Lecture 6
Liquid-Liquid Extraction (LLE)

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Intended learning outcome

1. To compare liquid-liquid extraction with distillation.
2. To calculate number of stages required for liquid-liquid extraction using similar concepts as in distillation (equilibrium curve and operating line).
3. To analyze several cases for contact between fluid stream (countercurrent and cocurrent directions, concentrated feed).
4. To derive analytical expression (Kremser equation) for determining the number of stages.

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Solvent Selection for liquid-liquid extraction

Ideal solvent:

1) High solubility towards solute	higher degree of extraction
2) Immiscible or only partially miscible with the diluent	easier to separate solvent
3) Chemically stable	less issues with degradation
4) Nontoxic	easy to handle
5) Noncorrosive	no damage to equipment
6) Environmental friendly	no damage to environment
7) Inexpensive (readily available)	low capital cost
8) Low viscosity	lower operating cost in mixing

Industrial perspective

Table 14.1-1 *Important applications of extraction*

Industry	Objective	Typical feed	Typical solvents	Remarks
Petroleum and petrochemicals	Dewaxing lubricating oils	Crude lube stocks	Glycols, furfural, cresol, liquid SO_2	Wide variety of solvents have been used
	Higher octane aromatic fuels	Aliphatic–aromatic mixtures	Glycols, sulfolane	Demand affected by legislation
	Desulfurization for reduced emissions	Sour distillates	Dilute aqueous base	Product is elemental sulfur after further reaction
	Butadiene–butene separation	Incompletely dehydrogenated feed	Aqueous copper complexes	Unreacted butene is recycled
Pharmaceuticals and foods	Concentrating impure antibiotics	Filtered fermentation beer	Amyl acetate, methylene chloride	Penicillin is a good example
	Refining fats and oils	Soybeans	Propane, hexane	Supercritical CO_2 is often suggested
	Sugar	Beets	Water	Major domestic sugar source
Metals	Concentrating copper for electrowinning	Acidic leach liquors	Hydroxyoximes in kerosene	pH changes are key
	Gold	Low-grade ore	Sodium cyanide solutions	Can be environmental problem
	Uranium and rare earth separations	Acidic leach liquors	Tertiary amines in kerosene	Future depends on nuclear power

Taken from Diffusion: Mass transfer in fluid system by Cussler

Separation of acetic acid from water: organic solvent (isopropyl ether) is used to extract acetic acid.

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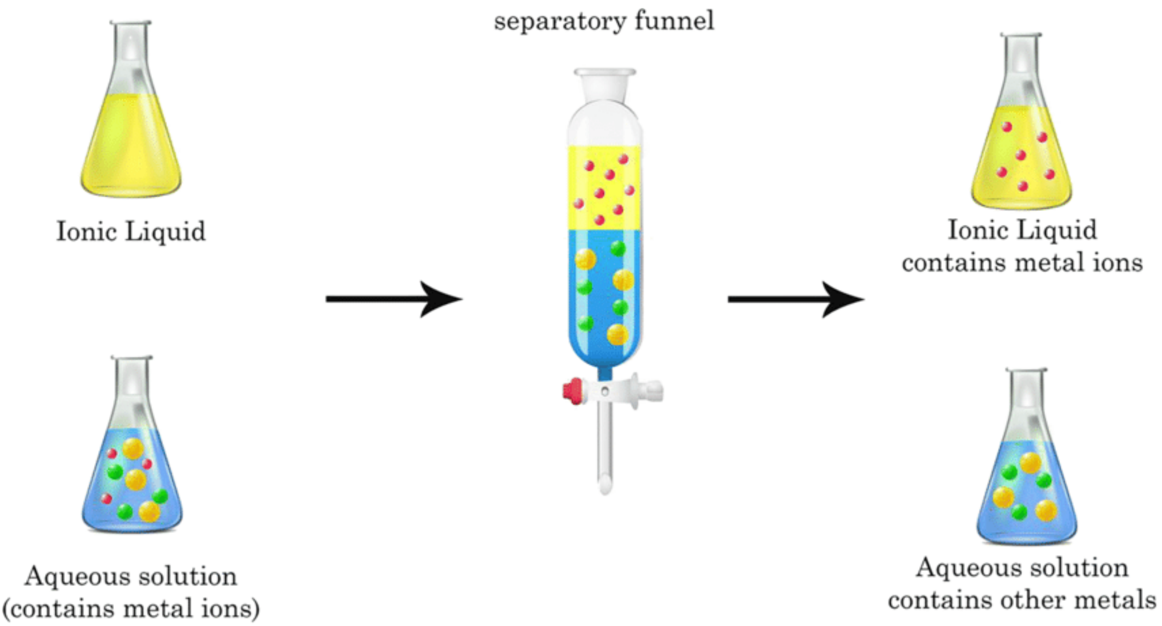
Degree of freedom
(number of variable vs. no of equation)

Solvent



Diluent: water

Source: Materials Circular Economy, 2, 10, 2020

Gibbs phase rule : $\mathscr{F} = 2 - N_{phase} + N_{component}$

Components: 3 (diluent, solute, solvent)

Phases: 2 (diluent, solvent)

Gibbs phase rule : $\mathscr{F} = 2 - 2 + 3 = 3$

Choice for independent variables

1. Pressure (isobaric operation, e.g., 1 bar)
2. Solute concentration in Feed
3. Temperature (isothermal operation) ← Different from distillation column where temperature varies in the column

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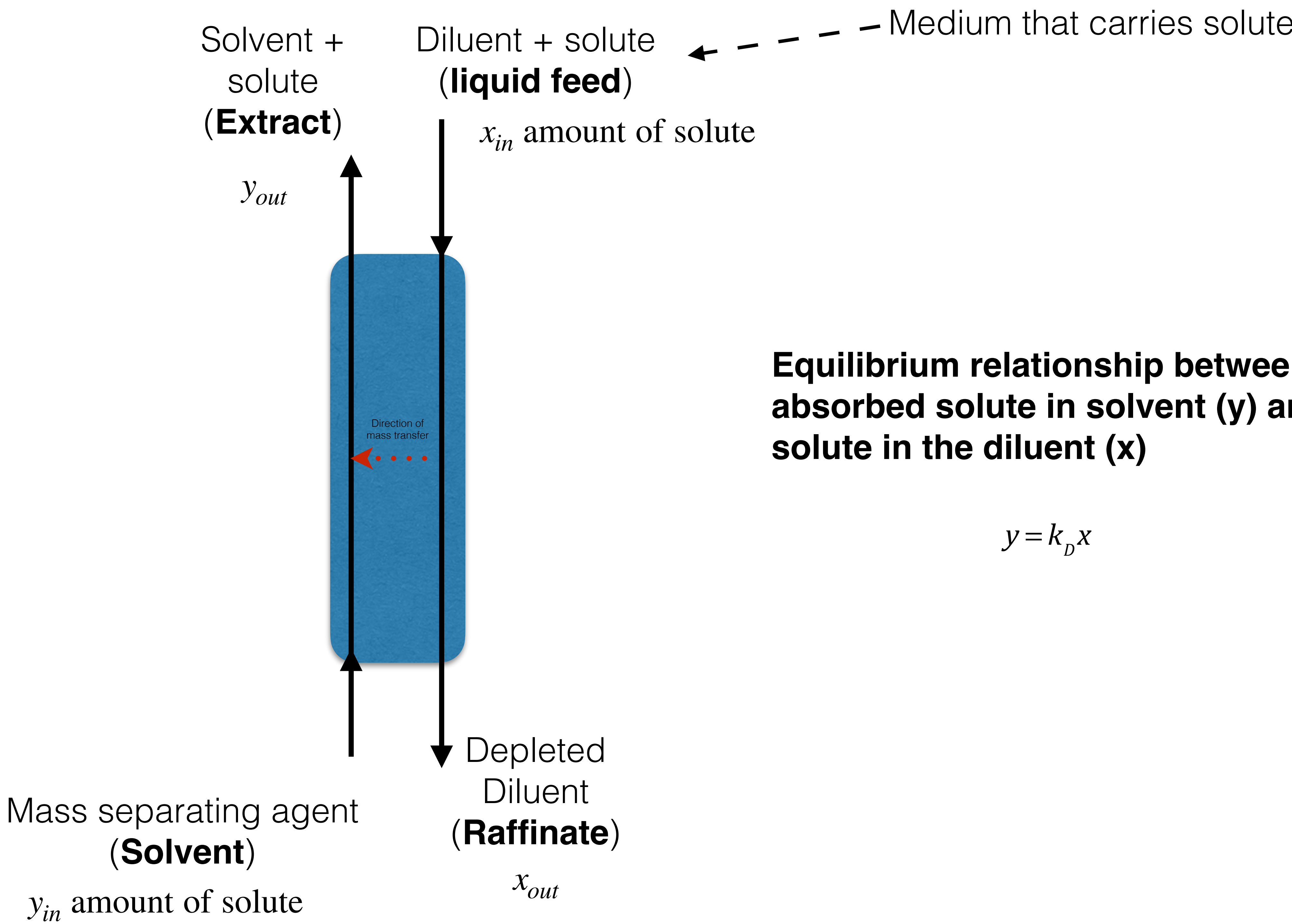
Liquid-liquid extraction carried out in continuous steady-state manner



Equilibrium relationship between absorbed solute in solvent (y) and solute in the diluent (x)

$$y = k_D x$$

Liquid-liquid extraction

Separation process	Equilibrium-stage	Steady-state
Distillation	Yes	Yes
Liquid-Liquid Extraction	Yes	Yes
Absorption	Yes	Yes
Membranes	No (diffusion)	Yes
Adsorption	No (diffusion, convection)	No

For LLE, we will setup the problem in similar manner to distillation.

Equilibrium relationship: y =f(x) between streams leaving an equilibrium stage.

Operating line: y =g(x) between streams that meet at the stage.

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Countercurrent extraction from a dilute solution using an immiscible solvent

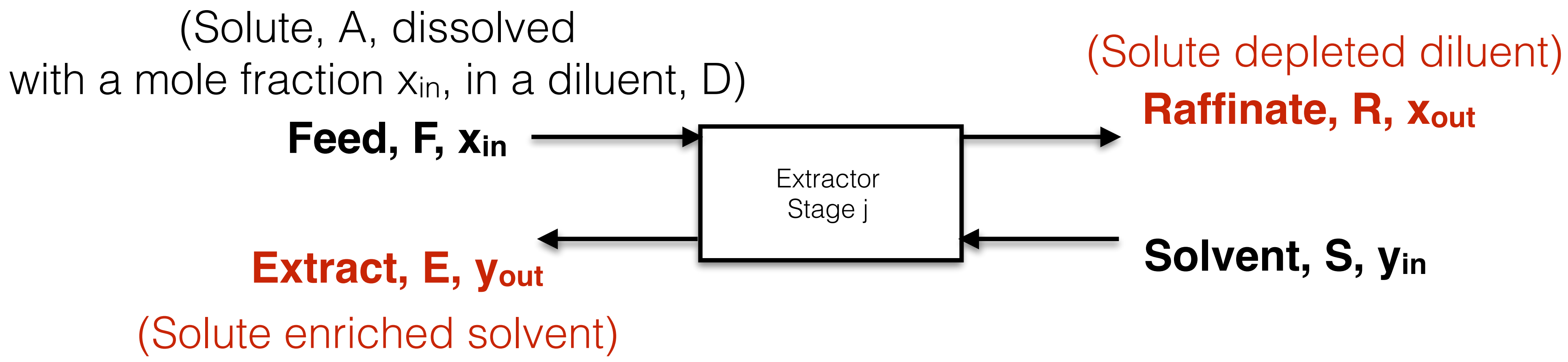
Key highlights

Dilute solution: A constant distribution ratio ($K_d = y/x$), independent of x

Immiscible phases (solvent and feed): Mass/mole balance becomes simple.

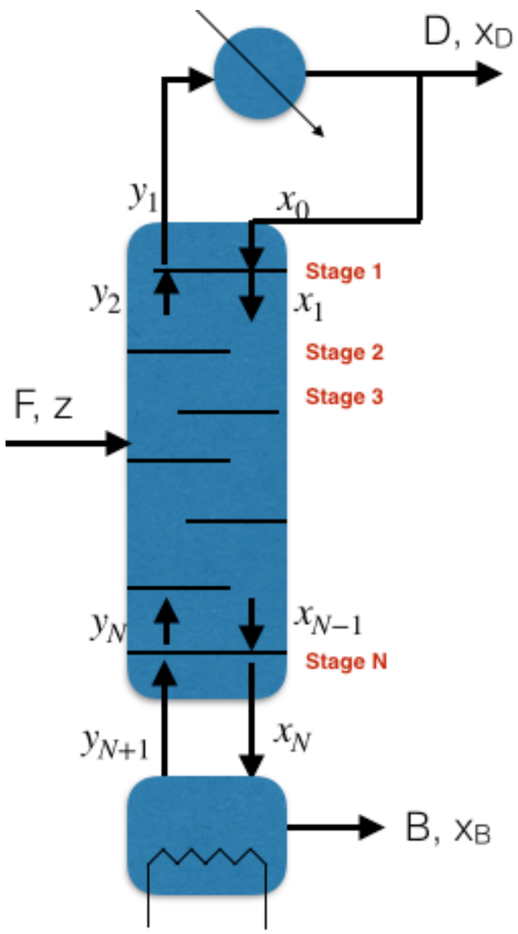
Countercurrent extraction: Most common configuration (feed and solvent phases flow in opposite direction).

With these info, we can model the operating line



Multi-staged Liquid-liquid extraction

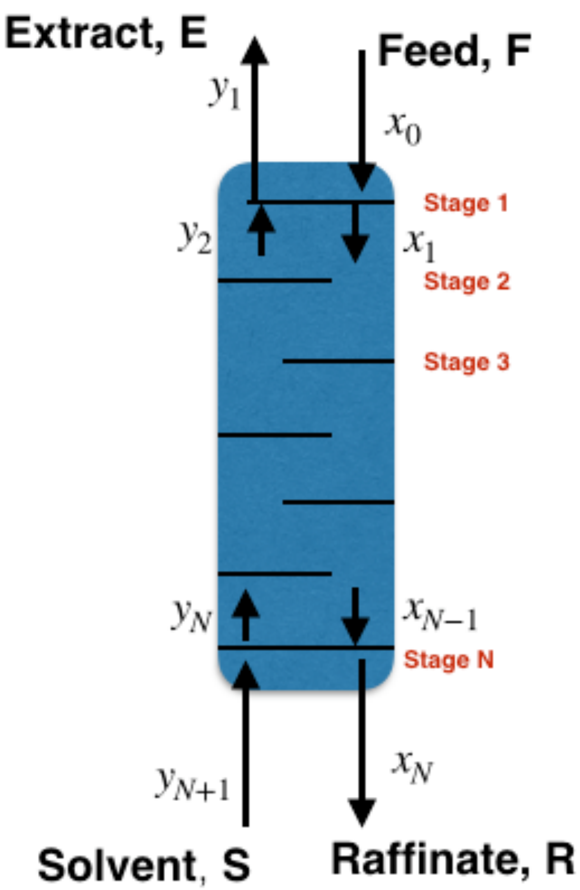
Analogy from the distillation column



At stage j

1. $\mathbf{x_j}$ and $\mathbf{y_j}$ are in equilibrium $K_d = f(T, P, pH)$

2. $\mathbf{(x_{j-1}, y_j)}$, and $\mathbf{(x_j, y_{j+1})}$ are part of the operating line



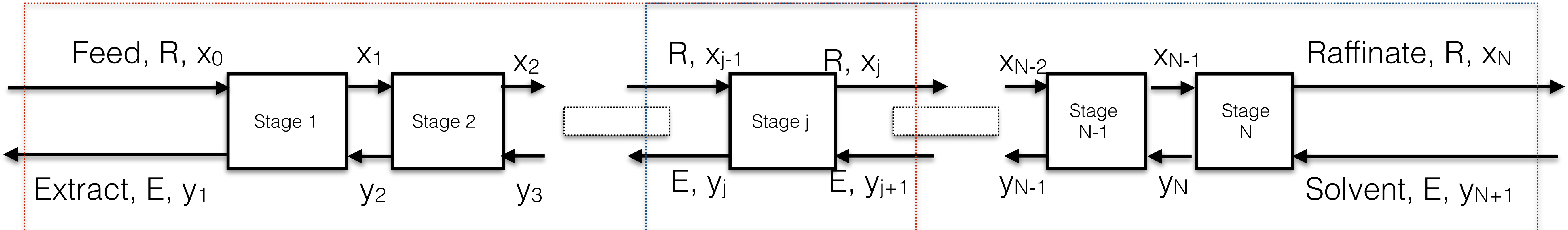
Dilute solution assumption:

S = E F = R

Similar to CMO assumption in distillation column

$$k_d = \frac{y_j}{x_j};$$ does not change from stage to stage (dilute assumption)

Multi-staged Liquid-liquid extraction: cascade diagram



$$Ey_{j+1} + Rx_0 = Ey_1 + Rx_j$$

$$Ey_j + Rx_N = Ey_{N+1} + Rx_{j-1}$$

$$y_{j+1} = \frac{R}{E}x_j + \left(y_1 - \frac{R}{E}x_0\right)$$

$$y_j = \frac{R}{E}x_{j-1} + \left(y_{N+1} - \frac{R}{E}x_N\right)$$

$$y = \frac{R}{E}x + \left(y_1 - \frac{R}{E}x_0\right) \qquad y = \frac{R}{E}x + \left(y_{N+1} - \frac{R}{E}x_N\right)$$

Operating line

You can choose one of these two equation depending upon what is specified (y_1 vs y_{N+1})

$$y_j = k_D x_j$$

Equilibrium line

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Multi-staged Liquid-liquid extraction: graphical method

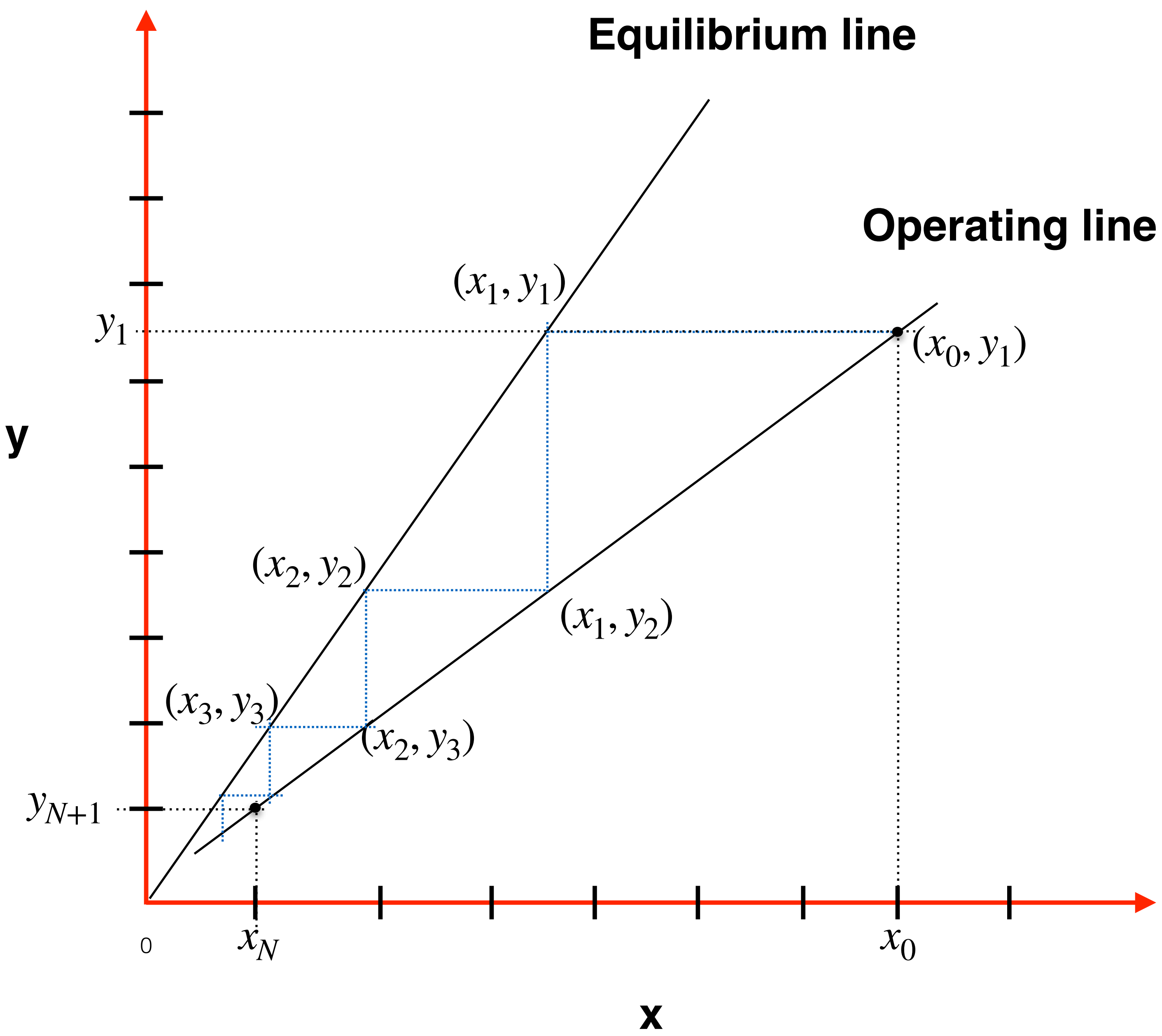
Operating line

$$y = \frac{R}{E}x + (y_1 - \frac{R}{E}x_0)$$

$$y = \frac{R}{E}x + (y_{N+1} - \frac{R}{E}x_N)$$

Equilibrium line

$$y = k_D x$$



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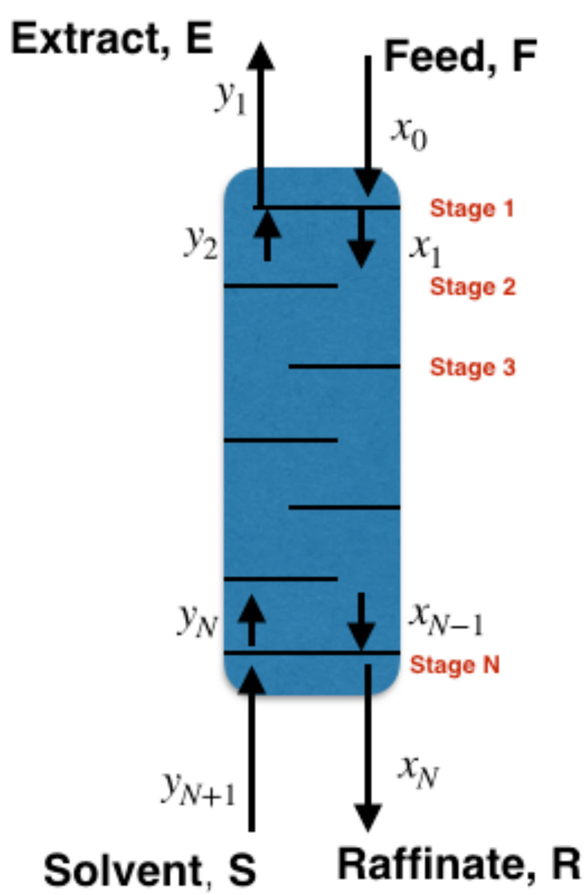
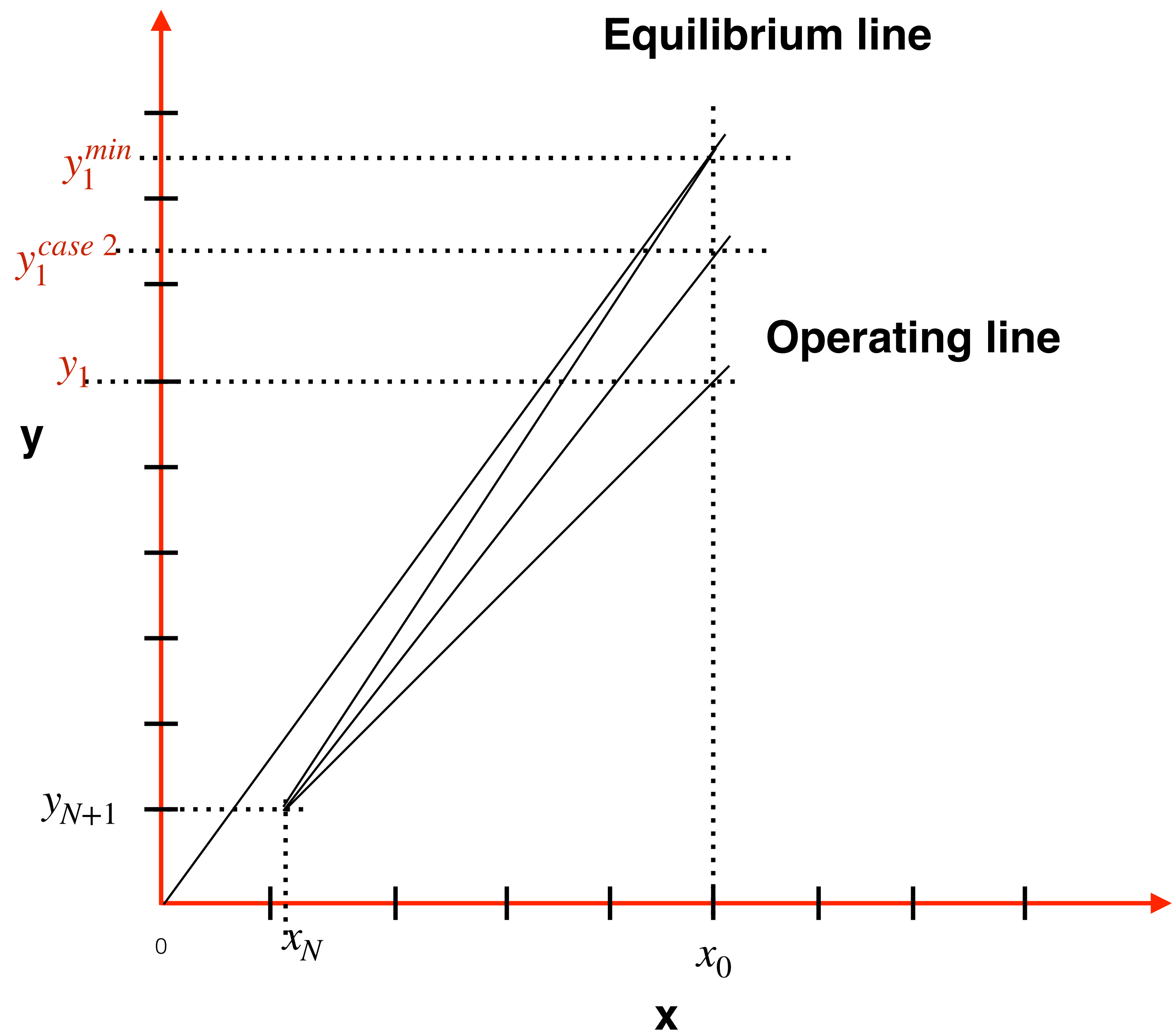
Minimum solvent flow rate

How operating line will change if I want to reduce the amount of solvent spent for extraction ?
How will this change extract composition (y_1) if one fixes desired x_N?

Operating line

$$y = \frac{R}{E}x + \left(y_1 - \frac{R}{E}x_0\right)$$





Quiz

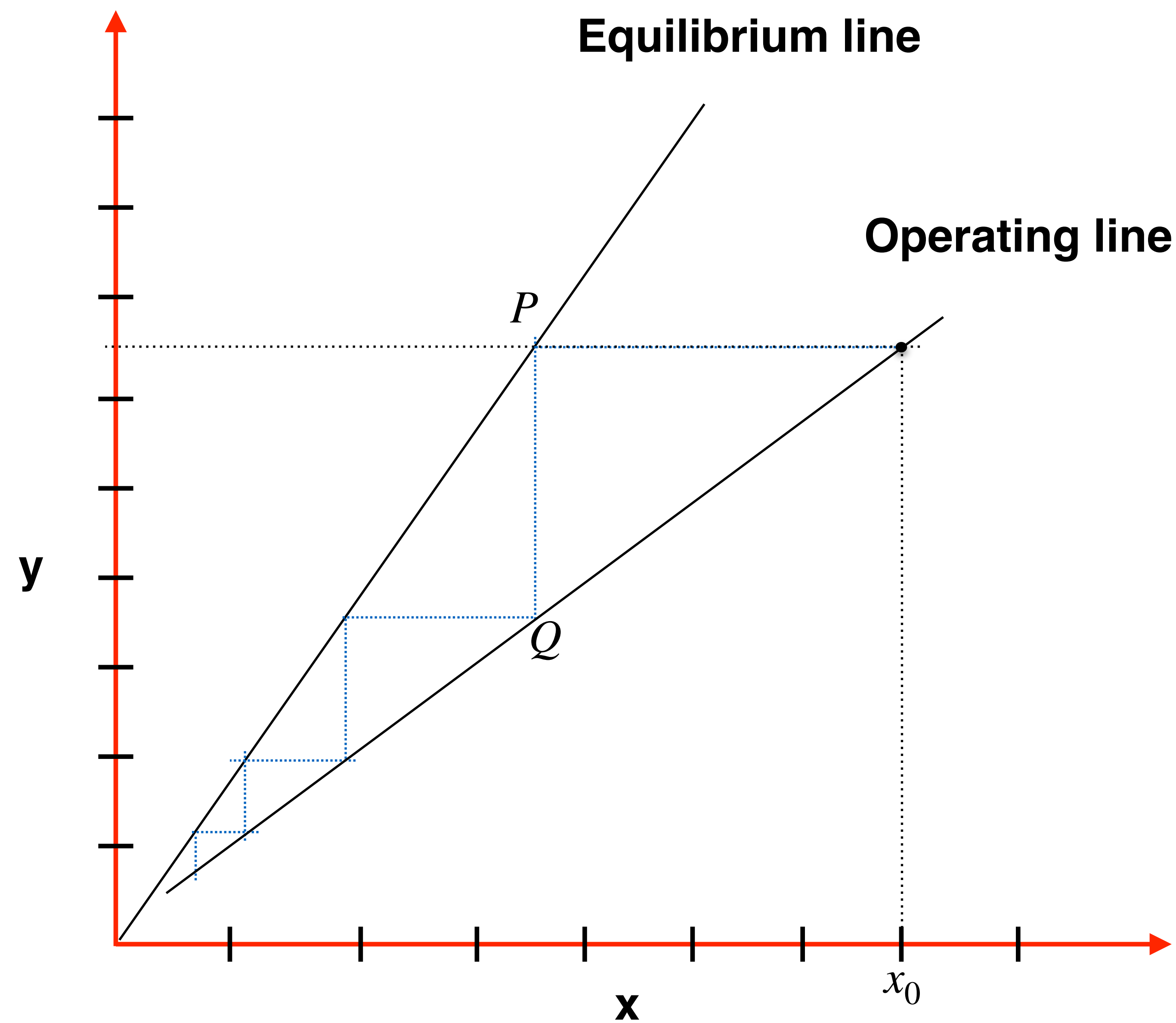
What do points P and Q represent in the context of liquid-liquid extraction?

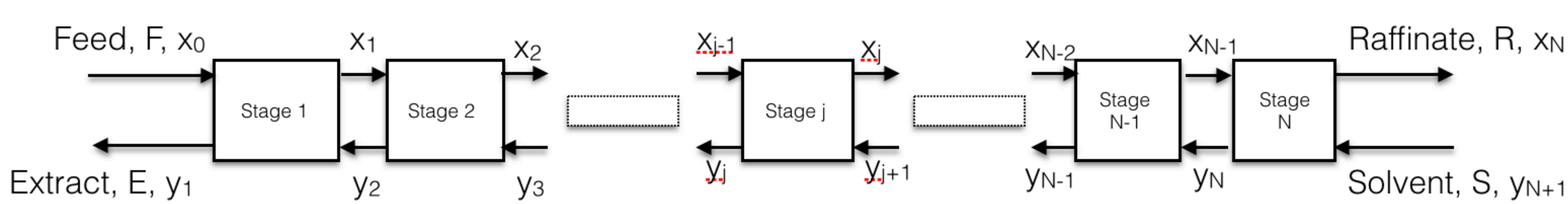
A. P is (x_2, y_1), Q is (x_2, y_2)

B. P is (x_1, y_1), Q is (x_2, y_2)

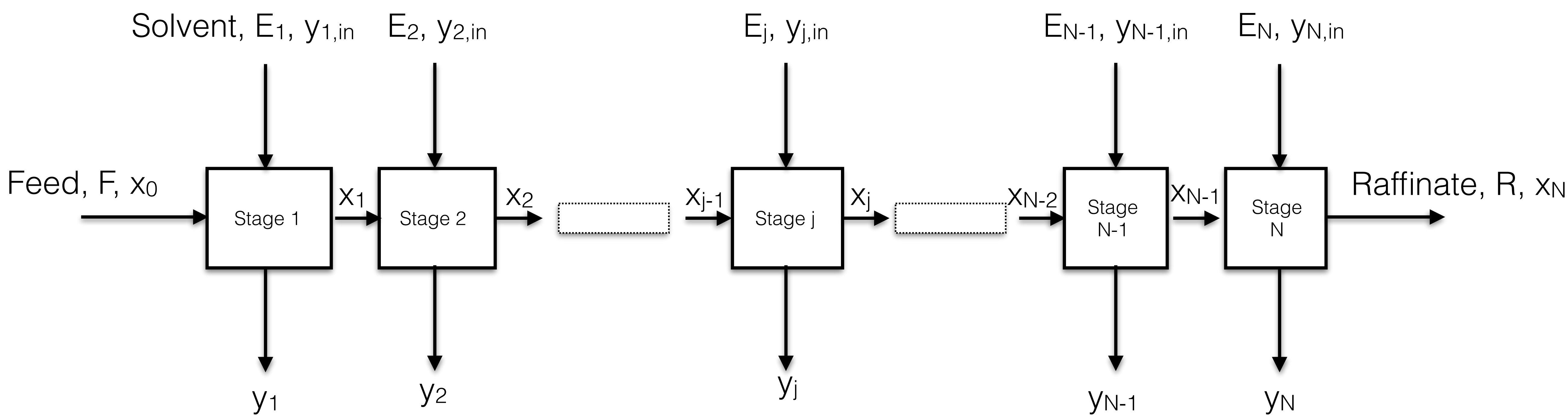
C. P is (x_2, y_1), Q is (x_1, y_2)

D. P is (x_1, y_1), Q is (x_1, y_2)





Cross-flow extraction from a dilute solution using an immiscible solvent



At stage j

1. $\mathbf{x_j}$ and $\mathbf{y_j}$ are in equilibrium K_d = f(T, P, pH, x) $y_j = k_D x_j$
2. $\mathbf{x_{j-1}}$, $\mathbf{y_{j,in}}$ is part of the operating line

Dilute solution:
A constant distribution ratio ($K_d = y/x$)

$E_{j,in} = E_{j,out}$ F = R

Similar to CMO

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Cross-flow extraction from a dilute solution using an immiscible solvent

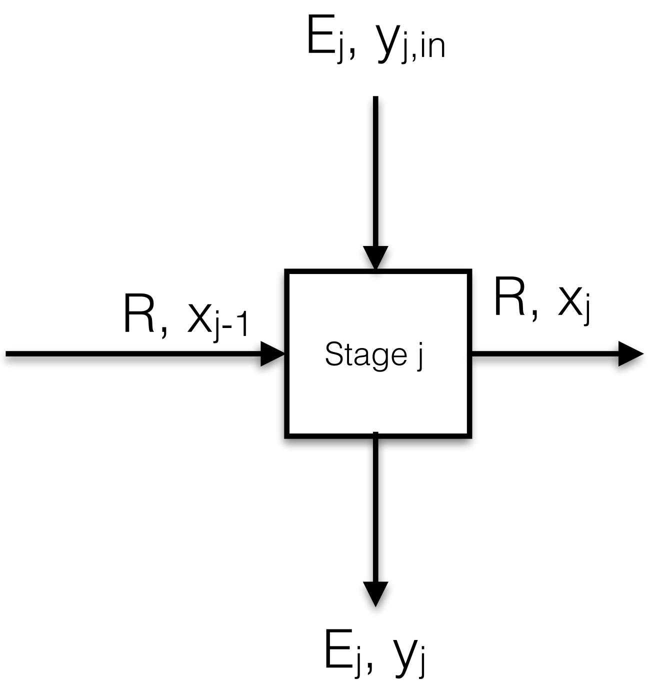
Operating equation

$$Rx_{j-1} + E_j y_{j,in} = Rx_j + E_j y_j$$

$$y_{j,in} = -\frac{R}{E}x_{j-1} + \left(\frac{R}{E}x_j + y_j\right)$$

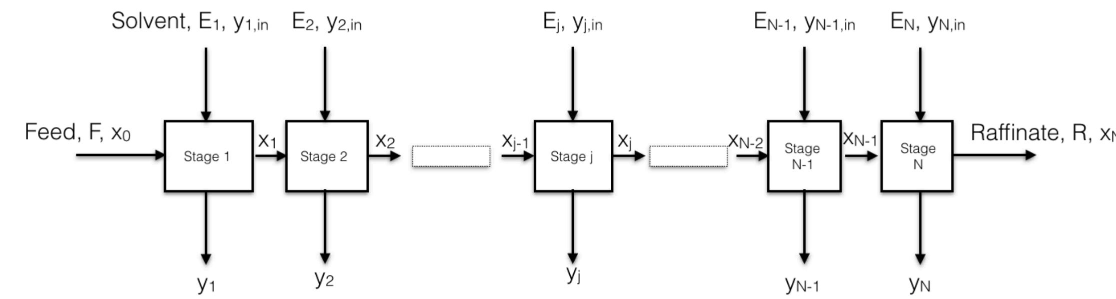
Operating equation

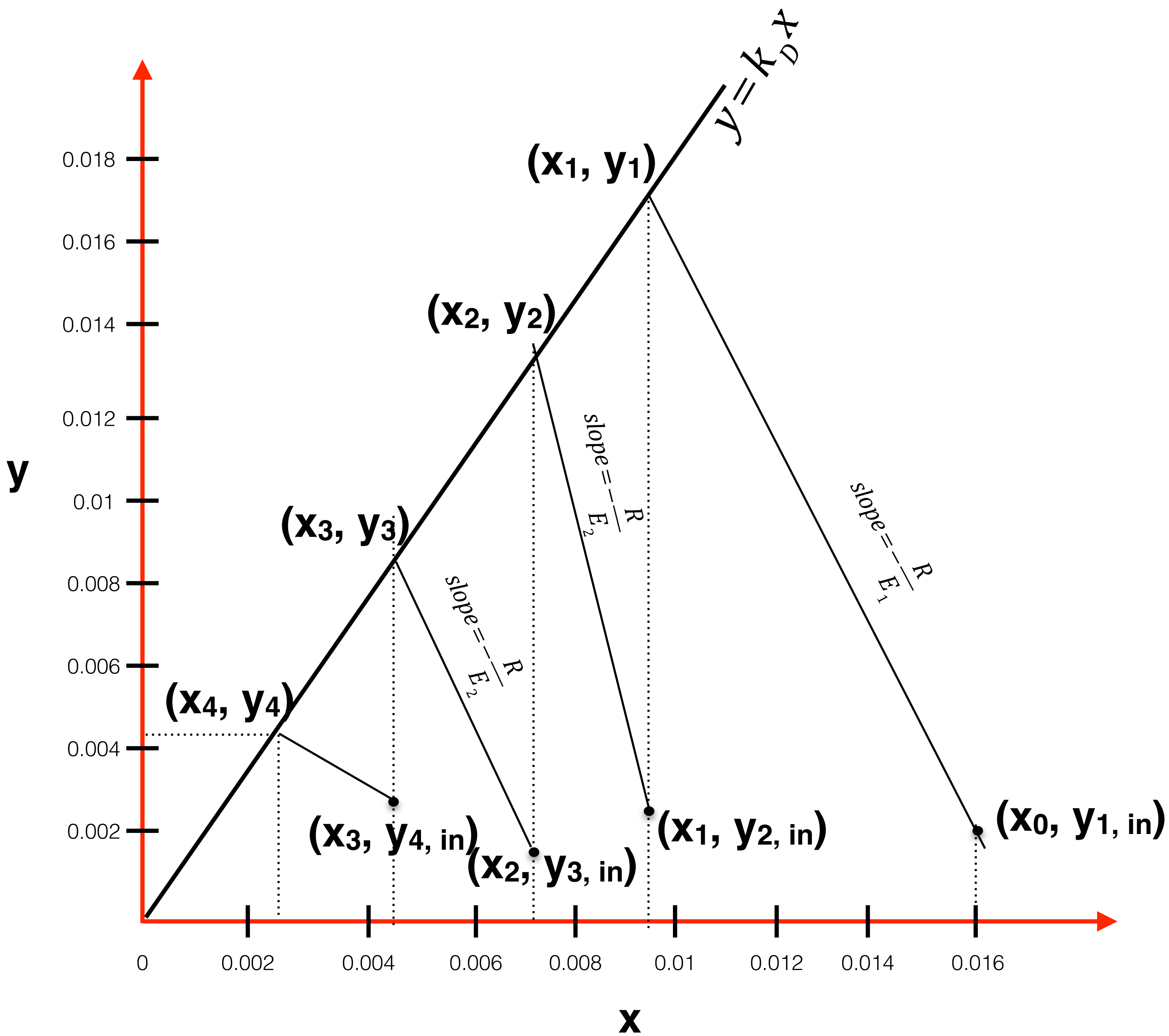
$$y_j = -\frac{R}{E_j}x_j + \left(\frac{R}{E_j}x_{j-1} + y_{j,in}\right)$$



Each stage may have a different operating equation!

Cross-flow extraction from a dilute solution using an immiscible solvent





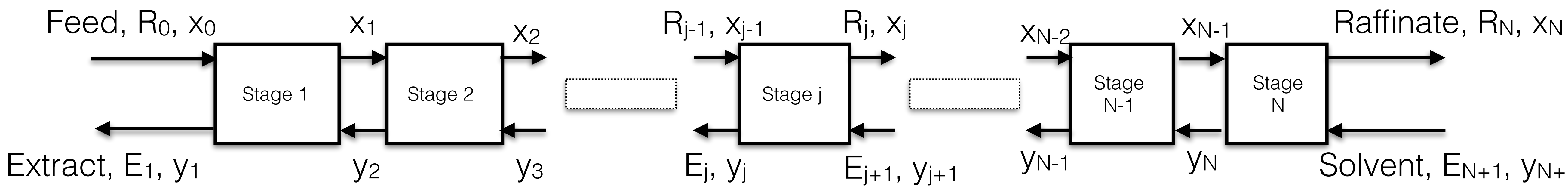
$$y_{j,in} = -\frac{R}{E} x_{j-1} + \left(\frac{R}{E} x_j + y_j \right)$$

$$y_j = -\frac{R}{E_j} x_j + \left(\frac{R}{E_j} x_{j-1} + y_{j,in} \right)$$

$$y_1 = -\frac{R}{E_1} x_1 + \left(\frac{R}{E_1} x_0 + y_{1,in} \right)$$

Concentrated immiscible extraction

Dilute solution assumptions are no longer valid: $K_d = f(T, P, pH, x)$



$$y_{j+1} = \frac{R_j}{E_{j+1}} x_j + \left(\frac{E_{N+1}}{E_{j+1}} y_{N+1} - \frac{R_N}{E_{j+1}} x_N \right)$$

Difficult to solve due to changing E and R

Solution: Use flow rate of diluent and pure solvent.
Use mole ratio instead of mole fraction.

Flow rate of diluent = F_D
Flow rate of solvent = F_S

For immiscible system,
F_D and F_S do not change between stages

$$X_j = \left(\frac{flow\ \ rate\ \ of\ \ solute}{flow\ \ rate\ \ of\ \ diluent, F_D} \right)_j = \frac{x_j}{1 - x_j}$$

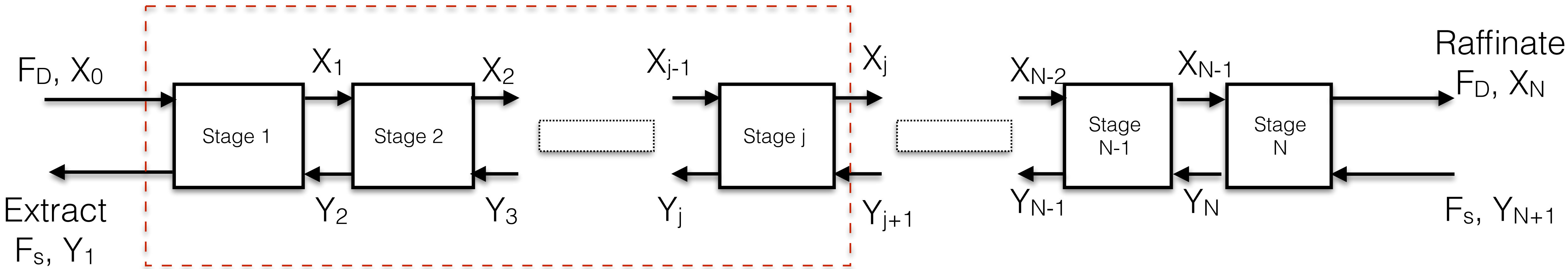
$$Y_j = \left(\frac{flow\ \ rate\ \ of\ \ solute}{flow\ \ rate\ \ of\ \ solvent, F_S} \right)_j = \frac{y_j}{1 - y_j}$$

(Flow rate of solute in diluent)$_j$ = $R_j x_j = F_D X_j$

(Flow rate of solute in solvent)$_j$ = $E_j x_j = F_S Y_j$

Concentrated immiscible extraction

$K_d = f(T, P, pH, X)$



Balance on solute for stage j

$$F_D X_0 + F_s Y_{j+1} = F_D X_j + F_s Y_1$$

$$Y_{j+1} = \frac{F_D}{F_s} X_j + \left(Y_1 - \frac{F_D}{F_s} X_0 \right)$$

$$Y_{j+1} = \frac{F_D}{F_s} X_j + \left(Y_{N+1} - \frac{F_D}{F_s} X_N \right)$$

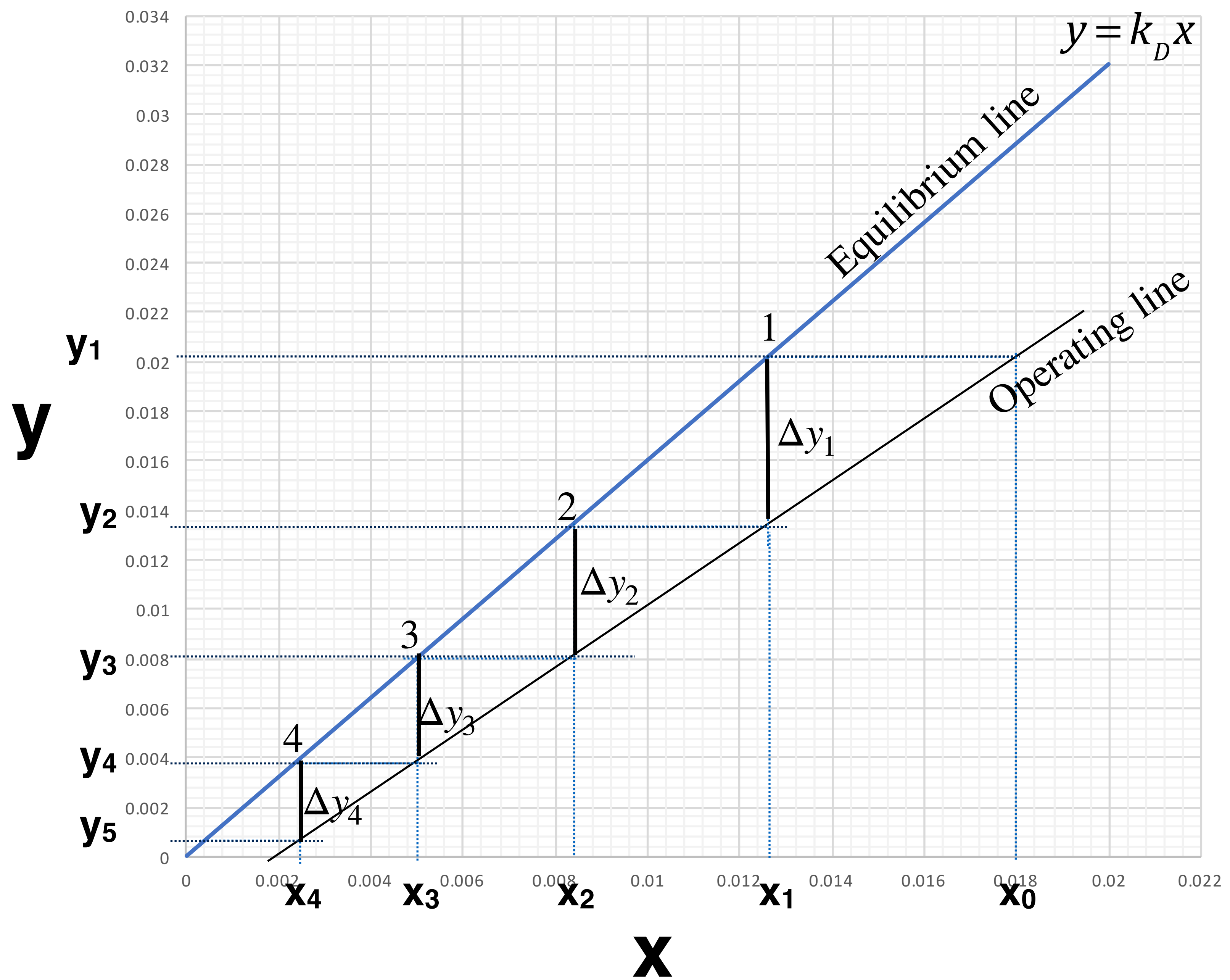
Kremser equation for analytical calculation

$$N = \frac{\ln\left[\frac{1}{A} + \left(1 - \frac{1}{A}\right)\left(\frac{y_0 - y_{N+1}}{y_0 - y_1}\right)\right]}{\ln A}$$

Kremser Equation

$$A = \frac{R}{k_D E}$$

$$y_0 = k_D x_0$$



Kremser equation for analytical calculation

$$y_1 - y_5 = (y_1 - y_2) + (y_2 - y_3) + (y_3 - y_4) + (y_4 - y_5)$$

Using equilibrium and operating lines

$$y_j = k_D x_j$$

$$y_{j+1} = \frac{R}{E} x_j + \left(y_{N+1} - \frac{R}{E} x_N \right)$$

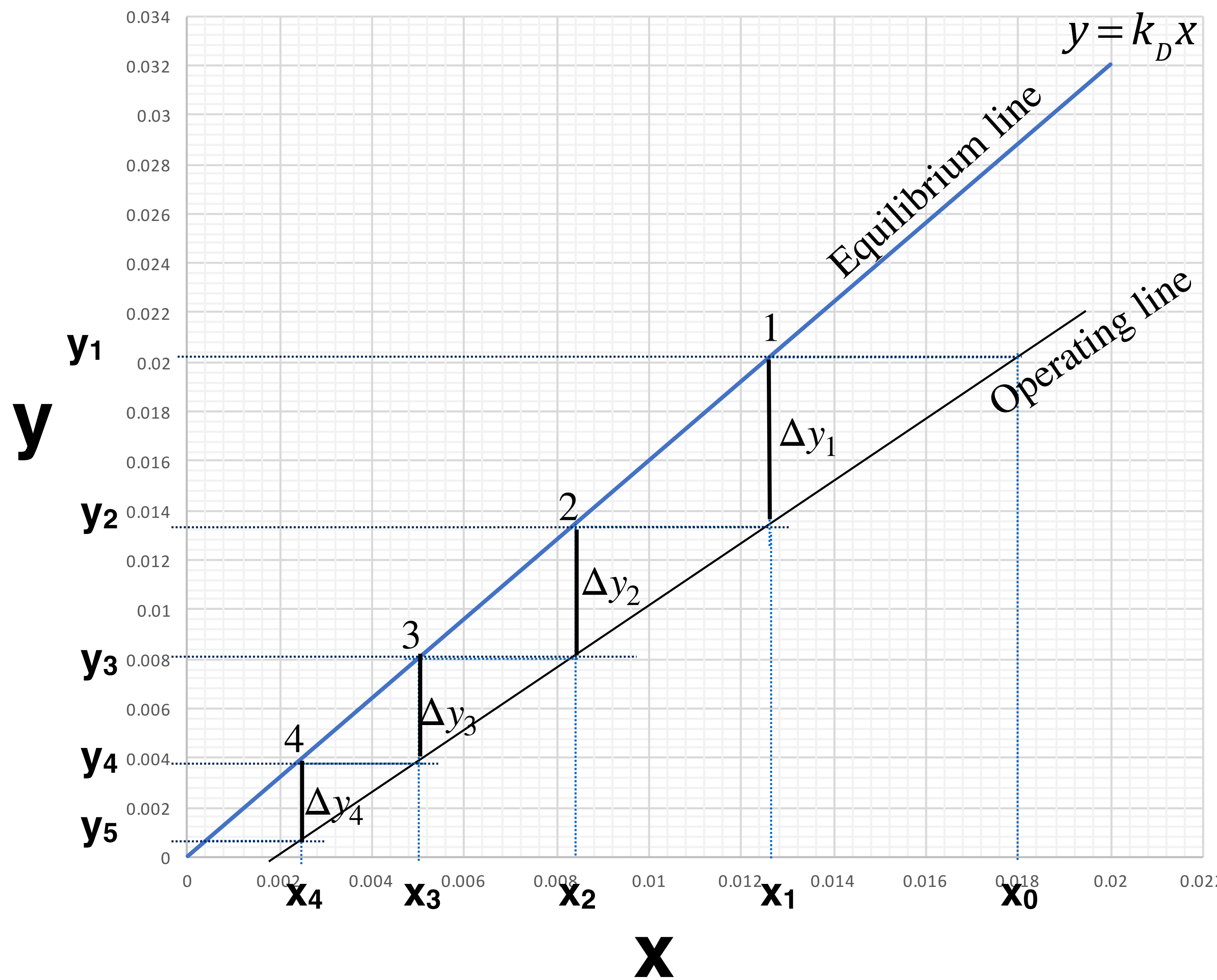
$$y_{j+1} = \frac{R}{E} x_j + C$$

$$\Delta y_1 = y_1 - y_2$$

$$\Delta y_j = y_j - y_{j+1}$$

$$\Delta y_j = k_D x_j - \left(\frac{R}{E} x_j + C \right)$$

$$\Delta y_j = \left(k_D - \frac{R}{E} \right) x_j - C$$



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Kremser equation for analytical calculation

$$\Delta y_j = \left(k_D - \frac{R}{E}\right)x_j - C$$

Δy_j is a simple function of x_j

$$\Delta y_j - \Delta y_{j+1} = \left[\left(k_D - \frac{R}{E}\right)x_j - C\right] - \left[\left(k_D - \frac{R}{E}\right)x_{j+1} - C\right]$$

$$= \left(k_D - \frac{R}{E}\right)\left(x_j - x_{j+1}\right)$$

$$= \left(k_D - \frac{R}{E}\right)\left(\frac{y_j}{k_D} - \frac{y_{j+1}}{k_D}\right)$$

$$= \left(1 - \frac{R}{k_D E}\right)\left(y_j - y_{j+1}\right) = \left(1 - \frac{R}{k_D E}\right)\Delta y_j$$

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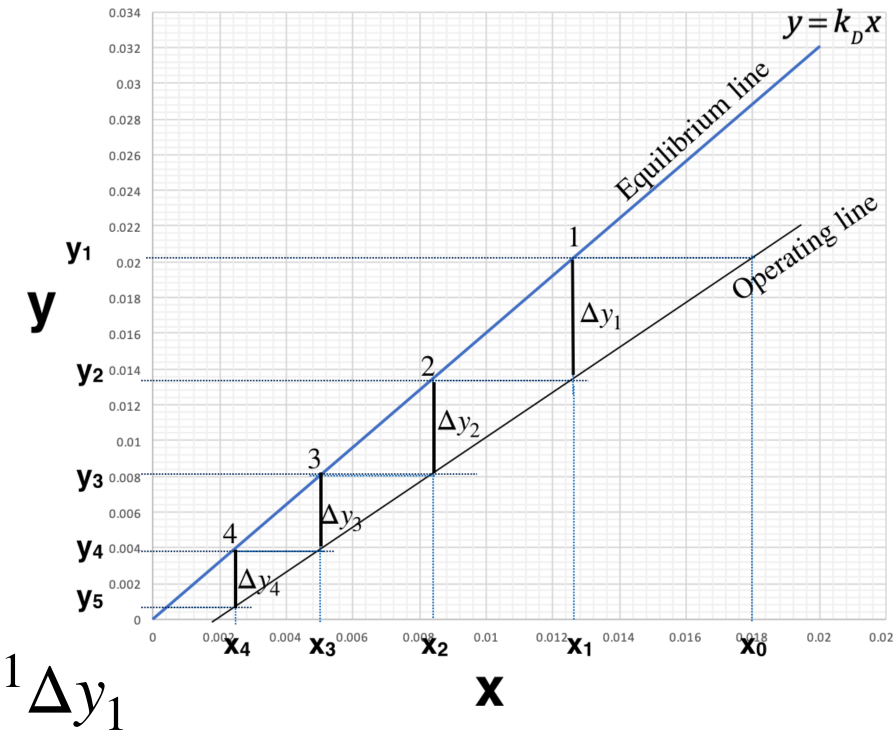
Kremser equation for analytical calculation



$$\cancel{\Delta y_j} - \Delta y_{j+1} = \left(\cancel{1} - \frac{R}{k_D E}\right)\Delta y_j \qquad \Delta y_{j+1} = \left(\frac{R}{k_D E}\right)\Delta y_j$$

$$\frac{R}{k_D E} = A \qquad \Rightarrow \Delta y_{j+1} = A\Delta y_j$$

$$\Delta y_2 = A\Delta y_1 \qquad \Rightarrow \Delta y_3 = A\Delta y_2 = A^2\Delta y_1 \qquad \Rightarrow \Delta y_N = A^{N-1}\Delta y_1$$

$$y_1 - y_{N+1} = (y_1 - y_2) + (y_2 - y_3) + (y_3 - y_4) + \ldots\ldots + (y_{N-1} - y_N) + (y_N - y_{N+1})$$

$$y_1 - y_{N+1} = \Delta y_1 + \Delta y_2 + \Delta y_3 + \ldots\ldots + \Delta y_{N-1} + \Delta y_N$$

$$\Rightarrow y_1 - y_{N+1} = \Delta y_1 + A\Delta y_1 + A^2\Delta y_1 + \ldots\ldots + A^{N-2}\Delta y_1 + A^{N-1}\Delta y_1$$

$$\Rightarrow y_1 - y_{N+1} = \left(1 + A + A^2 + \ldots\ldots + A^{N-2} + A^{N-1}\right)\Delta y_1$$

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Kremser equation for analytical calculation

$$1 + A + A^2 + A^3 + \dots + A^{N-2} + A^{N-1} = \left(\frac{1-A^N}{1-A}\right)$$

Geometric series

$$\Rightarrow y_1 - y_{N+1} = \left(1 + A + A^2 + \dots\dots + A^{N-2} + A^{N-1}\right)\Delta y_1 = \left(\frac{1-A^N}{1-A}\right)\Delta y_1$$

$$y_1 - y_{N+1} = \left(\frac{1-A^N}{1-A}\right)A\left(\Delta y_0\right) = \left(\frac{1-A^N}{\frac{1}{A}-1}\right)\left(y_0 - y_1\right)$$

$$\frac{1-A^N}{\frac{1}{A}-1} = \frac{y_1 - y_{N+1}}{y_0 - y_1}$$

$$\frac{1-A^N}{\frac{1}{A}-1} + 1 = \frac{y_1 - y_{N+1}}{y_0 - y_1} + 1$$

$$\frac{\frac{1}{A} - A^N}{\frac{1}{A}-1} = \frac{y_0 - y_{N+1}}{y_0 - y_1}$$

$$A^N = \frac{1}{A} + \left(1 - \frac{1}{A}\right)\frac{y_0 - y_{N+1}}{y_0 - y_1}$$

$$N = \frac{\ln\left[\frac{1}{A} + \left(1 - \frac{1}{A}\right)\left(\frac{y_0 - y_{N+1}}{y_0 - y_1}\right)\right]}{\ln A}$$

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Kremser equation for analytical calculation

$$N = \frac{\ln\left[\frac{1}{A} + \left(1 - \frac{1}{A}\right)\left(\frac{y_0 - y_{N+1}}{y_0 - y_1}\right)\right]}{\ln A}$$

Kremser Equation

$$y_0 = k_D x_0$$

$$A = \frac{R}{k_D E}$$