NATURAL PROCESSES.

Photosynthesis

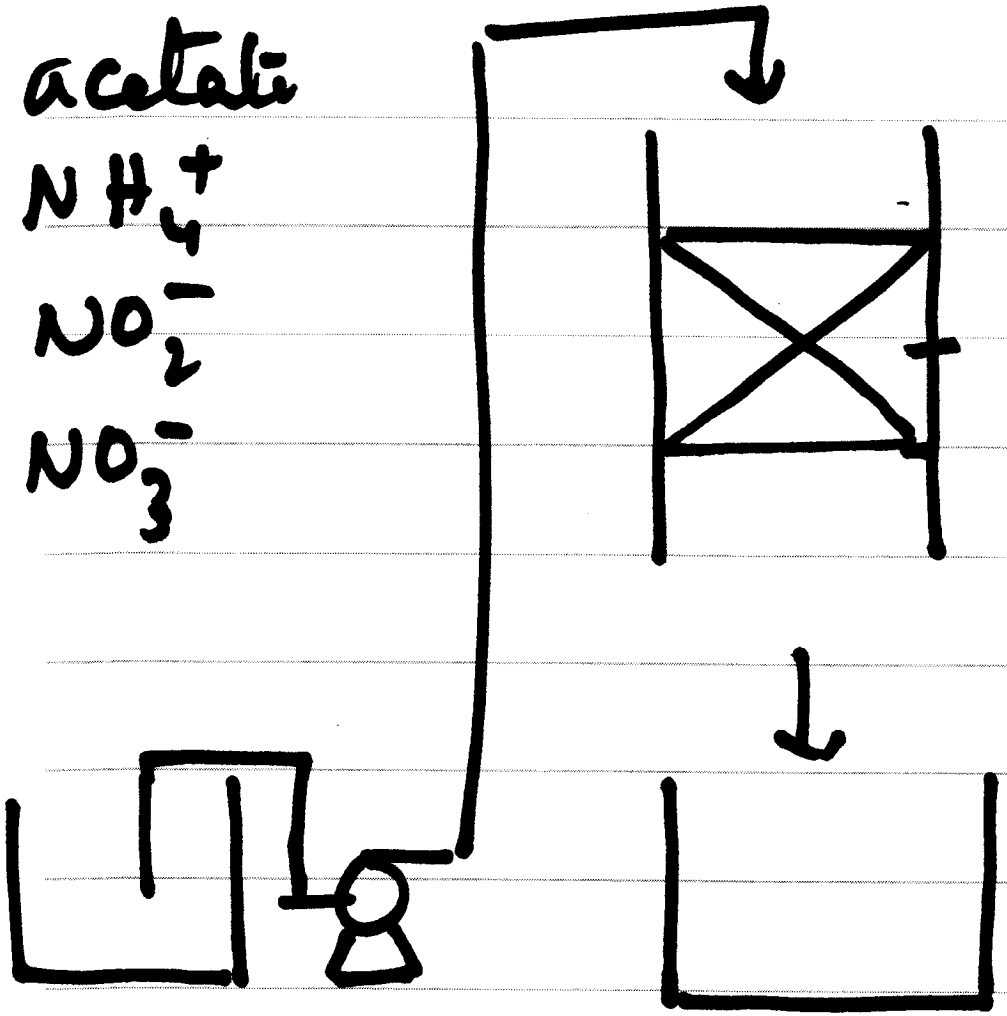
Respiration

N- fixation.

Nitrification.

Denitrification.

Methanogenesis



COD.

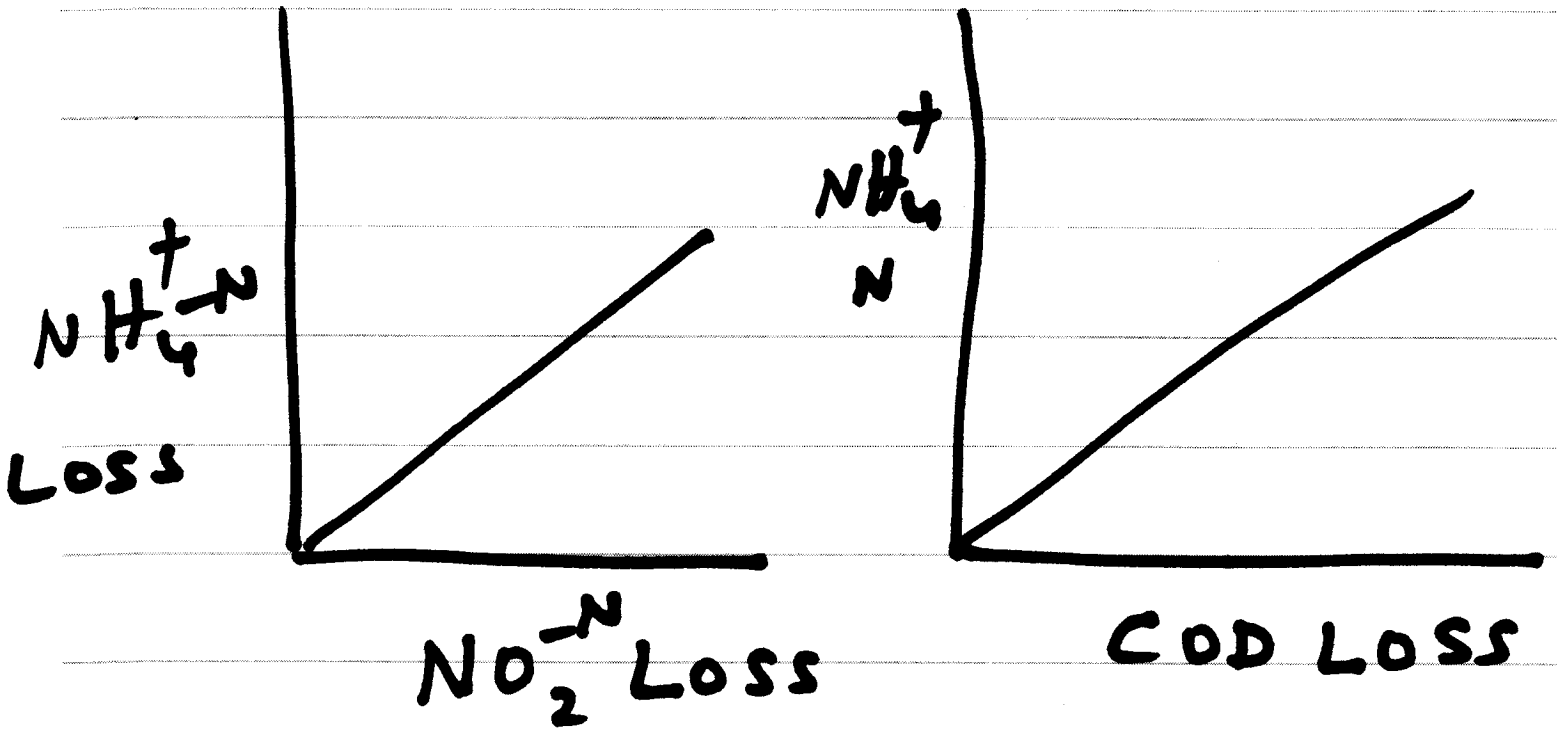
$NH_4^+ - N$

$NO_2^- - N$

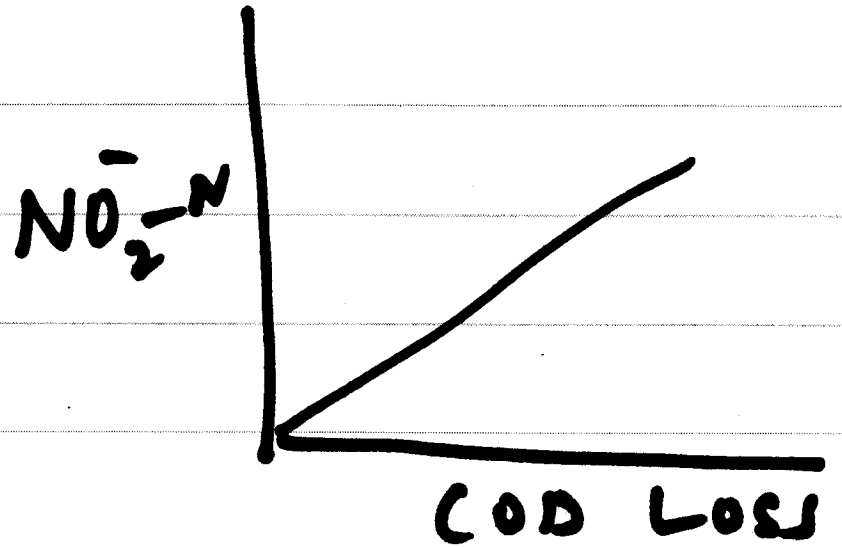
$NO_3^- - N$

Loss $\frac{NO_2^- - N}{NH_4^+ - N.}$

RUN	F	C/N	IN COD	OUT COD	IN NH_4-N	OUT NH_4-N	IN NO_2^--N	OUT NO_2-N	IN NO_3-N	OUT NO_3^-
3	3	1.86	1000	385.5	90.4	15.4	107.5	0.02	0	1.1
6	3	1.86	1000	435.5	51.1	6.3	59.8	0.7	0	2.7
12	6	1.86	1000	391.3	90.4	16.1	107.5	0.5	0	2.7
21	12	1.86	1000	400.7	90.4	17.2	107.5	2.2	0	4.1
30	3	0.93	1000	345.5	175	32.5	204.7	0.68	0	3.1
36	12	0.93	1000	374.8	175	35.3	204.7	5.2	0	2.3


NH_4^+-N Loss
NO_2^--N Loss

NH_4^+ N
COD Loss


NO_2^--N
COD Loss

X_1 $NO_2^- + H_2O + 2H^+ = NH_4^+ + 1.5O_2$ (1)

X_2 $NO_2^- + 0.5O_2 = NO_3^-$ (2)

X_3 $NH_4^+ + NO_2^- = N_2 + 2H_2O$ (3)

X_5 $CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$ (5)

X_4 Cell synthesis $= \alpha X_1$ (4)

$$\underline{NO_2^-} = A_0 - X_1 - X_2 - X_3 = A$$

$$NH_4^+ \qquad B_0 + X_1 - X_3 = B$$

$$NO_3^- \qquad C_0 + X_2 = C$$

$$X_1 = \frac{1}{2}\left[(A_0 - A) - (B_0 - B) + (C_0 - C)\right]$$

$$X_2 = C - C_0$$

$$X_3 = \frac{1}{2}\left[(A_0 - A) + (B_0 - B) + (C_0 - C)\right]$$

$$X_1 = 0.5\left[(A_0 - A) - (B_0 - B) + (C_0 - C)\right] F/V$$

$$X_2 = -(C_0 - C)\, F/V$$

$$X_3 = 0.5\left[(A_0 - A) + (B_0 - B) + (C_0 - C)\right] F/V.$$

$$X_4 = \alpha X_1$$

$$X_5 = (D_0 - D)\, F/V.$$

V: Reactor Vol

F: Flow

A - NO_2^-; B NH_4^+ C NO_3^-; D - COD

$NO_2^- - N$

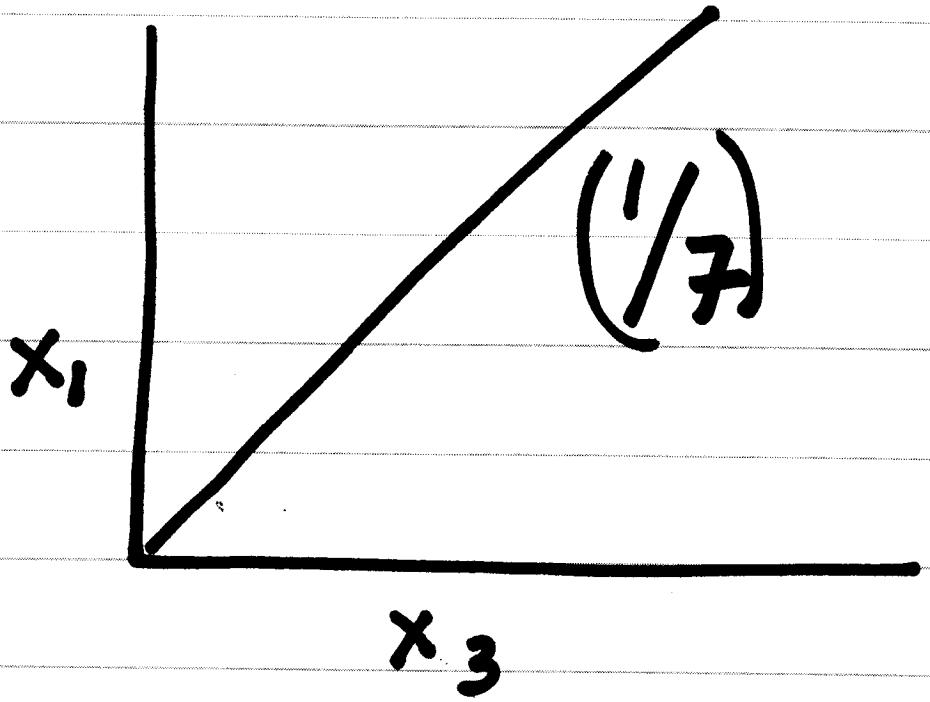
$NH_4 - N$

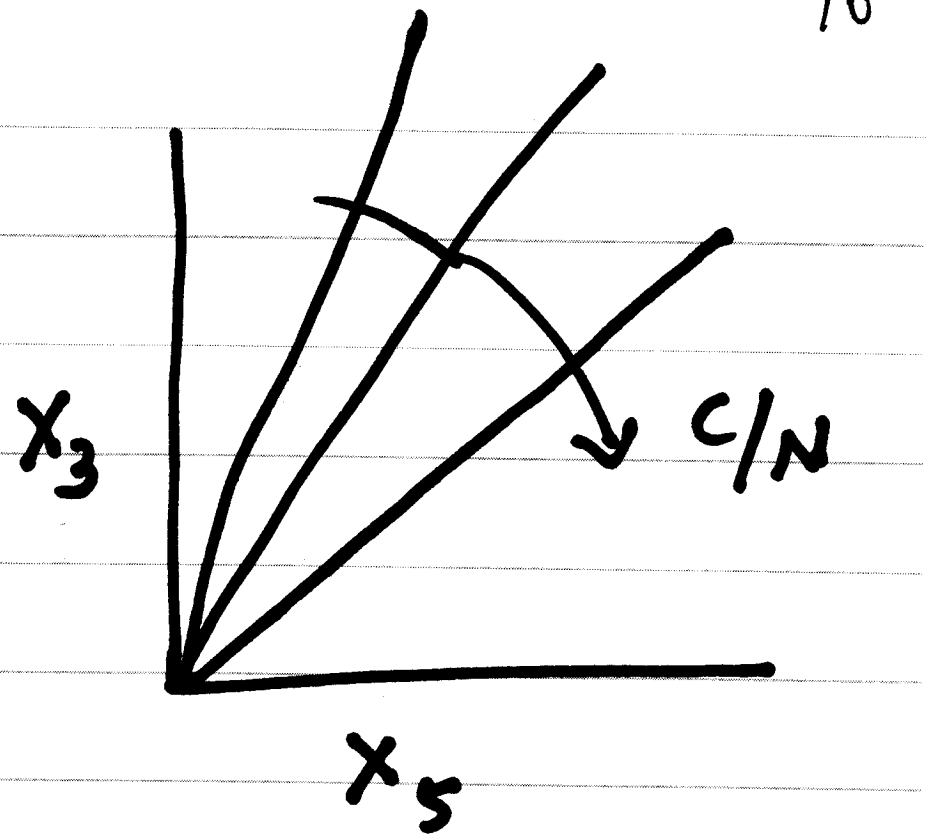
RUN	
3	~~1.42~~ 1.4 2
6	1.31
12	1.42
21	1.42
30	1.43
31	1.43

F	RUN	C_N	mg/L X_1	X_2	X_3	X_4	X_5
3	3	1.8	15.7		90.7		614
3	6	1.8	→ 5.8		50.6		524
6	12	1.8	→ 15		89.3		608
12	24	1.8	→ 14		87		600
3	30	.92	→ 29		171		655
12	36	.93	28.3		168		626

Lit/Hr

V = 20 Lit

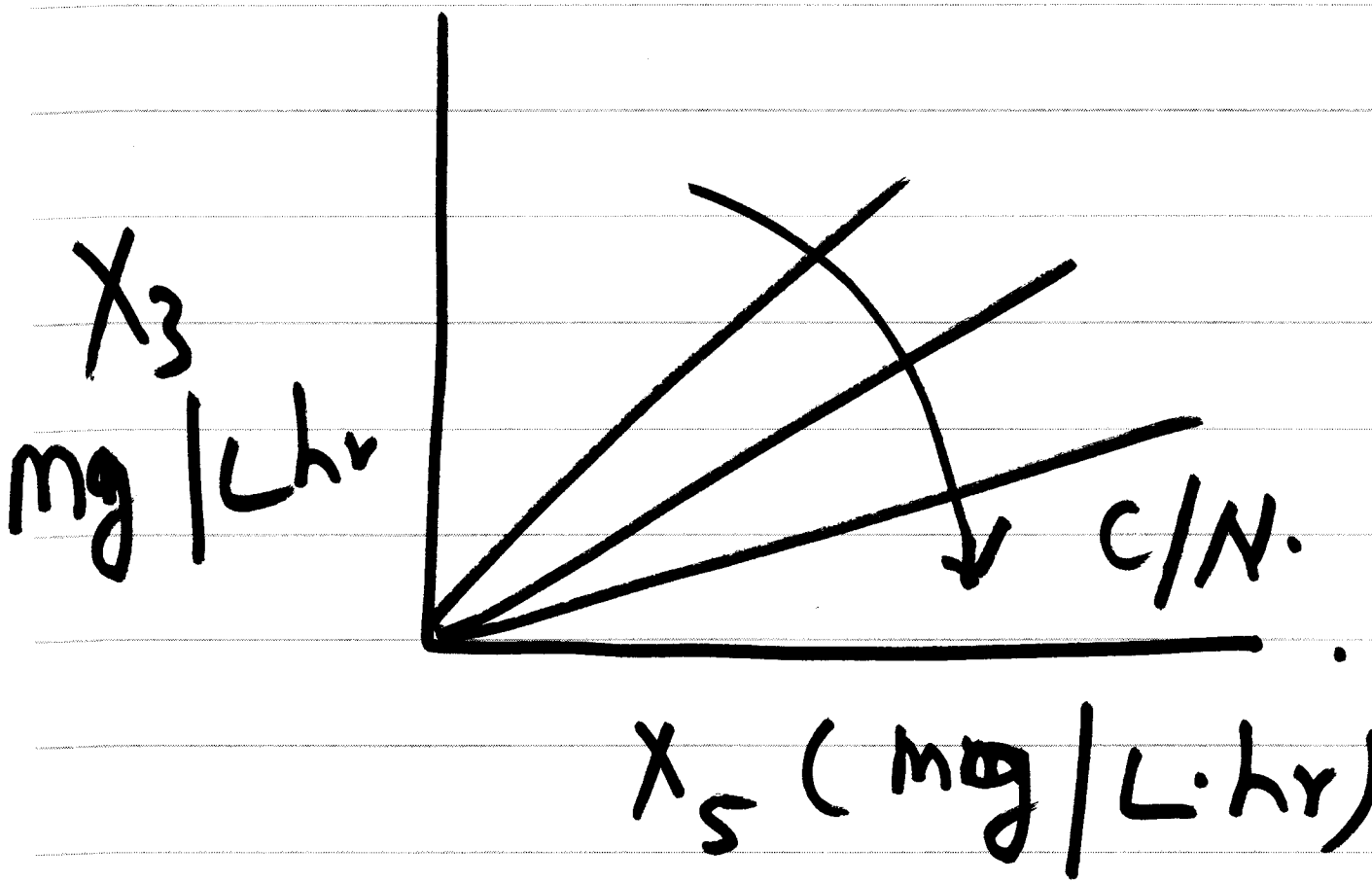




$$\frac{X_5}{X_3} = 2.84(C/N)$$

$\propto X_1 \Rightarrow X_4$

$$\frac{X_5}{X_4} = \frac{2.84\left(\frac{X_3}{X_1}\right)(C/N)}{\alpha}$$


X_3
mg/L·hr
C/N.
X_5 (mg/L·hr)

$$X_1 \Delta H_1 + X_2 \Delta H_2 + X_3 \Delta H_3 + X_4 \Delta H_4 + X_5 \Delta H_5 = 0$$

$X_3 = \lambda X_1$; $X_4 = \alpha X_1$ (C/N)

$$X_3 \left(\frac{\Delta H_1}{\lambda} + \Delta H_3 + \frac{\alpha}{\lambda} \Delta H_4 \right) + X_2 \Delta H_2 = -X_5 \Delta H_5$$

Plots of X_3 Vs X_5 can give $\frac{\alpha}{\lambda} \Delta H_4$

Since X_1 X_2 X_3 X_5 α, λ, ΔH_1, ΔH_2 ΔH_3 ΔH_5 are known

$$\alpha \Delta H_4 = 443 + 188 \text{ C/N}$$

Species	ΔG_f° kJ/mol	ΔH_f° kJ/mol
H_2O	−237	−285
NH_4^+ (aq)	−79.4	−132.5
NO_3^- (aq)	−110.35	−207.4
NO_2^- (aq)	−34.2	−104.6
CH_3COOH	−94.7	−483.5
H^+	0	0
O_2 / N_2	0	0
water (l)		−285.3
CO_2		−393

$\Delta H_1 =$ 18 kJ/g N $\Delta H_2 = -7.1$ kJ/g N

$\Delta H_3 = -25.5$ kJ/g N $\Delta H_5 = -14.5$ kJ/g COD acetat

$\Delta G_1 =$ 13.7 kJ/g N $\Delta G_2 = -5.4$ kJ/g N

$\Delta G_3 = -25.7$ kJ/g N ; $\Delta G_5 = -3.2$ kJ/g COD acetat

$\alpha \Delta G_4 =$

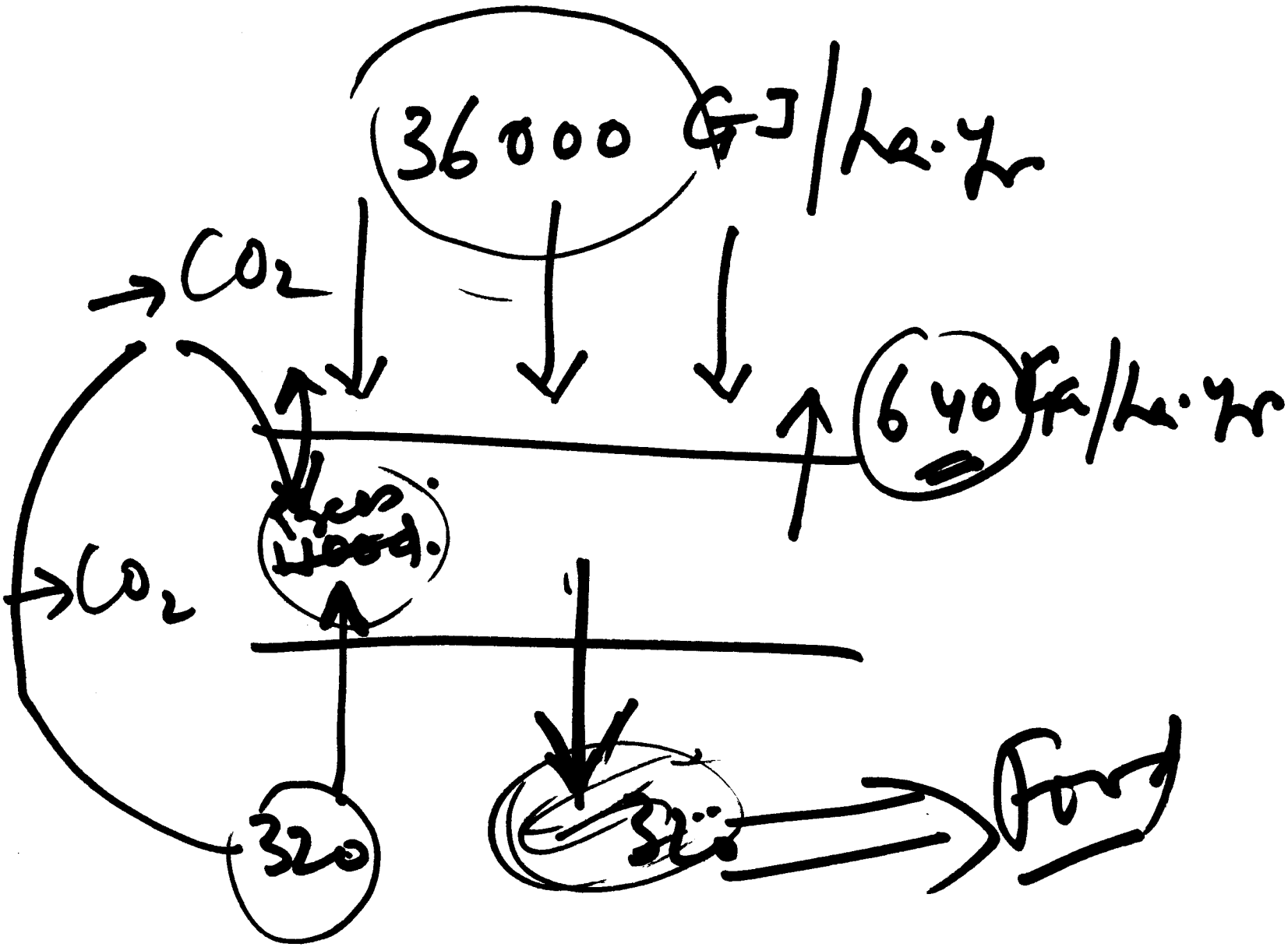
$$X_1 \Delta G + X_2 \Delta G_2 + X_3 \Delta G_3 + X_4 \Delta G_4 + X_5 \Delta G_5 = 0$$

$$X_3 = \lambda X_1 \quad \& \quad X_4 = \alpha X_1$$

$$X_3 \left(\frac{\Delta G_1}{\lambda} + \Delta G_3 + \alpha \Delta G_4 \right) + X_2 \Delta G_2 = X_5 \Delta G_5$$

gives

$$\alpha \Delta G_4 = \quad 235 + 44.5 \ \text{C/N}.$$


36000 GJ/ha·yr
CO2
640 GJ/ha·yr
CO2
320
Food

RESPIRATION PHOTOSYNTHESIS

$$nCO_2 + 2n\,H_2O + \text{Minerals (N P S K)}$$

$$+ \text{Sunlight} = (CH_2O\,N_x\,P_y\,S_z\,K_y)_n + nO_2$$

$$+ n\,H_2O$$

$x = 0.16 - 0.016$

$y: \quad 0.01 - 0.001$

$z = 0.02 - 0.002$

H

~~PHOTOSYNTHESIS~~ RESPIRATION

$$(CH_2O)_n + nH_2O + nO_2$$

$$\rightarrow nCO_2 + 2nH_2O + \underset{(NPSK)}{\text{Minerals}}$$

$$+ \text{Energy}$$

$x = 0.16 - 0.016$	Lower value terrestrial production.
$y = 0.01 - 0.001$	
$z = 0.02 - 0.002$	Higher value aquatic production.

N Fixation

$$N_2 + 2H_2O + \text{Energy} = NH_3 + O_2$$

Nitrification

$$NH_3 + CO_2 + 1.5\,O_2 = NO_2^- + H_2O + H^+ + \text{cells}$$

$$NO_2^- + CO_2 + 0.5\,O_2 = NO_3^- + \text{cells}$$

Denitrification

$$4\,NO_3^- + 2H_2O + \text{Energy} = 2N_2 + 5O_2 + 4\,OH^-$$

$$NH_4^+ + NO_2^- = N_2 + 2H_2O + \text{Energy}$$

ORGANICS →.

ACIDOGENESIS → METHANOGENESIS

$$4C_3H_7O_2NS + 6H_2O =$$

$$CH_3COOH + 6CO_2 + 4CH_4 + 4NH_3$$

$$+ 4H_2S$$

Mineral Weathering

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

Primary Mineral + CO_2 + H_2O

$$= M^{+n} + n\,HCO_3^- + \frac{\text{Soil}}{\frac{\text{Sand}}{\text{clay}}}$$