1. Consider a Carnot engine in which the working substance is at temperature T_{hw} as it absorbs heat from the hot reservoir, and at temperature T_{cw} as it expels heat to the cold reservoir. Under most circumstances the rates of heat transfer will be directly proportional to the temperature difference as follows:

$$\frac{Q_h}{\Delta t} = K\left(T_h - T_{hw}\right) \text{ and } \frac{Q_c}{\Delta t} = K\left(T_{cw} - T_c\right)$$

We assume here for simplicity that constant K are the same in these situation. And we also assume that both process take the same amount of time, so the Δt's are the same in both of these equations.

(a) Describe all the steps of Carnot cycle with proper processes, such as adiabatic. Then draw two diagrams (temperature versus entropy and pressure versus volume) with the steps you labeled. *(5%)*

(b) Assuming that no new entropy is created during the cycle except during the two heat transfer process, derive an equation that relates the four temperatures T_h, T_c, T_{hw}, and T_{cw}. *(5%)*

(c) Assuming that the time required for the two adiabatic steps is negligible, write down an expression for the power (work per unit time) output of this engine. Use thermodynamics first and second law to write the power entirely in terms of the four temperatures (and constant K), then eliminate T_{cw} using the result of part (b). *(5%)*

(d) Show that, for fixed T_h and T_c, the expression you found in part (c) has a maximum value at $T_{hw} = \frac{1}{2}\left(T_h + \sqrt{T_c / T_h}\right)$. Find the corresponding expression for T_{cw}. *(5%)*

(e) Show that the efficiency of this engine is $1 - \sqrt{T_c / T_h}$. Evaluate this efficiency numerically for a typical coal-fired steam turbine with $T_h = 600°C$ and $T_c = 25°C$, and compare the ideal Carnot efficiency for this temperature range. Which value is closer to the actual efficiency of a coal-fired power plant of approximately 40%? *(5%)*

(f) Based on thermodynamics, why do you think a fuel cell is usually much more efficient than a heat engine? *(5%)*

見背面

2. The surface forming the boundary between two given phases generally has a fixed thickness, regardless of its area. The additional Gibbs free energy of this surface is therefore directly proportional to its area; the constant of proportionality is called the surface tension, σ:

$$\sigma \equiv \frac{G_{\text{boundary}}}{A}.$$

If you have a blob of liquid in equilibrium with its vapor and you wish to stretch it into a shape that has the same volume but more surface area, then σ is the minimum work that you must perform, per unit of additional area, at fixed temperature and pressure.

(a) Consider a spherical droplet of water containing N_l molecules, surrounded by $N - N_l$ molecules of water vapor. Neglecting surface tension for the moment, write down a formula for the total Gibbs free energy of this system in terms of N, N_l, and the chemical potentials of the liquid and vapor. Rewrite N_l in terms of v_l, the volume per molecule in the liquid, and r, the radius of the droplet. *(5%)*

(b) Now add to your expression for G a term to represent the surface tension, written in terms of r and σ. *(5%)*

(c) Sketch a qualitative graph of G vs. r for both signs of $\mu_g - \mu_l$, and discuss the implications. For which sign of $\mu_g - \mu_l$ does there exist a nonzero equilibrium radius? Is this equilibrium stable? *(5%)*

(d) Let r_c represent the critical equilibrium radius that you discussed qualitatively in part (c). Find an expression for r_c in terms of $\mu_g - \mu_l$. Then rewrite the difference of chemical potentials in terms of the relative humidity (RH), assuming that the vapor behaves as an ideal gas. The relative humidity is defined in terms of equilibrium of a vapor with a flat surface, or with an infinitely large droplet. (Consider the reference pressure to be the vapor pressure in equilibrium with a flat surface of the liquid) *(5%)*

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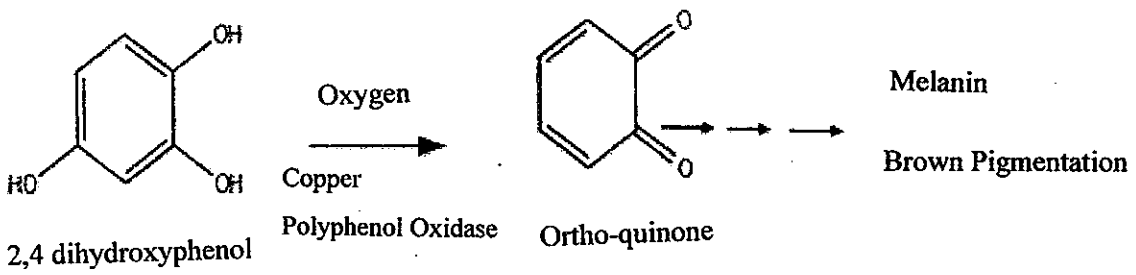
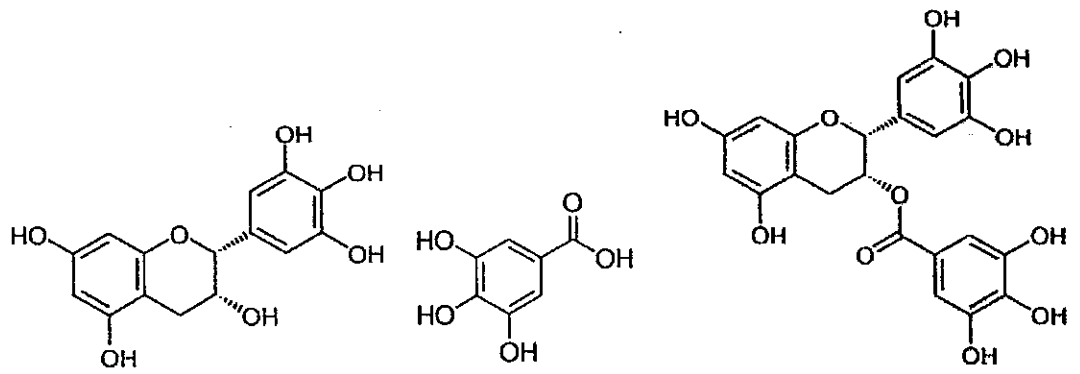
3. 讀完以下文章後，簡答文後所列問題，必要時請列出算式，中英文皆可 (50%)

食品褐變(Food browning)有化學性與酵素性反應。如蘋果接觸空氣中的氧分子，會因為組織中 Polyphenol oxidase 的催化，造成 Phenol 類的氧化而產生黃色的 Quinone，濃度一高視覺上就呈現棕色。



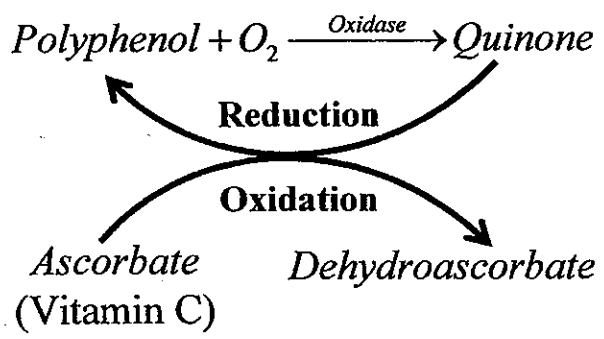
Browning catalyzed by phenol oxidation or copper ion

綠茶的澀味主成分的 Epigallocatechin gallate (化學構造如下圖)即是茶品褐變的主因。



Epicatechin (left), gallic acid (middle) and epigallocatechin gallate (right)

在茶葉發酵的過程中，上述的 Catechin 類化合物被從新鮮茶葉液泡中所釋放出來的 Polyphenol oxidase 催化其氧化過程而轉化成 Quinone 類化合物。此時新鮮茶葉組織中的維他命 C 會將其還原回來。



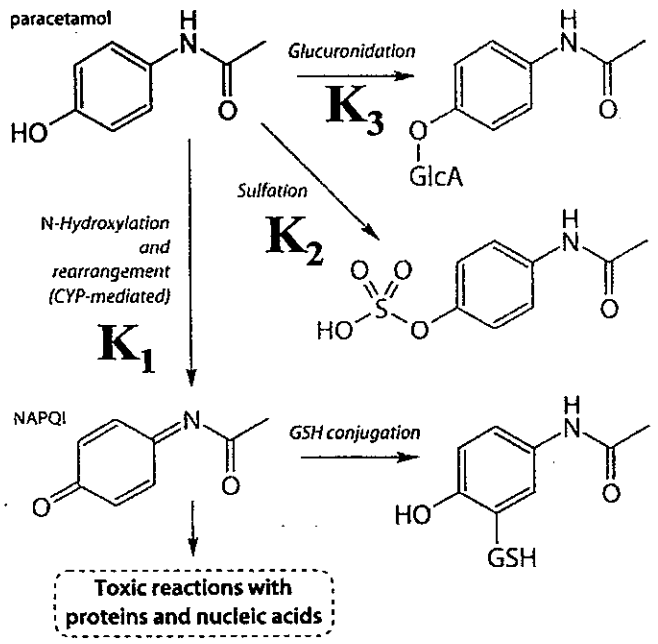
Chemical process during tea withering

日本煎茶的製程，即是在上圖的平衡中，以熱處理讓酵素失活。於是 Quinone 一直保持在低含量，沒有明顯的褐變過程，所以茶湯呈現翠綠色。烏龍茶的萎凋(發酵)過程，則是讓酵素作用，等到內含的維他命 C 用完，才開始褐變。

見背面

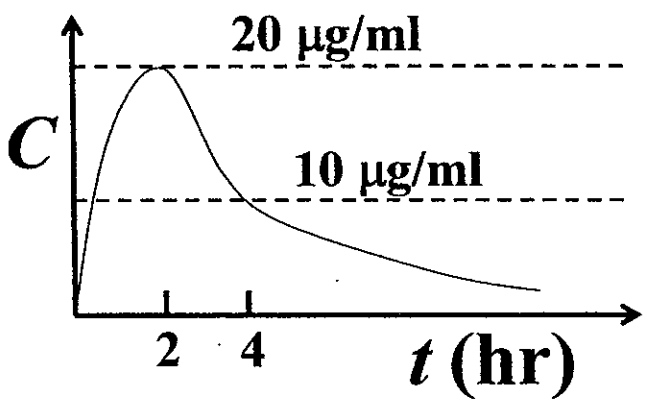
小明分別以放置於 25 度與 85 度 C 保溫箱的熱水泡烏龍茶，因為酵素已於製茶過程中失活，也沒有被萃取出來，但是由茶色發現褐變還是繼續進行。他將茶繼續放在 25 度與 85 度保溫箱中，定時採樣以分光光度計量測褐變速度，發現 85 度的褐變速率為 25 度的 3 倍。小明心想，100 度應該更快吧! 於是用煮沸的水萃取，但發現褐變速度反而比 85 度 C 還慢。百思不得其解後，於烏龍茶中擠入些許檸檬，發現褐變被逆轉了。

小明越想越頭痛吃了顆普拿疼，錠劑在胃內崩解後主成分 Paracetamol 於腸道以一定速度(K_{GI})被吸收，於兩小時內血中達到峰值濃度 20　g/ml，頭痛獲得緩解。但是，Paracetamol 於生理 pH (7.45)中屬於脂溶性，所以，肝臟進行如下圖三種類的 Biotransformation，將它轉化成水溶性物質由腎臟迅速排除。其中，速率常數為 K_1 的代謝路徑，是誘發肝毒性的主因。



Biotransformation of paracetamol in liver

所以，好景不常，超過 4 小時後，小明頭又痛了，此時血中濃度(C)降為 10　g/ml。



Plasma concentration of paracetamol after oral administration

在請問藥學專家後，專家說普拿疼半衰期只有約 2 小時，你可以試試普拿疼長效錠。然後給他一個微分方程式，說剛開始吃藥後腸道還有普拿疼時血中濃度變化如下式：

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$$\frac{dC}{dt} = K_{GI} - (K_1 + K_2 + K_3)C$$

若腸道沒有普拿疼時：

$$\frac{dC}{dt} = -(K_1 + K_2 + K_3)C$$

小明百思不解，找化工系同學用 Laplace transformation 分別解得：

$$C(t) = \frac{K_{GI}}{K_1 + K_2 + K_3}(1 - e^{-(K_1+K_2+K_3)t})$$ (剛吃藥後)

$$C(t) = C_p e^{-(K_1+K_2+K_3)t}$$ (腸道無藥，血中濃度過峰值 Cp 後)

有一天，小明頭又痛了，看了方程式心理更是霧煞煞。於是，吃了顆普拿疼，配了杯濃茶…….

請定性或定量回答以下問題

(a) 如何減低蘋果的褐變過程？（5 分）

(b) 如何評估日本煎茶的新鮮度？（5 分）

(c) 烏龍茶的萎凋過程中不時翻動茶葉的作用是什麼？（5 分）

(d) 西方歷史上茶是於 1610 年由荷蘭商人由東亞(可能是福建)引進歐洲，但歐洲人最後卻嗜喝完全發酵的紅茶，為什麼？（5 分）

(e) 使用沸騰過的熱水萃取後的烏龍茶，為何褐變速度反而低於用 85 度 C 的水來萃取？（5 分）

(f) 為何於茶中擠入檸檬會逆轉褐變過程？（5 分）

(g) K_{GI}, K_1, K_2, K_3 的單位為何？（5 分）

(h) 小明發現吃普拿疼配茶，可以讓普拿疼藥效超過 5 小時，請問是哪個速率常數發生怎樣的改變？試繪出吃普拿疼配茶與配開水後的血中濃度變化曲線，並比較之。(5 分)

(i) 藥劑師說阿斯匹靈傷胃、不宜配茶。普拿疼傷肝，但配茶卻可以減低普拿疼對肝臟的傷害。為什麼？（5 分）

(j) 小明改天吃了普拿疼長效錠，藥效維持 12 小時，請問是哪個速率常數發生怎樣的改變？試繪出吃一般普拿疼與普拿疼長效錠後的血中濃度變化曲線，並比較之。(5 分)

試題隨卷繳回