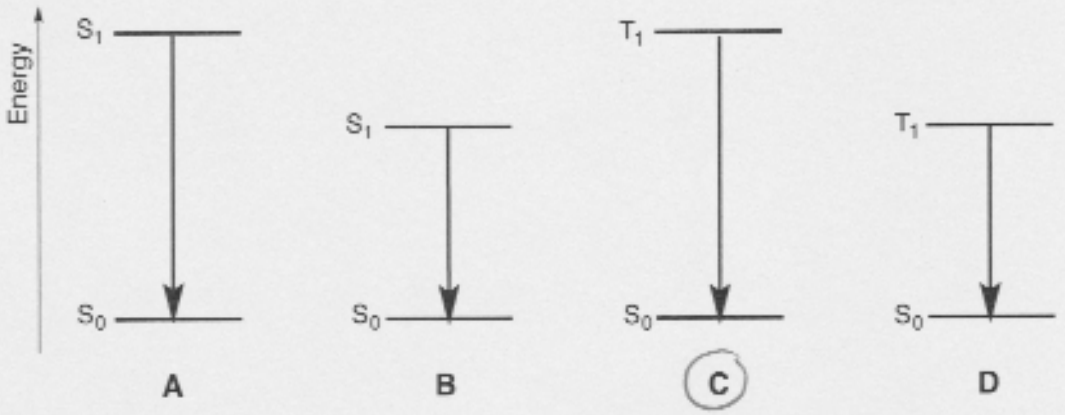
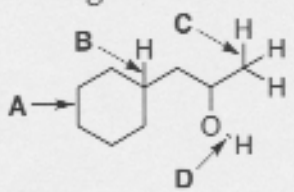
1. (16 pts) Short answers – one or two points each.

a) Among the 4 emissions below, which would have the longest lifetime and the shortest wavelength?



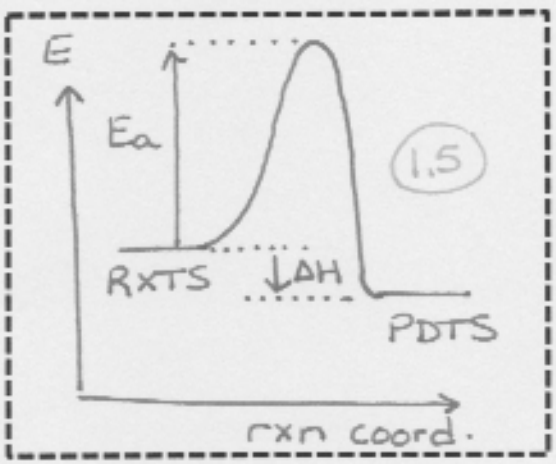
(1)

b) Classify the following indicated bonds (A to D) in order of *increasing* BDE.



A < B < C < D (2) (0.5 each)

c) In the box at right, draw the reaction profile for a reaction that is slow but slightly exothermic (label all parts of your diagram). If the temperature is increased, what are the relative effects on the rate and equilibrium point of the reaction?



(1.5)

Rate: $k \propto T$

(INCREASES) DECREASES NO CHANGE (1)

RXTS ⇄ PDTS + Δ

Equilibrium:

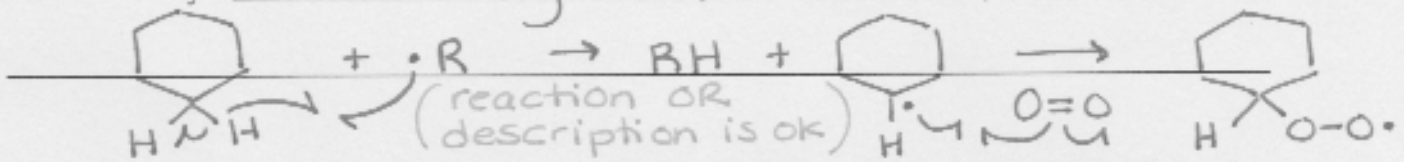
(TOWARDS REACTANTS) (1) TOWARDS PRODUCTS NO CHANGE

d) Of the different types of coal found in nature, the variety with the highest energy content is known as anthracite (1).

e) The chain length of a chain reaction is directly proportional to

initiation / termination termination / propagation (propagation / initiation) (1)

f) Cyclohexane is a very good "hydrogen donor", yet it is not considered to be an anti-oxidant. Why? The resulting radical reacts with O_2: (1)



g) The reaction A → products is a second order reaction in A. To find the rate constant, one can plot 1/[A] (0.5) vs. t (0.5). The unit of k is $M^{-1}\,s^{-1}$ (0.5).

h) Four identical Bunsen burners are supplied with 4 different fuels. If all the burners use the same gas flow, which fuel creates the largest flame?

Fuel	A	B	C	D
Flame Speed (cm/s)	20.7	16.6	44.9	53.2

(1)

i) Two ways to *maximize* the rate constant for a diffusion-controlled reaction are 1) use a solvent of low viscosity; 2) increase temperature (2)

j) The equilibrium between CO and CO_2 produced from the combustion of a hydrocarbon is temperature *and* pressure dependent. Predict the preferred equilibrium direction at:

i. high temperature & low pressure: CO favoured / CO_2 favoured (1)

ii. high pressure & low temperature: CO favoured / CO_2 favoured

k) The first synthetic organic compound of industrial and commercial success was

MAUVEINE TRINITROTOLUENE SULFURIC ACID VIOXX (1)

BONUS.

Draw a mechanism for the following. What is the name of this type of radical step?

$$CH_2O + O_2 \longrightarrow \cdot CHO + HO_2\cdot$$

(2)

BRANCHING.

2. (10 pts) FREE RADICALS

a) (5 pts) Derive the rate law and the overall reaction for the free radical chain reaction below. Label the scheme with step names and any rate constants you use.

$Cl_2 \xrightarrow{k_i} 2\,Cl\cdot$ INITIATION

$CH_4 + Cl\cdot \longrightarrow HCl + \cdot CH_3$ } PROPAGATION

$\cdot CH_3 + Cl_2 \xrightarrow{k_p} CH_3Cl + Cl\cdot$ } PROPAGATION

$2\,\cdot CH_3 \xrightarrow{k_t} CH_3CH_3$ TERMINATION

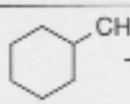
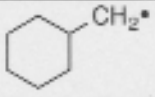
$\text{rate} = k_p[\cdot CH_3][Cl_2]$

$2k_i[Cl_2] = 2k_t[\cdot CH_3]^2$

$\therefore [\cdot CH_3] = \left(\frac{k_i}{k_t}\right)^{1/2}[Cl_2]^{1/2}$

$\therefore \text{rate} = k_p\left(\frac{k_i}{k_t}\right)^{1/2}[Cl_2]^{3/2}$

b) Use the table below to answer the following questions.

Reaction	Rate constant ($M^{-1}\,s^{-1}$)
$^tBuO\cdot + PhCH_2CH_3 \longrightarrow {}^tBuOH + Ph\dot{C}HCH_3$	1.0×10^6
$^tBuO\cdot + PhCH_3 \longrightarrow {}^tBuOH + PhCH_2\cdot$	2.3×10^5
$^tBuO\cdot +$  $\longrightarrow {}^tBuOH +$ 	1.7×10^4

(1 pt) These reactions are all examples of the radical-molecule reaction known as

(H) atom abstraction

(1.5 pts) Choose one of the reactions and draw the complete mechanism.

General: $^tBu\text{-}O\cdot + H\text{-}R \longrightarrow {}^tBuO\text{-}H + R\cdot$

(1 pt) Are the reactions expected to be exothermic or endothermic? EXOTHERMIC

(1.5 pts) Briefly explain the trend in the values of the observed reaction rate constants.

As BDE of the C-H bond decreases, $E_a \downarrow$ and thus $k \uparrow$.

3. (8 pts) THERMOCHEMISTRY

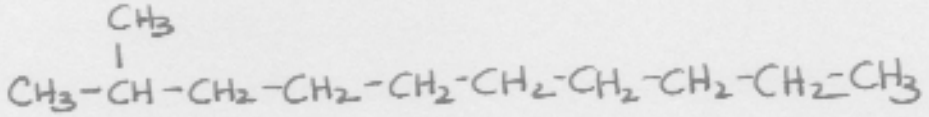
a) (1 pt) From the three following hydrocarbons, the best choice for a *diesel* fuel would be 2-methyldecane and for *gasoline*, 2-methyl-2-pentene

cyclohexane 2-methyl-2-pentene 2-methyldecane

b) (6 pts) Using the additivity table and the values below, calculate the enthalpies of combustion (in kJ/mol) of the two fuels you chose in part (a).

ΔH_f° of $CO_2(g)$ = –303.4 kJ/mol ΔH_f° of H_2O (l) = –286 kJ/mol

(A)



$\Delta H_f^\circ =$	$C-(H)_3(C)\times 3$	$3(-10.2)$
	$C-(H)(C)_3\times 1$	-1.90
	$C-(H)_2(C)_2\times 7$	$7(-4.93)$

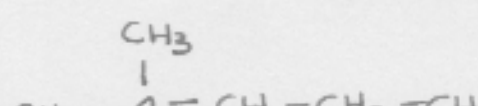
$\rightarrow -67.01 \frac{kcal}{mol} \times \frac{4.184\,kJ}{kcal} = -280.4$ kJ/mol

$C_{11}H_{24} + 17\,O_2 \rightarrow 11\,CO_2 + 12\,H_2O$

$\therefore \Delta H_{rxn}^\circ = [11\times(-303.4) + 12\times(-286)] - [(-280.4) + 17(0)]$

$= -6.49\times10^3$ kJ/mol

(B)



$\Delta H_f^\circ =$	$C-(H)_3(C_d)\times 2$	$2(-10.0)$
	$C_d-(C)_2\times 1$	10.34
	$C_d-(C)(H)\times 1$	8.59
	$C-(H)_2(C_d)(C)\times 1$	-4.76
	$C-(H)_3(C)\times 1$	-10.2

$\rightarrow -16.03 \frac{kcal}{mol} \times \frac{4.184\,kJ}{kcal} = -67.07$ kJ/mol

$C_6H_{12} + 9\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O$

$\therefore \Delta H_{rxn}^\circ = [6\times(-303.4) + 6\times(-286)] - [(-67.07) + 9\times(0)]$

$= -3.47\times10^3$ kJ/mol

c) (1 pt) Which fuel has a higher energy content on a per carbon atom basis?

(A) $\frac{-6.49\times10^3\,kJ}{11\ C\ atoms} = -590 \frac{kJ}{C}$ (B) $\frac{-3.47\times10^3\,kJ}{6\ C\ atoms} = -578 \frac{kJ}{C}$

$\therefore$ 2-METHYL-DECANE

4. (8 pts) ORGANIC FEEDSTOCKS

a) (1 pt) Complete the following reaction:

$CaC_2(s) + H_2O(l) \longrightarrow CaO(s) + H\text{-}C\equiv C\text{-}H\,(g)$

b) (2 pts) In the Bergius-Pier Process, coal is transformed in an oil-like feedstock by treating

it with a(n)	ACID	BASE	(METAL)	catalyst
with	LOW	(HIGH)	MEDIUM	hydrogen gas pressure.

c) (2 pts) Methane can be converted into a useful synthetic gas mixture called syn gas. What are the two components of syn gas? Write the chemical equation for one of the possible conversions seen in class.

Syn gas = $CO + H_2$

* any of the reactions seen in class are ok,

ex: $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$

d) (3 pts) Why are petroleum transformation processes (like cracking, reforming, etc.) necessary? What is the principal purpose of these transformations?

The SUPPLY of the desired fractions does not match the DEMAND for those materials. Thus, the purpose of petroleum refining is to convert useless HEAVY FRACTIONS into useful chemicals (instead of discarding them!).

5. (8 pts) COMBUSTION

a) (3 pts) Briefly describe the properties of the flame produced when the ports on a Bunsen burner are completely closed and completely open. What are the names of the two different flames?

CLOSED = DIFFUSION FLAME. Cooler flame, silent.
O_2 is brought to the flame surface by diffusion through air.

OPEN = PREMIXED FLAME. Hotter, noisier.
O_2 is mixed with the fuel before the flame surface.

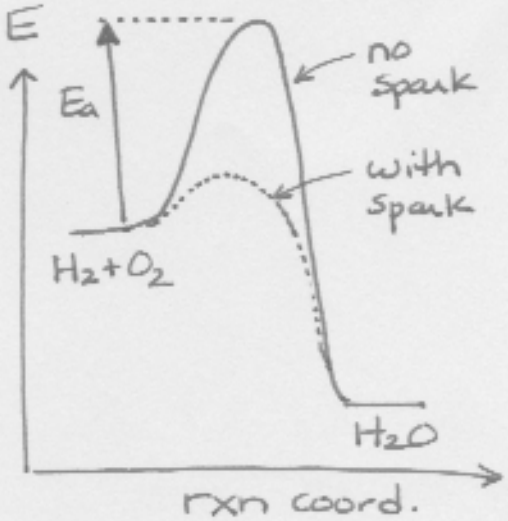
b) (2 pts) As the port is opened, the colour of the flame changes from yellow to mostly blue. What is the source of these two colours? Why is the colour changing?

YELLOW = blackbody radiation from soot particles
BLUE = excited state emission from carbonyls

Change from yellow → blue indicates improving combustion efficiency going from diffusion to pre-mixed flame (partial → complete combustion)

c) (3 pts) Mixtures of hydrogen and oxygen gas are stable at room temperature and atmospheric pressure. Why is a match required to induce combustion? You may draw a reaction profile to illustrate your answer.

$H_2 + O_2$ combustion has a high activation energy barrier (slow direct reaction). Adding a spark provides a source of radicals, creating an alternative mechanism with a much lower Ea!



6. (8 pts) ASSORTED

a) (3 pts) Below is a synthesis of MTBE. In the space underneath, add the catalyst used at each step and circle the relative pressure needed.

CATALYST:	ZEOLITE (LEWIS ACID)	METAL	ACID (H^+)
	LOW	(LOW)	LOW
PRESSURE:	HIGH	HIGH	(HIGH)
	(IRRELEVANT)	IRRELEVANT	IRRELEVANT

b) (2 pts) What does MTBE stand for? Why is it added to fuels?

- methyl-tert-butyl ether
- improves octane number (reduces knocking)

c) (3 pts) Thermal cracking of A, initiated by a methyl radical at 650°C, leads to one equivalent of each of the products B to E shown below. Draw a mechanism that explains the formation of B to E.