1/4}) + 2c\,(T_{\mathrm{ad}}^{1/2} - T_o^{1/2}) + \frac{4}{3}d\,(T_{\mathrm{ad}}^{3/4} - T_o^{3/4})$$



Substance	Formula	a	b	c	d
Carbon dioxide	CO_2	–55.6	30.5	–1.96	0
Carbon monoxide	CO	62.8	–22.6	4.6	–0.272
Oxygen	O_2	10.3	5.4	–0.18	0
Nitrogen	N_2	72	–26.9	5.19	–0.298
Hydrogen	H_2	79.5	–26.3	4.23	–0.197
Water	H_2O	180	–85.4	15.6	–0.858

Adapted from Table 20.2 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Adiabatic flame temperature calculations



$\dot n_{1\mathrm{R}},\dots,\dot n_{i\mathrm{R}},\dots,\dot n_{r\mathrm{R}}$

T_o, p_o

$\dot H^o_{\mathrm{R}}, \dot S^o_{\mathrm{R}}$

inlet bulk-flow state "R"

steady state reactor

$\sum_{i=1}^r \nu_i A_i = 0$

$\dot\epsilon \qquad \dot S_{\mathrm{irr}}$

$\dot n_{i\mathrm{P}} = \dot n_{i\mathrm{R}} + \nu_i\,\dot\epsilon$

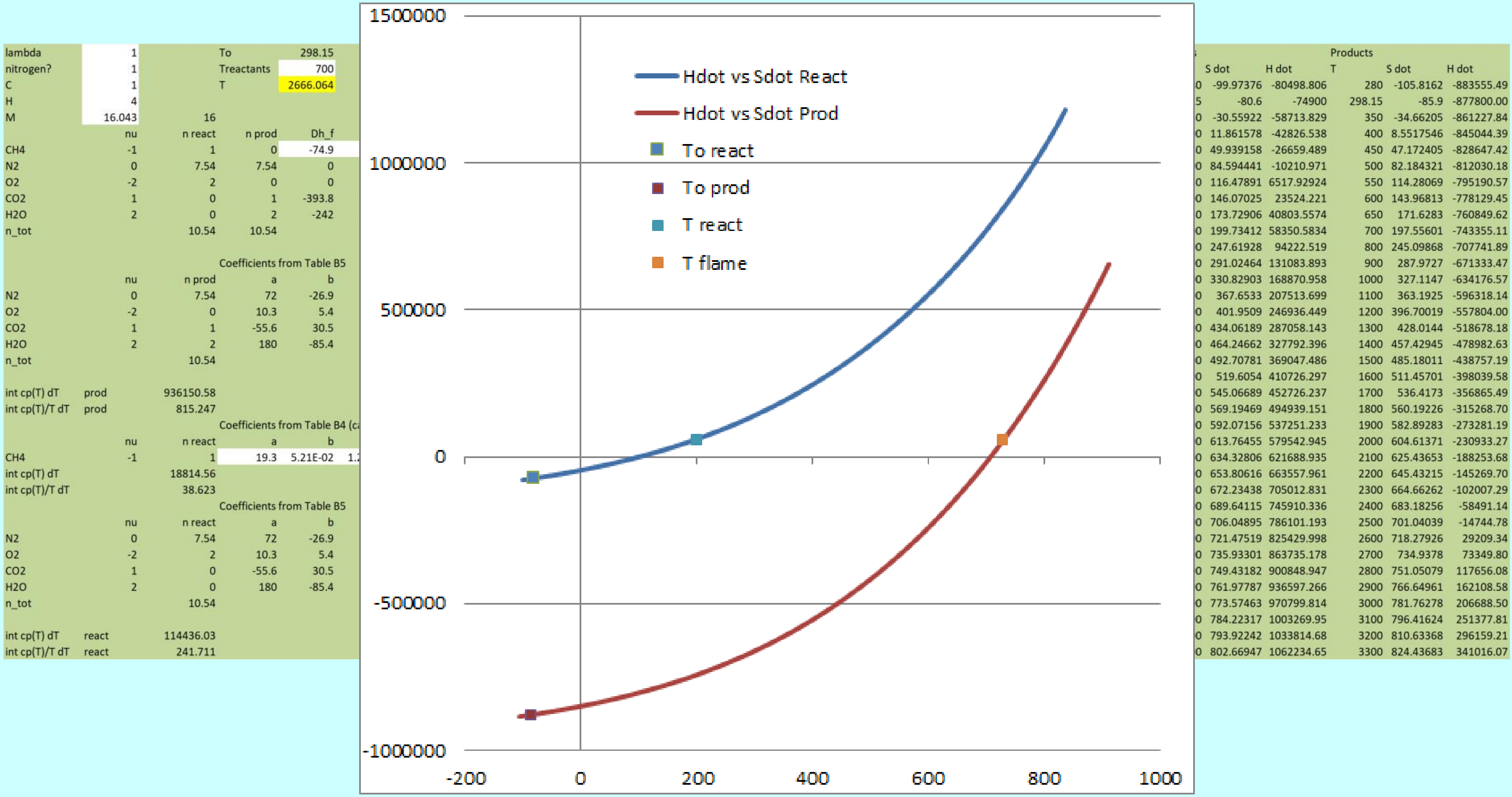
$\dot n_{1\mathrm{P}},\dots,\dot n_{i\mathrm{P}},\dots,\dot n_{r\mathrm{P}}$

T_{ad}, p_o

$\dot H_{\mathrm{P}}, \dot S_{\mathrm{P}}$

outlet bulk-flow state "P"

Steady-state constant-pressure burner

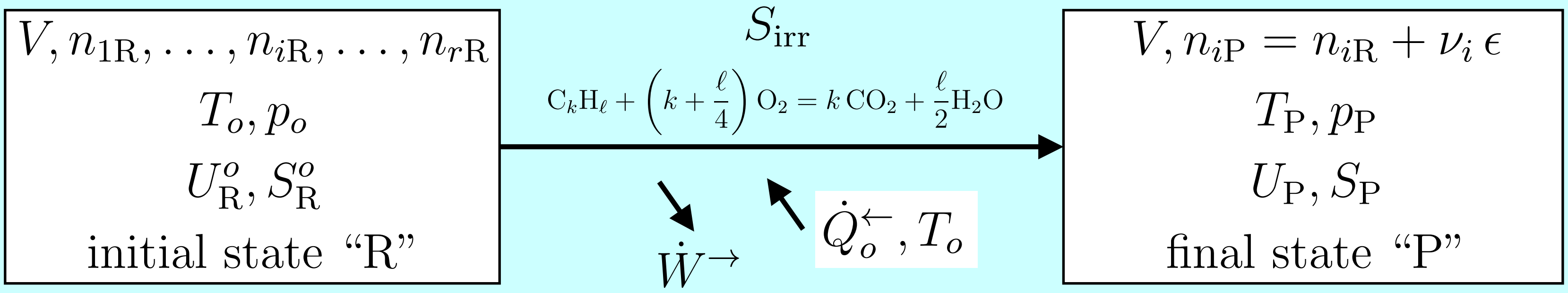


lambda	1		To	298.15
nitrogen?	1		Treactants	700
C	1		T	2666.064
H	4			
M	16.043	16		
	nu	n react	n prod	Dh_f
CH4	-1	1	0	-74.9
N2	0	7.54	7.54	0
O2	-2	2	0	0
CO2	1	0	1	-393.8
H2O	2	0	2	-242
n_tot		10.54	10.54	
			Coefficients from Table B5	
	nu	n prod	a	b
N2	0	7.54	72	-26.9
O2	-2	0	10.3	5.4
CO2	1	1	-55.6	30.5
H2O	2	2	180	-85.4
n_tot		10.54		
int cp(T) dT	prod	936150.58		
int cp(T)/T dT	prod	815.247		
			Coefficients from Table B4 (ca	
	nu	n react	a	b
CH4	-1	1	19.3	5.21E-02
int cp(T) dT		18814.56		
int cp(T)/T dT		38.623		
			Coefficients from Table B5	
	nu	n react	a	b
N2	0	7.54	72	-26.9
O2	-2	2	10.3	5.4
CO2	1	0	-55.6	30.5
H2O	2	0	180	-85.4
n_tot		10.54		
int cp(T) dT	react	114436.03		
int cp(T)/T dT	react	241.711		

		Products		
S dot	H dot	T	S dot	H dot
-99.97376	-80498.806	280	-105.8162	-883555.49
-80.6	-74900	298.15	-85.9	-877800.00
-30.55922	-58713.829	350	-34.66205	-861227.84
11.861578	-42826.538	400	8.5517546	-845044.39
49.939158	-26659.489	450	47.172405	-828647.42
84.594441	-10210.971	500	82.184321	-812030.18
116.47891	6517.92924	550	114.28069	-795190.57
146.07025	23524.221	600	143.96813	-778129.45
173.72906	40803.5574	650	171.6283	-760849.62
199.73412	58350.5834	700	197.55601	-743355.11
247.61928	94222.519	800	245.09868	-707741.89
291.02464	131083.893	900	287.9727	-671333.47
330.82903	168870.958	1000	327.1147	-634176.57
367.6533	207513.699	1100	363.1925	-596318.14
401.9509	246936.449	1200	396.70019	-557804.00
434.06189	287058.143	1300	428.0144	-518678.18
464.24662	327792.396	1400	457.42945	-478982.63
492.70781	369047.486	1500	485.18011	-438757.19
519.6054	410726.297	1600	511.45701	-398039.58
545.06689	452726.237	1700	536.4173	-356865.49
569.19469	494939.151	1800	560.19226	-315268.70
592.07156	537251.233	1900	582.89283	-273281.19
613.76455	579542.945	2000	604.61371	-230933.27
634.32806	621688.935	2100	625.43653	-188253.68
653.80616	663557.961	2200	645.43215	-145269.70
672.23438	705012.831	2300	664.66262	-102007.29
689.64115	745910.336	2400	683.18256	-58491.14
706.04895	786101.193	2500	701.04039	-14744.78
721.47519	825429.998	2600	718.27926	29209.34
735.93301	863735.178	2700	734.9378	73349.80
749.43182	900848.947	2800	751.05079	117656.08
761.97787	936597.266	2900	766.64961	162108.58
773.57463	970799.814	3000	781.76278	206688.50
784.22317	1003269.95	3100	796.41624	251377.81
793.92242	1033814.68	3200	810.63368	296159.21
802.66947	1062234.65	3300	824.43683	341016.07

E18-AdiabaticFlameTemperature(withEquilibrium).xlsx

Adiabatic flame temperature and pressure in a closed bomb



$V, n_{1\mathrm{R}}, \dots, n_{i\mathrm{R}}, \dots, n_{r\mathrm{R}}$

T_o, p_o

$U^o_{\mathrm{R}}, S^o_{\mathrm{R}}$

initial state "R"

S_{irr}

$\mathrm{C}_k\mathrm{H}_\ell + \left(k + \frac{\ell}{4}\right)\mathrm{O}_2 = k\,\mathrm{CO}_2 + \frac{\ell}{2}\mathrm{H}_2\mathrm{O}$

$\dot{W}^{\rightarrow}$

$\dot{Q}_o^{\leftarrow}, T_o$

$V, n_{i\mathrm{P}} = n_{i\mathrm{R}} + \nu_i\,\epsilon$

$T_{\mathrm{P}}, p_{\mathrm{P}}$

$U_{\mathrm{P}}, S_{\mathrm{P}}$

final state "P"

Volume balance (assuming GD mix of ideal gases): $V_{\mathrm{P}} = \dfrac{n_{\mathrm{P}} R T_{\mathrm{P}}}{p_{\mathrm{P}}} = V_{\mathrm{R}} = \dfrac{n_{\mathrm{R}} R T_o}{p_o}$

Heating value setup: $W^{\rightarrow} = 0,\ \epsilon = n_{\mathrm{C}_k\mathrm{H}_\ell},\ n_{\mathrm{P}} = n_{\mathrm{R}} + \nu\epsilon,\ \dfrac{p_{\mathrm{P}}}{p_o} = 1 + \nu\dfrac{\epsilon}{n_{\mathrm{R}}}$

$$U_P - U_R^o = -Q_o^{\rightarrow} = -\epsilon\,\mathrm{HV}^{\mathrm{bomb}}_{\mathrm{actual}} \quad \text{where} \quad \mathrm{HV}^{\mathrm{bomb}}_{\mathrm{actual}} = -\Delta u^o + \frac{n_{\mathrm{H_2O,f}}}{n_{\mathrm{C}_k\mathrm{H}_\ell}}\,u_{\mathrm{H_2O,fg}}(T_o)$$

Adiabatic flame temperature setup: $T_{\mathrm{P}} = T_{\mathrm{ad}},\ Q_o^{\rightarrow} = 0,\ W^{\rightarrow} = 0,\ \dfrac{p_{\mathrm{ad}}}{p_o} = \dfrac{T_{\mathrm{ad}}}{T_o}\left(1 + \nu\dfrac{\epsilon}{n_{\mathrm{R}}}\right)$

$$0 = U_P(T_{\mathrm{ad}}) - U_R^o = U_P(T_{\mathrm{ad}}) - U_P^o + U_P^o - U_R^o = n_{\mathrm{P}}\int_{T_o}^{T_{\mathrm{ad}}} \sum_i y_{i\mathrm{P}}\, c_{v,ii}(T')\,\mathrm{d}T' - \epsilon\,\mathrm{HV}^{\mathrm{bomb}}_{\mathrm{actual}} \Rightarrow \begin{array}{c}\text{solve}\\ \text{for } T_{\mathrm{ad}}\end{array}$$

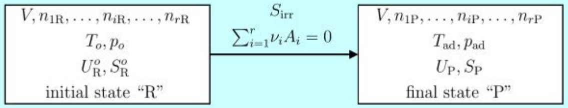
$$\dot{S}_{\mathrm{irr}} = S_P(T_{\mathrm{ad}}, p_{\mathrm{ad}}) - S_R^o = S_P(T_{\mathrm{ad}}, p_{\mathrm{ad}}) - S_P^o + S_P^o - S_R^o$$

$$= n_{\mathrm{P}}\int_{T_o}^{T_{\mathrm{ad}}} \frac{\sum_i y_{i\mathrm{P}}\, c_{p,ii}(T')}{T'}\,\mathrm{d}T' - n_{\mathrm{P}} R \ln\frac{p_{\mathrm{ad}}}{p_o} + \epsilon\,\Delta s^o \approx -(0.22 \div 0.26)\,\epsilon\,\frac{\Delta g^o}{T_o}$$

Typical values of $\dfrac{T_o \dot{S}_{\mathrm{irr}}}{-\dot{\epsilon}\Delta g^o}$ are in the range 22% to 26%

Adiabatic flame temperature

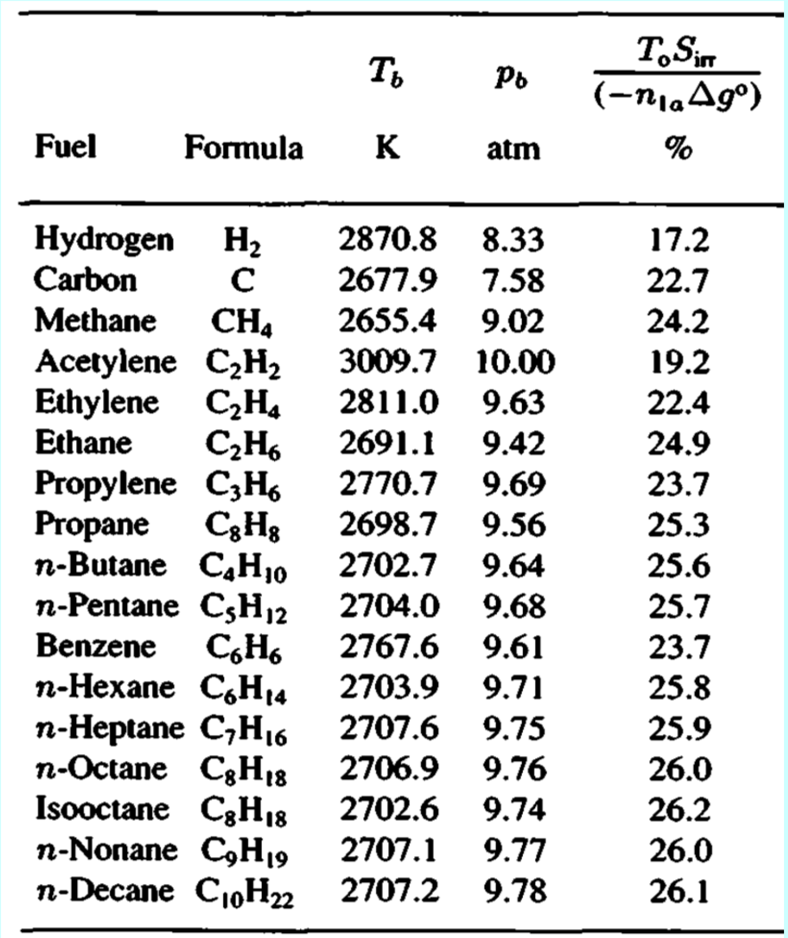
Closed fixed-volume combustion chamber



$V, n_{1\mathrm{R}}, \ldots, n_{i\mathrm{R}}, \ldots, n_{r\mathrm{R}}$
T_o, p_o
$U^o_{\mathrm{R}}, S^o_{\mathrm{R}}$
initial state “R”

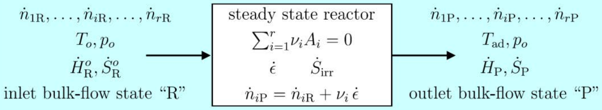
S_{irr}
$\sum_{i=1}^{r} \nu_i A_i = 0$

$V, n_{1\mathrm{P}}, \ldots, n_{i\mathrm{P}}, \ldots, n_{r\mathrm{P}}$
$T_{\mathrm{ad}}, p_{\mathrm{ad}}$
$U_{\mathrm{P}}, S_{\mathrm{P}}$
final state “P”



Fuel	Formula	T_b K	p_b atm	$\frac{T_o S_{\mathrm{irr}}}{(-n_{1a}\Delta g^o)}$ %
Hydrogen	H_2	2870.8	8.33	17.2
Carbon	C	2677.9	7.58	22.7
Methane	CH_4	2655.4	9.02	24.2
Acetylene	C_2H_2	3009.7	10.00	19.2
Ethylene	C_2H_4	2811.0	9.63	22.4
Ethane	C_2H_6	2691.1	9.42	24.9
Propylene	C_3H_6	2770.7	9.69	23.7
Propane	C_8H_8	2698.7	9.56	25.3
n-Butane	C_4H_{10}	2702.7	9.64	25.6
n-Pentane	C_5H_{12}	2704.0	9.68	25.7
Benzene	C_6H_6	2767.6	9.61	23.7
n-Hexane	C_6H_{14}	2703.9	9.71	25.8
n-Heptane	C_7H_{16}	2707.6	9.75	25.9
n-Octane	C_8H_{18}	2706.9	9.76	26.0
Isooctane	C_8H_{18}	2702.6	9.74	26.2
n-Nonane	C_9H_{19}	2707.1	9.77	26.0
n-Decane	$C_{10}H_{22}$	2707.2	9.78	26.1

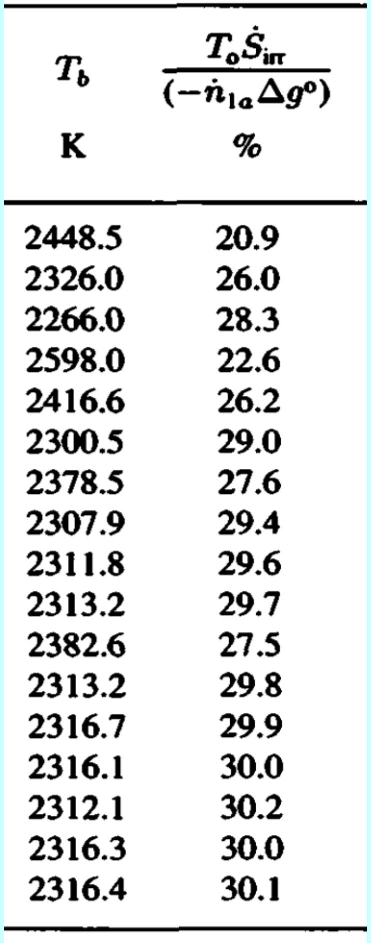
Steady-state constant-pressure burner



$\dot{n}_{1\mathrm{R}}, \ldots, \dot{n}_{i\mathrm{R}}, \ldots, \dot{n}_{r\mathrm{R}}$
T_o, p_o
$\dot{H}^o_{\mathrm{R}}, \dot{S}^o_{\mathrm{R}}$
inlet bulk-flow state “R”

steady state reactor
$\sum_{i=1}^{r} \nu_i A_i = 0$
$\dot{\epsilon} \qquad \dot{S}_{\mathrm{irr}}$
$\dot{n}_{i\mathrm{P}} = \dot{n}_{i\mathrm{R}} + \nu_i\,\dot{\epsilon}$

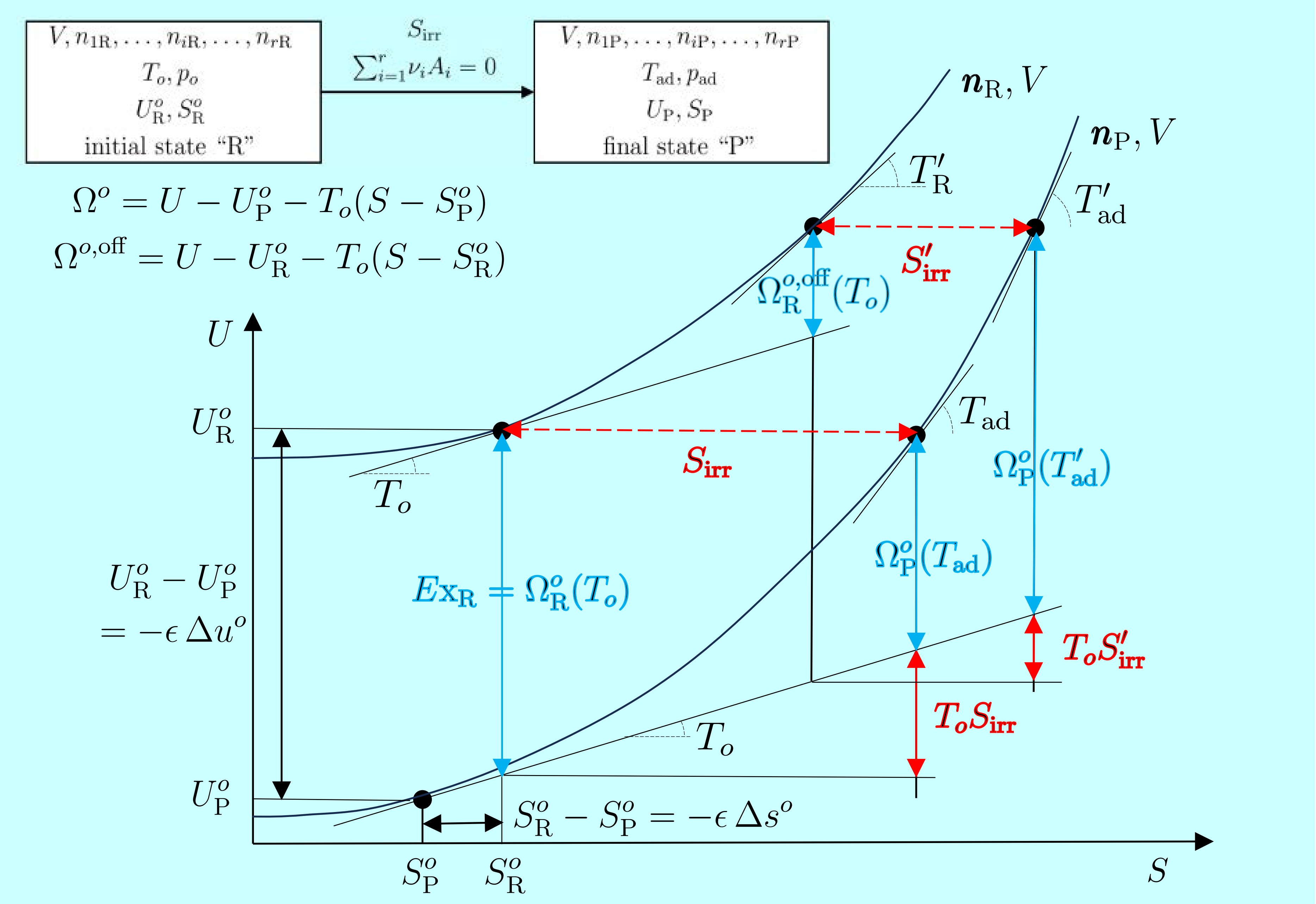
$\dot{n}_{1\mathrm{P}}, \ldots, \dot{n}_{i\mathrm{P}}, \ldots, \dot{n}_{r\mathrm{P}}$
T_{ad}, p_o
$\dot{H}_{\mathrm{P}}, \dot{S}_{\mathrm{P}}$
outlet bulk-flow state “P”



T_b K	$\frac{T_o \dot{S}_{\mathrm{irr}}}{(-\dot{n}_{1a}\Delta g^o)}$ %
2448.5	20.9
2326.0	26.0
2266.0	28.3
2598.0	22.6
2416.6	26.2
2300.5	29.0
2378.5	27.6
2307.9	29.4
2311.8	29.6
2313.2	29.7
2382.6	27.5
2313.2	29.8
2316.7	29.9
2316.1	30.0
2312.1	30.2
2316.3	30.0
2316.4	30.1

Adapted from Figures 31.8 and 31.9 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Summary on an energy vs entropy diagram



$V, n_{1\mathrm{R}}, \dots, n_{i\mathrm{R}}, \dots, n_{r\mathrm{R}}$

T_o, p_o

$U^o_\mathrm{R}, S^o_\mathrm{R}$

initial state "R"

S_irr

$\sum_{i=1}^r \nu_i A_i = 0$

$V, n_{1\mathrm{P}}, \dots, n_{i\mathrm{P}}, \dots, n_{r\mathrm{P}}$

$T_\mathrm{ad}, p_\mathrm{ad}$

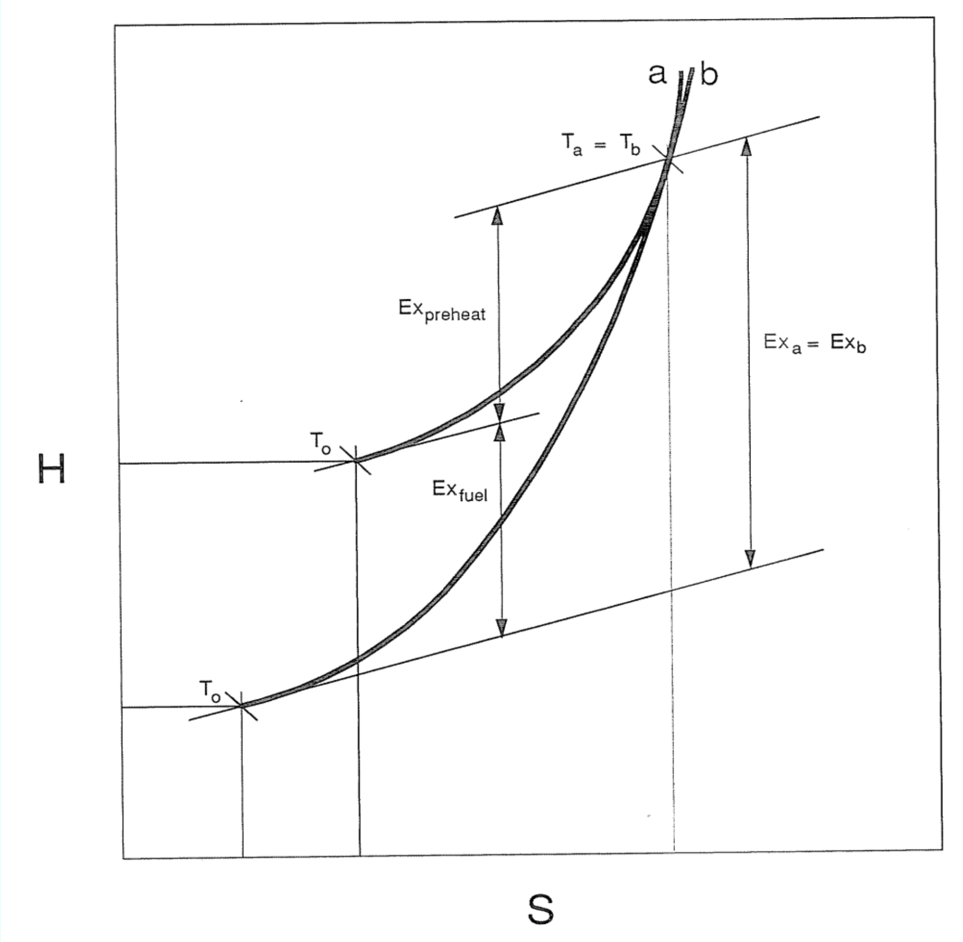
$U_\mathrm{P}, S_\mathrm{P}$

final state "P"

$$\Omega^o = U - U^o_\mathrm{P} - T_o(S - S^o_\mathrm{P})$$

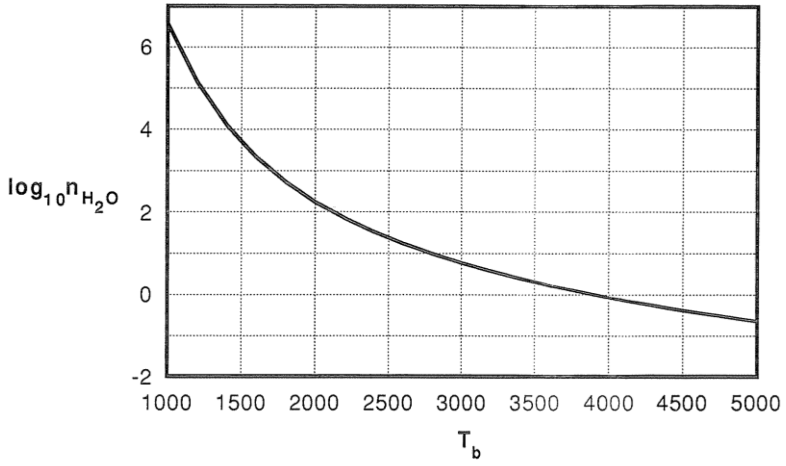
$$\Omega^{o,\mathrm{off}} = U - U^o_\mathrm{R} - T_o(S - S^o_\mathrm{R})$$

Is a reversible combustion possible?



For $n_{H_2} = 1\ mol$, $n_{O_2} = 1/2\ mol$ and $p_b = p_o$ we find

$$n_{H_2O}\left(\frac{3}{2} + n_{H_2O}\right)^{1/2} = \left(\frac{1}{2}\right)^{-1/2} \exp\left(-6.866 + \frac{29911}{T_b}\right)$$



Figures 3 and 4 from G.P. Beretta, A.M. Lezzi, A. Niro, and M. Silvestri, On the concept of a reversible flame, in Energy for the Transition Age, FLOWERS '92, Edited by S.S. Stecco and M.J. Moran, Nova Science Pu. Inc., New York, Additional Proceedings, pp. 165-177 (1992).

The question was first raised and discussed in Keenan (1941) and Obert (1948,1973), and later also by Richter & Knoche (1983), Dunbar & Lior (1994).

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