Thermodynamics **Test June 20th 2023**

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

NAME, First Name :

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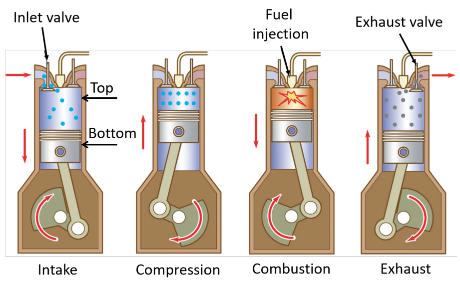
Duration : 3 h - All documents and all calculators authorised - No computer or tablet, no wifi no 4/5G

Thermodynamic data

Diesel molar mass : $M_{C_{12}H_{23}} = 167\,\text{g/mol}$
Diesel standard molar formation enthalpy : $\Delta_f H^\circ_{298(C_{12}H_{23}(l))} = 50.1\,\text{kJ/mol}$
Diesel standard molar formation entropy : $\Delta_f S^\circ_{298(C_{12}H_{23}(l))} = 74.8\,\text{J/(mol K)}$

1 Diesel engine (10 points)



Diesel fuel (or diesel oil) is a liquid mixture of alkanes and cycloalkanes (average chemical formula $C_{12}H_{23}$) largely used in the automotive transportation. A car diesel engine (a type of internal combustion engine) is a combustion piston-cylinder device operating typically on four-stroke cycle. A stroke represents a movement of the piston inside the cylinder from bottom to top or from top to bottom (see figure on the right, not to scale).
The four successive strokes of the cycle are :

- A) "Intake" : the inlet valve is open, the piston descends from the top and pulls 0.2 moles of dry air in the cylinder (state 1, piston at the bottom, $T_1 = 25\,°\text{C}$, $P_1 = 1\,\text{bar}$, V_1).
- B) "Compression" : the cylinder valves are closed, the piston goes up and compresses adiabatically reversibly the dry air (state 2, piston at the top, $T_2 = 643\,°\text{C}$, $P_2 = 25\,\text{bar}$, V_2).
- C) "Combustion" : liquid fuel is suddenly injected in the cylinder. Once the system is closed, the fuel combustion takes place at constant pressure during the beginning of the piston descent. When the combustion is completed (state 3, piston in between top and bottom, $T_3 = 1791\,°\text{C}$, $P_3 = P_2$, V_3) the piston continues its descent expanding adiabatically reversibly the combustion gases until reaching the bottom (state 4, T_4, P_4, $V_4 = V_1$) ; then gases cool down to T_1 at constant volume $V_4 = V_1$.
- D) "Exhaust" : the piston rises, the exhaust valve opens and the combustion gases are expelled. At the end of the fourth stroke, the piston is at the top, exhaust valve closes and the inlet valves opens to start again from intake.

By using the data provided and by clearly explicating your reasoning :

Question 1 Draw a qualitative PV diagram showing all strokes (A, B, C and D) and all states (1, 2, 3 and 4) of the diesel cycle.

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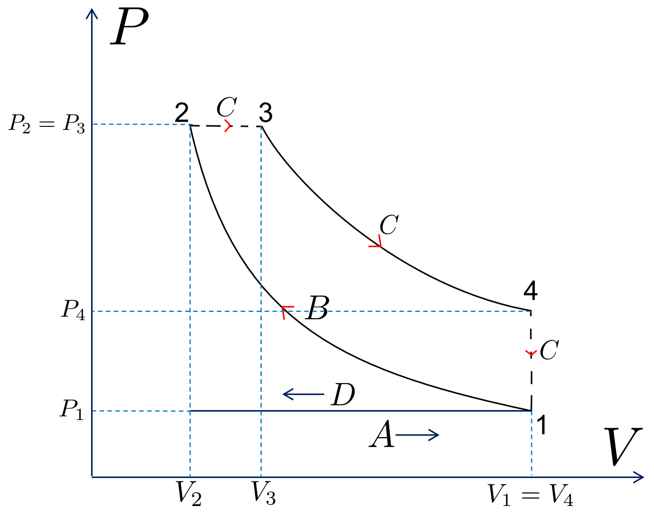

(1 pts)

Question 2 Give the compression work $W_{pf_{(1-2)}}$ as a function of data given in the text.

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Close system, adiabatic process : first law states $\Delta_t U_{(1-2)} = W_{pf_{(1-2)}}$ leading to (ideal gas) : $W_{pf_{(1-2)}} = n_{air}\bar{C}_{V_{m(air)}}(T_2 - T_1)$. (0.75 pts)

Question 3 What is the numerical value of $W_{pf_{(1-2)}}$ in kJ ?

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■ +	☐ 0	☐ 1	☐ 2	☐ 3	☐ 4	■ 5	☐ 6	☐ 7	☐ 8	☐ 9
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Question 4 Let us now focus on the combustion of the liquid diesel at 298 K and 1 bar giving gaseous water. Write the reaction of combustion of one mole of diesel.

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$C_{12}H_{23(l)} + \frac{71}{4}\ O_{2(g)} \rightarrow 12\ CO_{2(g)} + \frac{23}{2}\ H_2O_{(g)}$ (0.5 pts).

Question 5 Give the literal expression of $\Delta_r H^\circ_{298}$ of the combustion of one mole of diesel.

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Hess's law : $\Delta_r H^\circ_{298} = \nu_{(H_2O)} \Delta_f H^\circ_{298(H_2O_{(g)})} + \nu_{(CO_2)} \Delta_f H^\circ_{298(CO_{2(g)})} + -\nu_{(C_{12}H_{23})} \Delta_f H^\circ_{298(C_{12}H_{23(l)})} - \nu_{(O_2)} \Delta_f H^\circ_{298(O_{2(g)})}$ (0.5 pts).

Question 6 What is the numerical value of $\Delta_r H^\circ_{298}$ in MJ/mol ?

	[ ] 0	[ ] 1	[ ] 2	[ ] 3	[ ] 4	[ ] 5	[ ] 6	[x] 7	[ ] 8	[ ] 9
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[ ] +	[ ] 0	[ ] 1	[ ] 2	[ ] 3	[ ] 4	[x] 5	[ ] 6	[ ] 7	[ ] 8	[ ] 9
[x] −	[ ] 0	[ ] 1	[ ] 2	[ ] 3	[ ] 4	[x] 5	[ ] 6	[ ] 7	[ ] 8	[ ] 9

Question 7 Give the literal expression of $\Delta_r U^\circ_{298}$ of the combustion of one mole of diesel.

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Enthalpy definition : $H = U + PV$. So, the enthalpy variation is $\Delta_t H = \Delta_t U + \Delta_t(PV)$. For an ideal gas $PV = nRT$ leading to for isothermal processes : $\Delta_t H = \Delta_t U + RT\Delta_t(n)$. So :

$\Delta_r U^\circ_{298} = \Delta_r H^\circ_{298} - RT\Delta_t \nu_g$ with $\Delta_t \nu_g = 12 + \frac{23}{2} - \frac{71}{4}$ (0.5 pts).

Question 8 What is the numerical value of $\Delta_r U^\circ_{298}$ in MJ/mol ?

	[ ] 0	[ ] 1	[ ] 2	[ ] 3	[ ] 4	[ ] 5	[ ] 6	[x] 7	[ ] 8	[ ] 9
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Question 9 Give the literal expression of the S_{cre} of the combustion of one mole of diesel.

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For isothermal and isobaric chemical reactions $\Delta_t S_\sigma = \xi \cdot \Delta_r S^\circ_{298}$ and $S_{ex} = \frac{\xi \cdot \Delta_r H^\circ_{298}}{T}$ leading to (2nd law) : $S_{cre} = \xi \cdot \Delta_r S^\circ_{298} - \frac{\xi \cdot \Delta_r H^\circ_{298}}{T}$ with $\Delta_r S^\circ_{298} = \nu_{(H_2O)} S^\circ_{298(H_2O_{(g)})} + \nu_{(CO_2)} S^\circ_{298(CO_{2(g)})} - \nu_{(C_{12}H_{23})} S^\circ_{298(C_{12}H_{23(l)})} - \nu_{(O_2)} S^\circ_{298(O_{2(g)})}$, $\xi = 1\,\text{mol}$ and $T = 298\,\text{K}$ (1 pts).

Question 10 What is the numerical value of S_{cre} at 298 K (in kJ/(mol K)) ?

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Question 11 Give the RICE chart of the diesel combustion in the engine $\left(\frac{n_{air}}{n_{C_{12}H_{23}}} = 140\right)$, specifying the value of ξ_{max} (extent of reaction) and the quantity of all species at equilibrium.

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R	$C_{12}H_{23(l)}$	$\frac{71}{4}O_{2(g)}$	$12CO_{2(g)}$	$\frac{23}{2}H_2O_{(g)}$
I	$\frac{0.2}{140}$	0.04	0	0
C	$-\xi$	$-\frac{71}{4}\xi$	12ξ	$\frac{23}{2}\xi$
E	$\frac{0.2}{140} - \xi_{max}$	$0.04 - \frac{71}{4}\xi_{max}$	$12\xi_{max}$	$\frac{23}{2}\xi_{max}$
E	$=0$	$=0.0146$	$=0.0171$	$=0.0164$

with $\xi_{max} = 0.2/140$ mol (1 pts)

Question 12 Let's now go back to the Diesel engine. Give the literal expression of the heat Q_{hot} exchanged by the engine with the hot source considering that, from now on the mixture of combustion gases is an ideal diatomic gas of total moles $n_{comb\ gas} = 0.2$:

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Close system, constant pressure process (1st law) : $\Delta_t H = Q$. This leads for an ideal diatomic gas to :

$Q_{hot} = n_{comb\ gas}\bar{C}_{P_{m(comb\ gas)}}(T_3 - T_2)$ (0.75 pts).

Question 13 What is the numerical value of Q_{hot} in kJ ?

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■+ | ☐0 ☐1 ☐2 ☐3 ☐4 ☐5 ■6 ☐7 ☐8 ☐9

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Question 14 Give the literal expression of temperature T_4 obtained at the end of the adiabatic reversible expansion 3-4 as a function of V_4, V_3, T_3, $\bar{C}_{V_{m(comb\ gas)}}$ and R :

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Adiabatic reversible compression (first principle) : $P_3V_3^{\gamma} = P_4V_4^{\gamma}$ leading to : $T_3V_3^{\gamma-1} = T_4V_4^{\gamma-1}$ leading to :

$T_4 = T_3\left(\frac{V_3}{V_4}\right)^{\frac{R}{\bar{C}_{V_{m(comb\ gas)}}}}$ (0.75 pts)

Question 15 What is the numerical value of T_4 (in °C) ?

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Question 16 Give the literal expression of the expansion work $W_{pf_{(2-4)}}$ obtained by the complete descent of the piston between states 2 and 4 as a function of data given in the text.

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The total expansion work is $W_{pf_{(2-4)}} = W_{pf_{(2-3)}} + W_{pf_{(3-4)}}$ with $W_{pf_{(2-3)}}$ taking place at constant pressure and $W_{pf_{(3-4)}}$ in adiabatic conditions leading to :
$W_{pf_{(2-4)}} = -P_2(V_3 - V_2) + n_{(comb\ gas)}\bar{C}_{V_{m(comb\ gas)}}(T_4 - T_3)$ (0.75 pts).

Question 17 What is the numerical value of $W_{pf_{(2-4)}}$ in kJ ?

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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 18 Give the literal expression of the real efficiency η_{real} of the Diesel engine as a function of data given in the text.

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The real efficiency of the Diesel engine is : $\eta_{\text{real}} = \frac{\text{useful energy}}{\text{input energy}}$ leading to : $\eta_{\text{real}} = \frac{W_{pf_{(1-2)}} + W_{pf_{(3-4)}}}{Q_{hot_{2-3}}}$ (0.5 pts).

Question 19 What is the numerical value of the real efficiency η_{real} ?

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☐0 ☐1 ■2 ☐3 ☐4 ☐5 ☐6 ☐7 ☐8 ☐9

2 Opening a jam jar (4 points)

It's strawberry season. You've decided to make jam. In your kitchen ($T_0 = 25\,°C$ and $P_0 = 1\,atm$), you mix the fruit and sugar and bring to the boil. The temperature of the mixture reaches $T_b = 100\,°C$. When the jam is ready, you put it in a jar.

The jar is like a perfect, undeformable cylinder of radius $R = 6\,cm$ and height $h = 12\,cm$. You fill it with jam up to a height of 10.0 cm, leaving 2.0 cm of air space. Immediatly after, you place the lid (also dimensionally stable) on the jar **without screwing it on**. There is no air leak between the inside and outside of the jar thanks to a rubber joint. Once the jar has cooled down to the kitchen temperature, you'll notice that it's sealed, meaning that it's very difficult to open.

Data : temperature of the kitchen : $T_0 = 25\,°\text{C}$, Pressure in the kitchen $P_0 = 1\,\text{atm}$, vapor pressure of water at T_0 : P_0^{VS} =3 kPa.

Question 20 Assuming the gas at the top of the jam inside the jar is dry air at T_b when the lid is placed, give the pressure inside the jar (in bar) after the jar has cooled down.

■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 21 Give the value of the force (in N) to apply to open the jar.

□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 22 Assuming now that the gas on top of the jam inside the jar is humid air (with $RH = 50\%$) at T_b when the lid is placed, give the expression of the force to apply to open the jar after cooling as a function of R, RH, T_b, P_0, P_0^{VS} and T_0.

□Vide □Faux □1 □2 □3 □4 ■5

The gas on top of the jam is a mixture of water and air. The vapor pressure of water at $T_b = 100\,°\text{C}$ is $P_0 = 1\,\text{atm}$ and the partial pressure of water is then : $\frac{RH}{100}P_0$ (0.5 pts).

The partial pressure of air at T_b is then $(1 - \frac{RH}{100})P_0$ (0.5 pts).

After cooling, at T_0, the partial pressure of air is $(1-\frac{RH}{100})\frac{T_0}{T_b}P_0$ (0.5 pts) and the partial pressure of water is P_0^{VS} =3 kPa.

The final pressure inside the jar is : $(1 - \frac{RH}{100})\frac{T_0}{T_b}P_0 + P_0^{VS}$. (0.5 pts)

The force applied is the pressure difference between the inside and the outside of of jar multiplied by the surface of the lid :

$$F = \left\{P_0\left[1-(1-\frac{RH}{100})\frac{T_0}{T_i}\right] - P_0^{VS}\right\}\pi R^2$$ (0.5 pts).

Question 23 Give the value of the force (in N) to apply to open the jar.

☐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

3 Payback on a photovoltaic panel (6 points)

Photovoltaic panels are based on silicon semiconductor technology, which requires a great deal of energy (mostly electricity) to manufacture. This energy, known as "embodied energy", is some kind of energy debt that the panel must repay over its lifetime. The time it takes to repay this debt is known as the "energy payback time". The embodied energy of a solar panel is $E_e = 583\,\text{kWh/m}^2$. The map of average photovoltaic potential power (figure 1) and the map of carbon intensity of electricity (figure 2) are given. Finally, we consider that the efficiency of photovoltaic panels is 0.125.

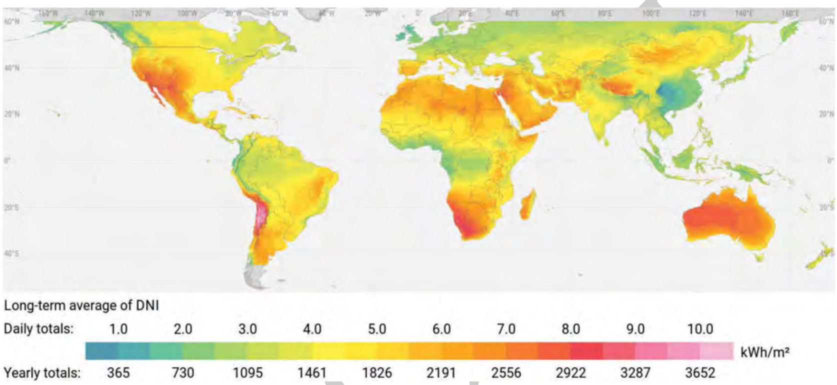

FIGURE 1 – In 2020, the Energy Sector Management Assistance Program published a map of average photovoltaic power potential. It represents the average power that a photovoltaic panel would receive if deployed, in a given area of the globe.

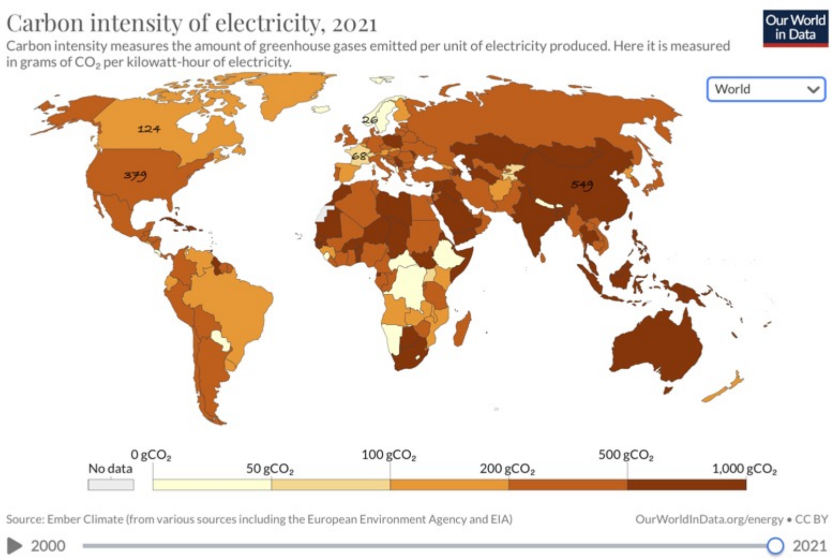

FIGURE 2 – Carbon intensity of electricity produced in different countries.

Question 24 What is the payback time in terms of CO_2 emissions for a solar panel installed in different parts of the world (using France and China as examples) and manufactured in different parts of the world (using the same countries) ? ☐Vide ☐Faux ☐1 ☐2 ☐3 ☐4 ☐5 ■6

Own the problem : We are given the PhotoVoltaic (PV) power potenial : $E_p^F = 1400\,\mathrm{kWh/m^2/year}$ and $E_p^C = 1500\,\mathrm{kWh/m^2/year}$ in France and China resp. (0.5 pts)), the carbon intensity of electricity : $I_{CO_2}^F = 68\,\mathrm{gCO2/kWh}$ and $I_{CO_2}^C = 549\,\mathrm{gCO2/kWh}$ in France and China resp. (0.5 pts)), the usage time in year of the pannel : n_y, the payback time in year of the pannel : n_y^0, the efficiency of a photovoltaic pannel : η. (0.5 pts).

Resolution strategy : We are going to calculate the CO_2 debt per square meter of PV pannel as a function of lifetime and find n_y for with the debt is back to zero. (0.5 pts)

Resolution : The initial debt is $E_e I_{CO_2}^i$, where i is either F of C represent the country of fabrication. (0.5 pts)

Each year, the PV pannel injects CO_2 free electricity, saving $E_p^j \eta I_{CO_2}^j$, where j stands for the country where the pannel is installed. (0.5 pts)

The debt is therefore : $E_e I_{CO_2}^i - n_y E_p^j \eta I_{CO_2}^j$ (0.5 pts), leading to a payback time :

$$n_y^0 = \frac{E_e I_{CO_2}^i}{E_p^j \eta I_{CO_2}^j}$$ (0.5 pts)

n_y^0 (year)	Made in Fr.	Made in Ch.
Installed in Fr.	4	28
Installed in Ch.	1	4

(1 pts)

Critical look : Installing in France PV pannel made in China does not make much sense since the payback time is 28 years, more than the expeted lifetime of a PV pannel. However, PV pannels made in France are worth installing anywhere ! (1 pts)