Thermodynamics **Test June 13th 2022**

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⟵ Please enter you student number, and write your name above.

NAME, First Name :

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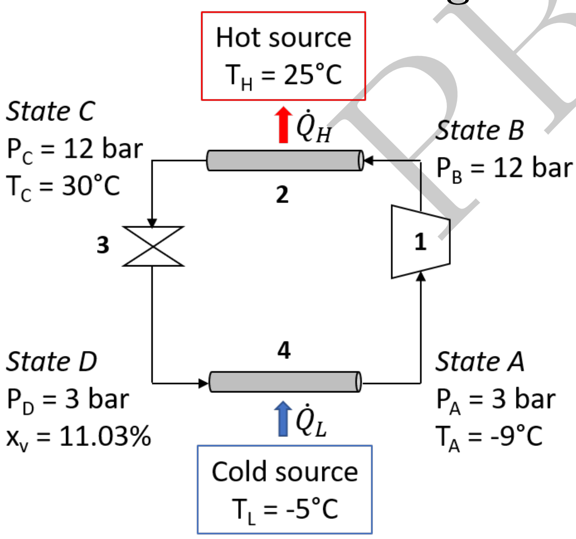
Duration : 3 h - All documents and all calculators authorised - No computer or tablet, no wifi no 4/5G

PROJET

Ammonia : thermodynamic data

$\bar{C}_v(\mathrm{NH_3}) = 28.00\,\mathrm{J/(molK)}$
$\bar{C}_p(\mathrm{NH_3}) = 36.31\,\mathrm{J/(molK)}$
$\Delta_{\mathrm{vap}}H_{303}(\mathrm{NH_3}) = 1146\,\mathrm{kJ/kg}$
$\Delta_{\mathrm{vap}}H_{264}(\mathrm{NH_3}) = 1294\,\mathrm{kJ/kg}$

1 Ammonia as refrigerant fluid (8 points)



The use of ammonia as refrigerant fluid started in France in 1850's and then it spread worldwide being used to create ice, keep food cold, and in air conditioners. Nowadays, due to its lower cost and environmental impact, ammonia is largely used as replacement of CFC's and Freon as refrigerant fluid for cold storage of food and for large scale cooling requirements such as large office buildings, hospitals, ice rinks.

Let's now study the ammonia-based refrigerator used in ice rinks to avoid ice melting. This cycle is schematised in the picture and is made of :

1) an adiabatic compressor ;
2, 4) two isobaric heat exchangers ;
3) an adiabatic expansion valve ($W_{CD} = 0$).

The fluid starts in state A as a saturated vapour [1] at 3 bar (mass flow rate $\dot{m}(\mathrm{NH_3}) = 161\,\mathrm{kg/h}$) and, after the compression and the successive heat exchange with external air (hot source) arrives to the state C as a saturated liquid [2]. After the expansion, the fluid is in state D at the liquid/vapour equilibrium ($x_v = n_{\mathrm{gas}}/n_{\mathrm{tot}} = 11.03\%$) and it goes back to state A by exchanging heat with the ice rink (cold source).

1. A vapour that is about to condensate (vapour and liquid are at equilibrium).
2. A liquid that is about to vaporise (vapour and liquid are at equilibrium).

Pour votre examen, imprimez de préférence les documents compilés à l'aide de auto-multiple-choice.

Question 1 Give the literal expression of temperature T_B^{irrev} as function of P_B, P_A, T_A, R, $\bar{C}_v(\text{NH}_3)$ and $\bar{C}_p(\text{NH}_3)$ considering an irreversible compression.

☐ Vide ☐ 0 ☐ 1 ☐ 2 ■ 3

Adiabatic irreversible compression (first principle) : $\Delta U = Q + W$ leading to : $n\bar{C}_v(\text{NH}_3)(T_B^{\text{irrev}} - T_A) = -P_B(V_B - V_A) = -nR(T_B^{\text{irrev}} - T_A P_B/P_A)$ leading to : $T_B^{\text{irrev}} = T_A \frac{RP_B/P_A + \bar{C}_v(\text{NH}_3)}{\bar{C}_p(\text{NH}_3)}$ (0.75 pts)

Question 2 Give the literal expression of temperature T_B^{rev} as function of P_B, P_A, T_A, $\bar{C}_v(\text{NH}_3)$ and $\bar{C}_p(\text{NH}_3)$ considering an reversible compression

☐ Vide ☐ 0 ☐ 1 ☐ 2 ■ 3

Adiabatic reversible compression (first principle) : $P_A V_A^\gamma = P_B V_B^\gamma$ leading to : $P_A^{1-\gamma} T_A^\gamma = P_B^{1-\gamma} T_B^\gamma$ leading to : $T_B^{\text{rev}} = T_A \left(\frac{P_A}{P_B}\right)^{\frac{\bar{C}_v(\text{NH}_3)}{\bar{C}_p(\text{NH}_3)} - 1}$ (0.75 pts)

Question 3 What is the numerical value of T_B^{rev} (in °C) ?

■ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐ 8 ☐ 9
☐ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐ 8 ■ 9
■ 0 ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐ 8 ☐ 9

Question 4 Considering from now on that the compression is irreversible and that $T_B^{\text{irrev}} = T_B = 172.26\,°\text{C}$, give the power $\dot{W}_{AB}$ transferred during the compression as a function of data given in the text.

☐ Vide ☐ 0 ☐ 1 ☐ 2 ■ 3

The work $W_{AB} = -P_B(V_B - V_A)$, leading to : $\dot{W}_{AB} = -\dot{n}R(T_B^{\text{irrev}} - T_A P_B/P_A)$ and finally $\dot{W}_{AB} = -\frac{\dot{m}(\text{NH}_3)}{M(\text{NH}_3)} R(T_B^{\text{irrev}} - T_A P_B/P_A)$ or the work is $W_{AB} = \Delta U$, leading to : $\dot{W}_{AB} = \frac{\dot{m}(\text{NH}_3)}{M(\text{NH}_3)} \bar{C}_v(\text{NH}_3)(T_B^{\text{irrev}} - T_A)$. (0.75 pts)

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Question 5 What is the numerical value of $\dot{W}_{AB}$ (kW) ?

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☐0 ☐1 ☐2 ■3 ☐4 ☐5 ☐6 ☐7 ☐8 ☐9
■+ .
☐− ☐0 ☐1 ☐2 ☐3 ■4 ☐5 ☐6 ☐7 ☐8 ☐9

Question 6 Gives the expression of the rate of entropy created $\dot{S}_{\text{cre}}$ during the compression.

☐Vide ☐0 ☐1 ☐2 ☐3 ■4

$\dot{S}_{\text{cr}} = \Delta\dot{S}_\sigma - \dot{S}_{\text{ex}} = \Delta\dot{U} - \dot{W} - \dot{S}_{\text{ex}}$ with $\dot{S}_{\text{ex}} = 0$ (adiabatic), leading to : $\dot{S}_{\text{cr}} = \dot{n}\bar{C}_v(\text{CH}_3)\ln(T_B^{\text{irrev}}/T_A) + \dot{n}R\ln(V_B/V_A)$. Finally : $\dot{S}_{\text{cr}} = \frac{\dot{m}(\text{CH}_3)}{M(\text{CH}_3)}\left[\bar{C}_p(\text{CH}_3)\ln\left(\frac{T_B^{\text{irrev}}}{T_A}\right) + R\ln\left(\frac{P_A}{P_B}\right)\right]$ (1 pts). We can also directly decompose the transformation from A to B^{irrev} into A to B^{rev} and B^{rev} to B^{irrev}, leading to : $\dot{S}_{\text{cr}} = \frac{\dot{m}(\text{CH}_3)}{M(\text{CH}_3)}\bar{C}_p(\text{CH}_3)\ln\left(\frac{T_B^{\text{irrev}}}{T_B^{\text{rev}}}\right)$

Question 7 What is the numerical value of $\dot{S}_{\text{cre}}$ (in J/(K s)) ?

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☐0 ☐1 ☐2 ☐3 ☐4 ☐5 ■6 ☐7 ☐8 ☐9

Question 8 Gives the expression of the rate of heat exchanged $\dot{Q}_H$ with the hot source between states B and C as a function of data given in the text.

☐Vide ☐0 ☐1 ☐2 ■3

The vapour will heat until its liquid / vapour equilibrium temperature at 12 bar, leading to : $\dot{Q}_H = \dot{m}(\text{CH}_3)\left[\frac{\bar{C}_p(\text{CH}_3)}{M(\text{CH}_3)}\left(T_C - T_B^{\text{irrev}}\right) - \Delta_{\text{vap}}H_{303}\right]$ (0.75 pts).

Question 9 What is the numerical value of $\dot{Q}_H$ (in kW) ?

☐0 ☐1 ☐2 ☐3 ☐4 ☐5 ■6 ☐7 ☐8 ☐9
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Question 10 Gives the expression of the rate of heat exchanged $\dot{Q}_L$ with the cold source between states D and A as a function of data given in the text.

□ Vide □ 0 □ 1 □ 2 ■ 3

In states D and A, the fluid is in equilibrium between vapour and liquid. As $P_D = P_A$, $T_D = T_A$, leading to : $\dot{Q}_L = \dot{m}(\mathrm{CH_3})(1 - x_v)\Delta_{\mathrm{vap}}H_{240}$ (0.75 pts).

Question 11 What is the numerical value of $\dot{Q}_L$ (in kW) ?

	□ 0	□ 1	□ 2	□ 3	□ 4	■ 5	□ 6	□ 7	□ 8	□ 9
	□ 0	■ 1	□ 2	□ 3	□ 4	□ 5	□ 6	□ 7	□ 8	□ 9
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□ −	□ 0	□ 1	□ 2	□ 3	□ 4	■ 5	□ 6	□ 7	□ 8	□ 9

Question 12 What is the numerical value of $\dot{Q}_L + \dot{Q}_H + \dot{W}_{AB}$ (in kW) ?

	■ 0	□ 1	□ 2	□ 3	□ 4	□ 5	□ 6	□ 7	□ 8	□ 9
	■ 0	□ 1	□ 2	□ 3	□ 4	□ 5	□ 6	□ 7	□ 8	□ 9
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□ −	■ 0	□ 1	□ 2	□ 3	□ 4	□ 5	□ 6	□ 7	□ 8	□ 9

Question 13 What is the numerical value of the real COP COP^{real} ?

	□ 0	□ 1	□ 2	■ 3	□ 4	□ 5	□ 6	□ 7	□ 8	□ 9
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■ +	□ 0	□ 1	□ 2	□ 3	□ 4	□ 5	□ 6	□ 7	■ 8	□ 9
□ −	□ 0	□ 1	□ 2	□ 3	□ 4	□ 5	■ 6	□ 7	□ 8	□ 9

Question 14 Demonstrate the expression of the ideal COP COP^{ideal} of the thermal machine as a function of data given in the text.

□ Vide □ 0 □ 1 ■ 2

The ideal COP is : $COP^{\mathrm{ideal}} = \frac{\dot{Q}_L}{\dot{W}^{\mathrm{rev}}_{AB} + \dot{W}^{\mathrm{rev}}_{CD}}$. The first principle applied to the whole machine leads to : $\Delta\dot{U} = \dot{Q}_L + \dot{Q}_H + \dot{W}_{AB} + \dot{W}_{CD} = 0$. The second principle applied to the whole machine leads to $\Delta\dot{S}_\sigma = \frac{\dot{Q}_L}{T_L} + \frac{\dot{Q}_H}{T_H} = 0$. Mixing these three equations leads finally to : $COP^{\mathrm{ideal}} = \frac{T_L}{T_H - T_L}$ (0.5 pts).

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Question 15 What is the numerical value of the ideal COP COP^{ideal} ?

☐0 ☐1 ☐2 ☐3 ☐4 ☐5 ☐6 ☐7 ■8 ☐9
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■+ | ☐0 ☐1 ☐2 ☐3 ☐4 ☐5 ☐6 ☐7 ☐8 ■9
☐− | ☐0 ☐1 ☐2 ■3 ☐4 ☐5 ☐6 ☐7 ☐8 ☐9

Question 16 Cite some sources of irreversibility.

☐Vide ☐0 ☐1 ■2

Irreversibility is mostly due to (i) the energy of the expansion is not recovered ; (ii) the compression is irreversible ; (iii) thermal exchanges are irreversible. (0.5 pts) .

2 Ammonia as fuel (5 points)

Among the different applications of ammonia, one concerns its possible use as carbon-free fuel as replacement of current fossile fuels. Indeed, several studies are currently carried on to produce ammonia from carbon-free sources and then, burn it as a fuel. This exercice concerns the combustion of gaseous ammonia at 298 K and 1 bar giving gaseous nitrogen and gaseous water.

Question 17 Write the combustion reaction of **one** mole of ammonia.

☐Vide ☐0 ☐1 ■2

$NH_{3(g)} + \frac{3}{4}\ O_{2(g)} \rightarrow \frac{1}{2}\ N_{2(g)} + \frac{3}{2}\ H_2O_{(g)}$ (0.5 pts) .

Question 18 Give the expression of the standard reaction enthalpy $\Delta_r H$ of the combustion of **one** mole of ammonia.

☐Vide ☐0 ☐1 ■2

$\Delta_r H = \frac{3}{2}\Delta_f H(H_2O_{(g)}) - \Delta_f H(NH_{3(g)})$ (0.5 pts) .

Question 19 What is the numerical value of $\Delta_r H$ (in kJ/mol) ?

☐0 ☐1 ☐2 ■3 ☐4 ☐5 ☐6 ☐7 ☐8 ☐9
☐+ | ☐0 ■1 ☐2 ☐3 ☐4 ☐5 ☐6 ☐7 ☐8 ☐9
■− | ☐0 ☐1 ☐2 ☐3 ☐4 ☐5 ☐6 ■7 ☐8 ☐9

Question 20 What is the numerical value of the standard reaction energy $\Delta_r U$ of **one** mole of ammonia.(in kJ/mol) ?

☐0 ☐1 ☐2 ■3 ☐4 ☐5 ☐6 ☐7 ☐8 ☐9
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■− | ☐0 ☐1 ☐2 ☐3 ☐4 ☐5 ☐6 ■7 ☐8 ☐9

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Question 21 Give the expression of the created entropy S_{cre} of this reaction as a function of temperature T.

□ Vide □ 0 □ 1 ■ 2

The created entropy is : $S_{\text{cre}} = S_\sigma - S_{\text{ex}} = \Delta_r S - \frac{\Delta_r H}{T_{298}}$, leading to : $S_{\text{cre}} = \frac{1}{2}\Delta_f S(N_{2(g)}) + \frac{3}{2}\Delta_f S(H_2O_{(g)}) - \Delta_f S(NH_{3(g)}) - \frac{3}{4}\Delta_f S(O_{2(g)}) - \frac{\Delta_r H}{T}$ (0.5 pts).

Question 22 What is the numerical value of S_{cre} at 298 K (in kJ/mol/K) ?

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■ + □ 0 ■ 1 □ 2 □ 3 □ 4 □ 5 □ 6 □ 7 □ 8 □ 9

□ − ■ 0 □ 1 □ 2 □ 3 □ 4 □ 5 □ 6 □ 7 □ 8 □ 9

Question 23 At 298 K, the combustion reaction of ammonia is :

□ Impossible ■ Irreversible □ Reversible

Question 24 Give the RICE chart of the combustion reaction of ammonia for 1 mol of ammonia in air with molar ratio of air equals to r ($n_{\text{air}}/n_{NH_3} = r$).

□ Vide □ 0 □ 1 □ 2 □ 3 ■ 4

R	$NH_{3(g)}$	$\frac{3}{4}O_{2(g)}$	$\frac{1}{2}N_{2(g)}$	$\frac{3}{2}H_2O_{(g)}$
I	1	$\frac{r}{5}$	$\frac{4r}{5}$	0
C	$-\xi$	$-\frac{3}{4}\xi$	$\frac{1}{2}\xi$	$\frac{3}{2}\xi$
E	$1-\xi$	$r/5 - \frac{3}{4}\xi$	$\frac{4}{5}r + \frac{1}{2}\xi$	$\frac{3}{2}\xi$

(1 pts)

Question 25 What is the minimal value of r for the combustion to be complete ?

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□ 0 □ 1 □ 2 □ 3 □ 4 □ 5 □ 6 ■ 7 □ 8 □ 9

□ 0 □ 1 □ 2 □ 3 □ 4 ■ 5 □ 6 □ 7 □ 8 □ 9

Question 26 If $r = 4$, what is the value of ξ_M at the end of the reaction ?

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■ 0 □ 1 □ 2 □ 3 □ 4 □ 5 □ 6 □ 7 □ 8 □ 9

■ 0 □ 1 □ 2 □ 3 □ 4 □ 5 □ 6 □ 7 □ 8 □ 9

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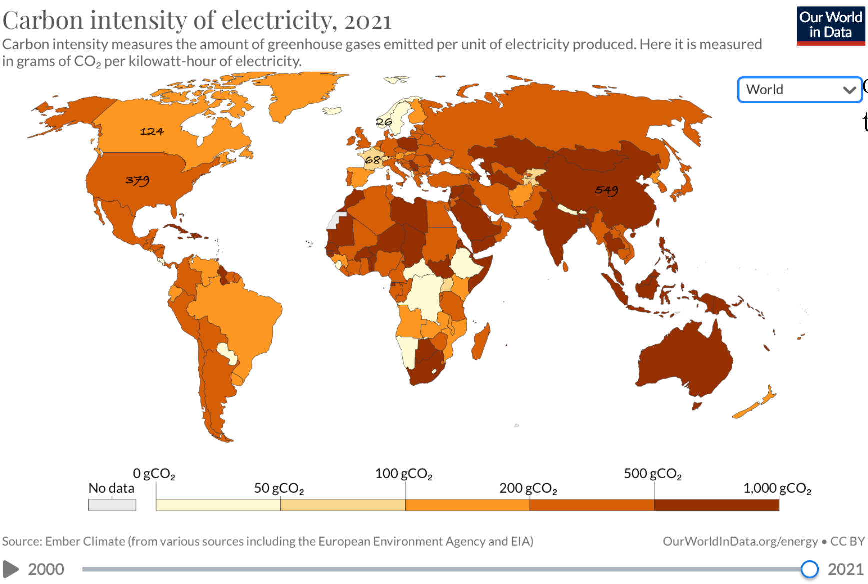
Question 27 Prove that the flame temperature T_f obtained by the combustion of an initial mixture of ammonia in air with molar ratio of air equals to r ($n_{\text{air}}/n_{\text{NH}_3} = r$, such that no reactant remains) and by considering that a fraction η of the heat released by the combustion is lost to the surroundings and that the heat capacities are independent of the temperature is :

$$T_f = T_0 - \frac{(1-\eta)\Delta_r H_{298}}{\eta\left[C_p(\text{NH}_3) + \frac{3}{4}C_p(\text{O}_2) + 3C_p(\text{N}_2)\right] + (1-\eta)\left[\frac{7}{2}C_p(\text{N}_2) + \frac{3}{2}C_p(\text{H}_2\text{O})\right]}$$

☐ Vide ☐ 0 ☐ 1 ☐ 2 ☐ 3 ■ 4

From the RICE chart and the fact that no reactant remains, we know that $\xi_M = 1$ and $r = \frac{15}{4}$ (0.25 pts).
Then, we write that the fraction $(1-\eta)$ of the enthalpy of the reaction at T_f is used to heat the reactants : $(1-\eta)\Delta_r H_{T_f} + \int_{T_0}^{T_f}\left[C_p(\text{NH}_3) + \frac{3}{4}C_p(\text{O}_2) + 3C_p(\text{N}_2)\right]dT = 0$ (0.25 pts).
Then we use the fact that ΔH is a state function so that : $\Delta_r H_{T_f} + \int_{T_0}^{T_f}\left[C_p(\text{NH}_3) + \frac{3}{4}C_p(\text{O}_2) + 3C_p(\text{N}_2)\right]dT = \Delta_r H_{298} + \int_{T_0}^{T_f}\left[\frac{7}{2}C_p(\text{N}_2) + \frac{3}{2}C_p(\text{H}_2\text{O})\right]dT$ (0.25 pts).
Subtracting the first equation to the second one multiplied by $(1-\eta)$ leads to the proposed form (0.25 pts).

3 Carbon assessment of an electric car (7pts)



An average car needs 180 W.h/km of mechanical energy to move and transport passengers.

Cars can be powered by :

- a gasoline engine (efficiency $\eta^{\text{gas}} = 0.25$). Gasoline is considered as C_8H_{18}. Its combustion releases carbon dioxide and water. The heat of formation of gasoline is $\Delta_f H_{C_8H_{18}} = -250$ kJ/mol and its density is $\rho = 700\,\text{kg/m}^3$.
- an electric engine (efficiency $\eta^{\text{elec}}{=}0.85$) powered by a set of batteries (efficiency $\eta^{\text{bat}}{=}0.8$).

Extraction and production of gasoline emits 720 g of CO_2 per litter. The production of a battery for an electric car emits 6000 kg of CO_2. The life span of cars is $L = 150\,000$ km. The Carbon intensity of electricity (mass of CO_2 per kWh of electricity produced) is given in the map.

Question 28 Estimate the net gain in CO_2 per km of an electric vehicle compared to a gasoline one.

Vide Faux 1 2 3 4 5 6 7

Own the problem : We have to calculate and compare the emission of CO_2 per km of gasoline ($m_{CO_2}^{gas}$) and electric ($m_{CO_2}^{elec}$) cars.
We are given (undefined variables) the energy E per km needed by a car, the mass of CO_2 $m_{CO_2}^{Prod(Bat)}$ emitted for the production of batteries, the mass of CO_2 $m_{CO_2}^{\mathrm{Prod(Gas)}}$ released per volume of gasoline produced and the mass of CO_2 released per electric energy produced in various countries $m_{CO_2}^{Prod(Elec)}$. We define the number of mols of gasoline $n_{C_8H_{18}}$ needed per km, the combustion enthalpy of gasoline $\Delta_r H$ (assumed independent of temperature).
Resolution strategy : (i) For gasoline cars, we are going to add the amount of CO_2 released by combustion and emitted during gasoline production. (ii) For the electric cars, we are going to add the amount CO_2 emitted during electricity and battery production. CO_2 emissions of gasoline and electric car will finally be compared and discussed.
Resolution : The reaction of combustion of diesel is :
$C_8H_{18} + 25/2\ O_2 \rightarrow 8\ CO_2 + 9\ H_2O$
So that $\Delta_r H = 8\Delta_f H(CO_2) + 9\Delta_f H(H_2O) - \Delta_f H_{C_8H_{18}}$. We also know that $E = \eta^{\mathrm{gas}}\Delta_r H n_{C_8H_{18}}$. The mass of CO_2 generated by combustion is : $8M_{CO_2}E/(\eta^{\mathrm{gas}}\Delta_r H)$ The mass of CO_2 necessary to gasoline production is : $m_{CO_2}^{\mathrm{Prod(Gas)}} M_{C_8H_{18}} E/(\eta^{\mathrm{gas}}\Delta_r H\rho)$. The total mass of CO_2 for gasoline cars is :
$m_{CO_2}^{\mathrm{gas}} = \frac{E}{\eta^{\mathrm{gas}}}\frac{8M_{CO_2} + m_{CO_2}^{\mathrm{Prod(Gas)}} M_{C_8H_{18}}/\rho}{8\Delta_f H(CO_2) + 9\Delta_f H(H_2O) - \Delta_f H_{C_8H_{18}}}$. N.A : $m_{CO_2}^{tot} = 183\,\mathrm{g/km}$.
The amount of electricity necessary to move the car is $E/(\eta^{\mathrm{elec}}\eta^{bat})$. The mass of CO_2 necessary to electricity production is $m_{CO_2}^{\mathrm{Prod(Elec)}} E/(\eta^{\mathrm{elec}}\eta^{bat})$. The cost of battery production in CO_2 is $m_{CO_2}^{Prod(Bat)}/L$. The total mass of CO_2 for electric cars is :
$m_{CO_2}^{\mathrm{elec}} = \frac{m_{CO_2}^{\mathrm{Prod(Elec)}} E}{\eta^{\mathrm{elec}}\eta^{\mathrm{bat}}} + \frac{m_{CO_2}^{\mathrm{Prod(Bat)}}}{L}$, which gives $58\,\mathrm{g/km}$ in France and $185\,\mathrm{g/km}$ in China.
Critical look : There is almost a factor 3 of reduction of CO_2 emission if electric cars are replaced by gasoline cars in France, but no gain if it were to be in China.

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