Thermodynamics of Life

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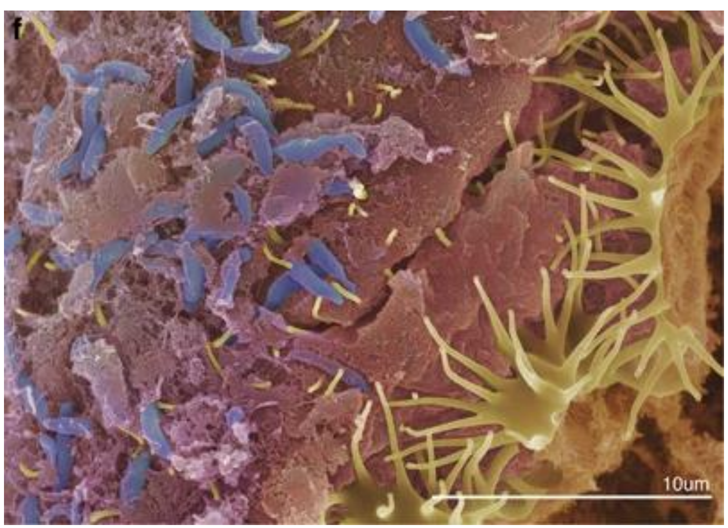
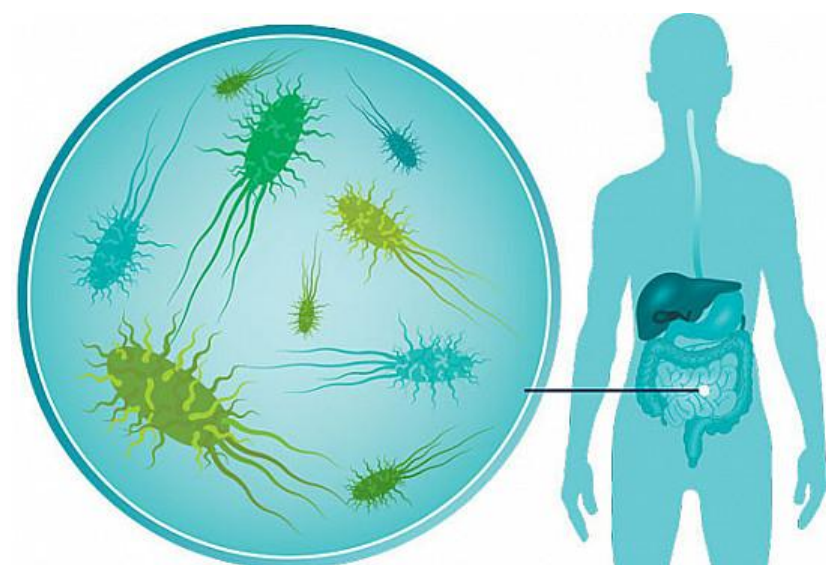
Boundaries





Boundaries

- Open, closed, adiabatic and isolated systems

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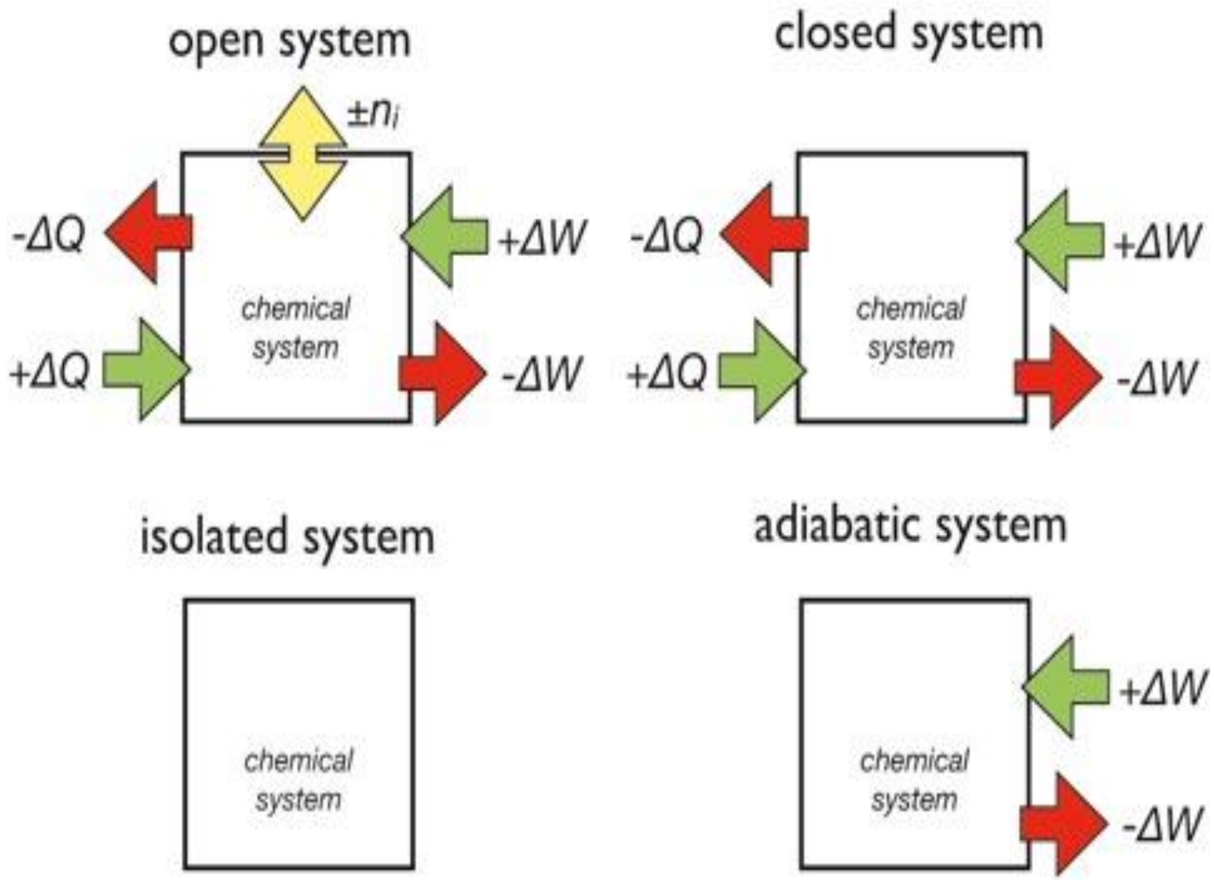
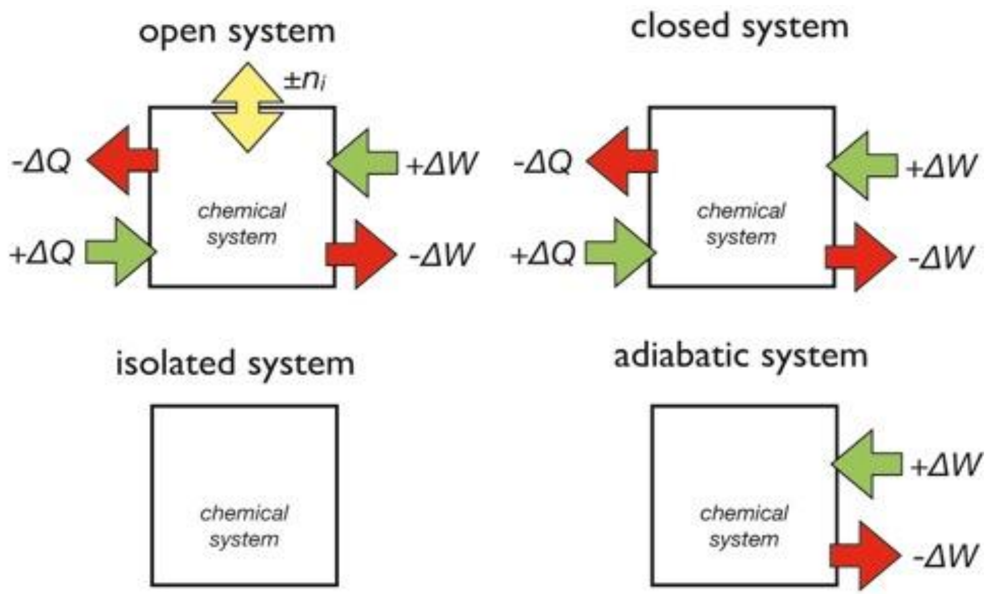


Boundaries

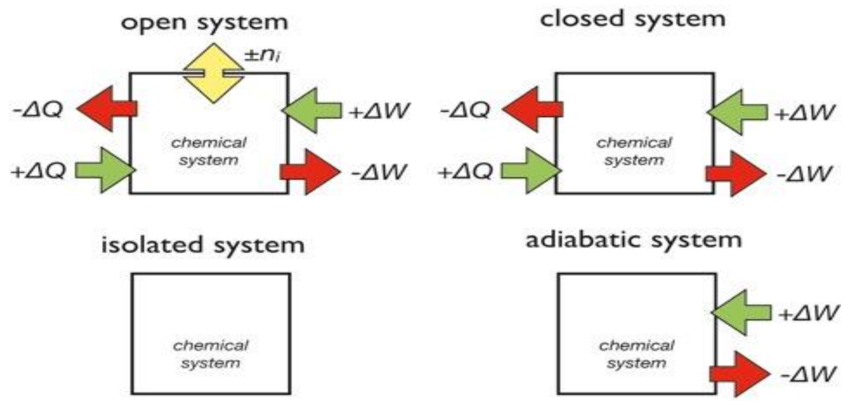
- Open, closed, adiabatic and isolated systems



- What should be the criteria to define boundaries?

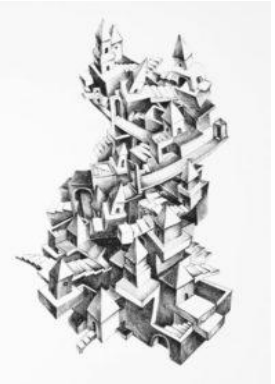
Boundaries

- Open, closed, adiabatic and isolated systems

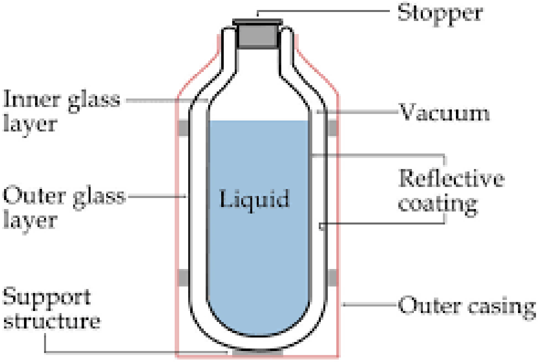


- What should be the criteria to define boundaries?

"Penthesilea is different. You advance for hours and it is not clear to you whether you are already in the city's midst or still outside it. Like a lake with low shores lost in swamps, so Penthesilea spreads for miles around, a soupy city diluted in the plain; pale buildings back to back in mangy fields, among plank fences and corrugated iron sheds."
Invisible cities, Italo Calvino

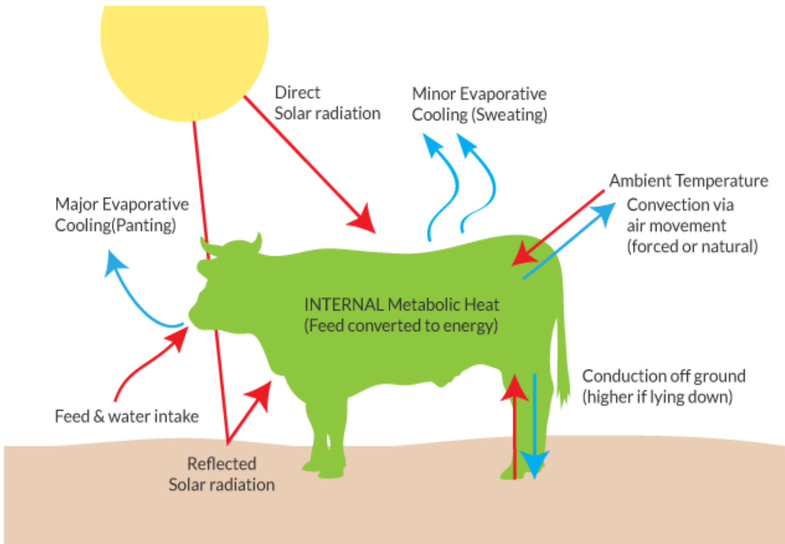


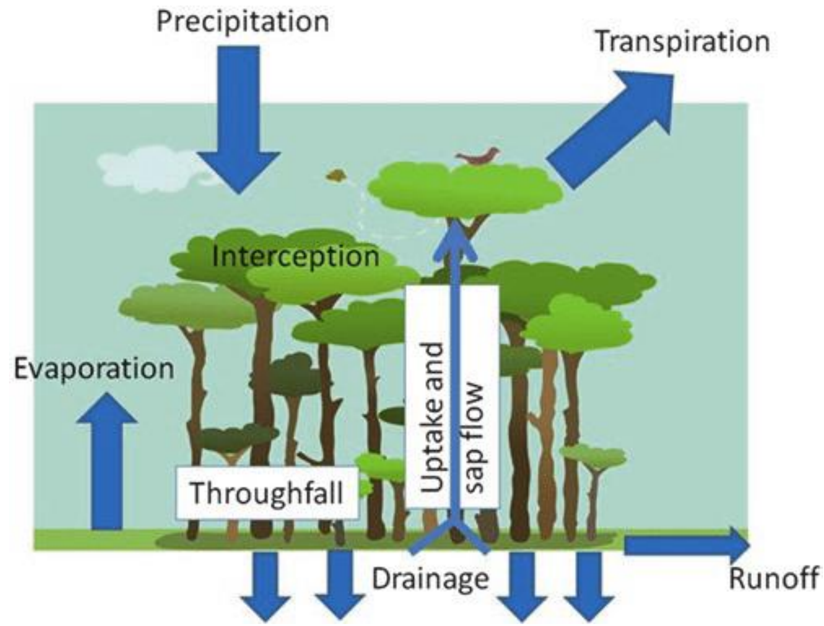
Isolated Systems

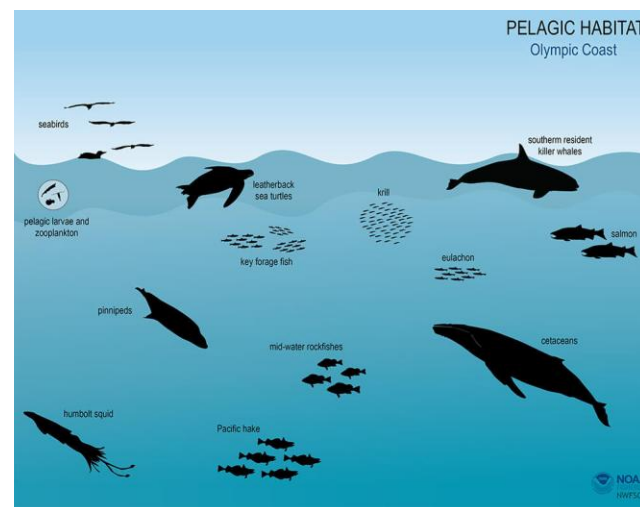


Closed Systems

Open Systems

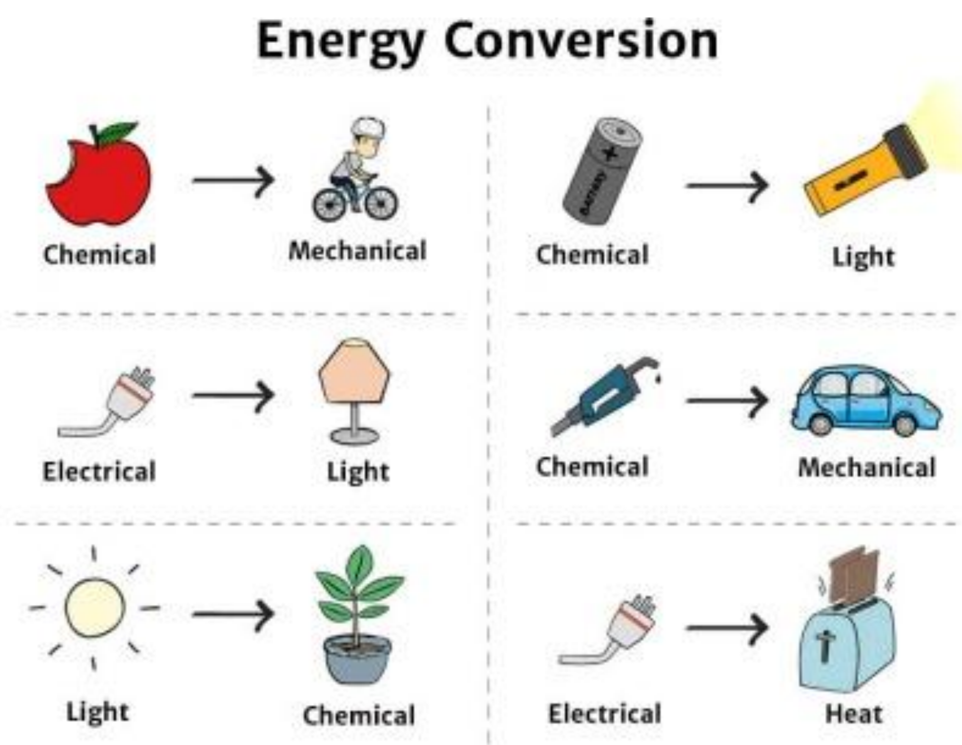






First Law of Thermodynamics

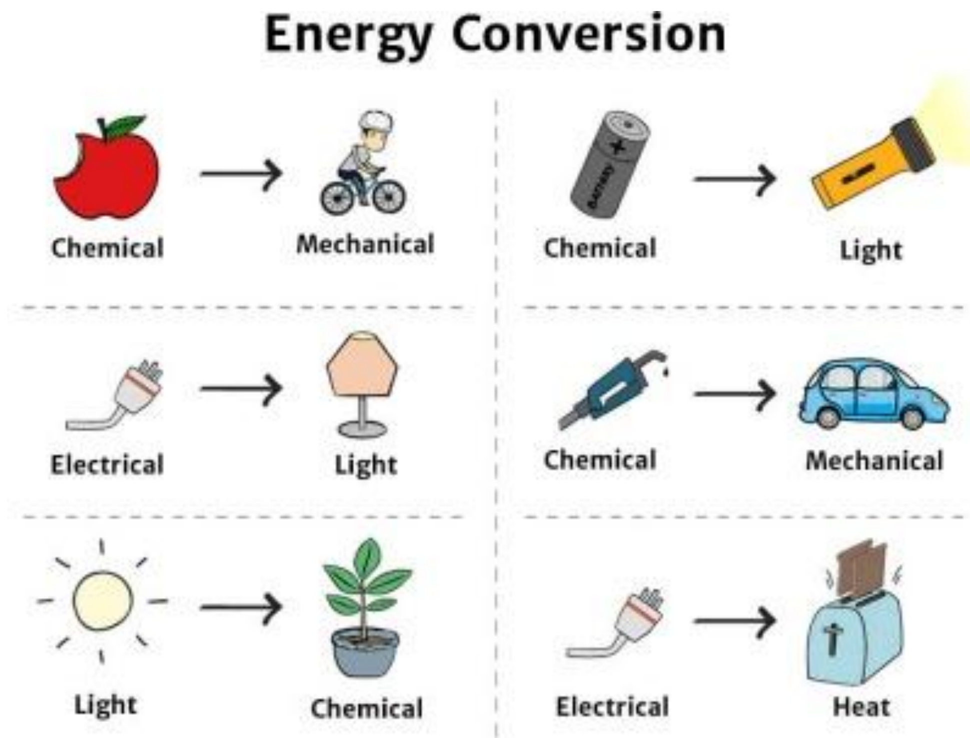
- <u>Energy is always conserved. Energy cannot be destroyed nor created. Energy can only be transformed</u>



First Law of Thermodynamics

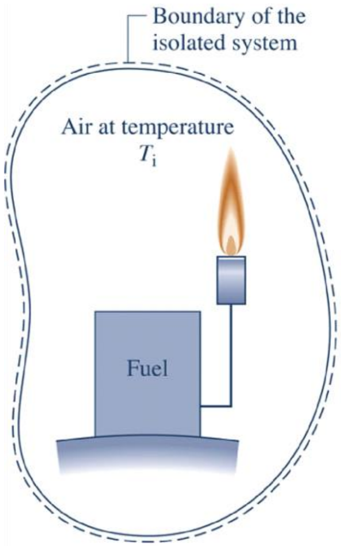
- Energy efficiency: not all input energy is transformed into useful output

$$\eta = \frac{\dot{Q}}{\dot{W}}$$

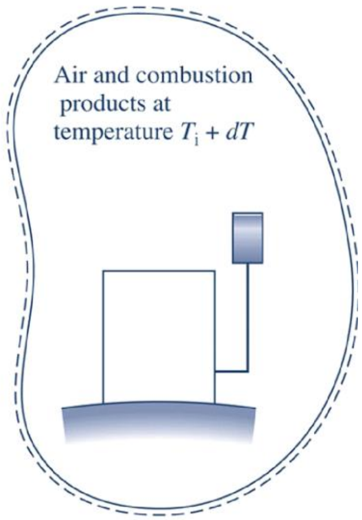


Energy Balance in Isolated Systems

- Energy is always conserved. Energy cannot be destroyed nor created. Energy can only be transformed.
- Energy change?



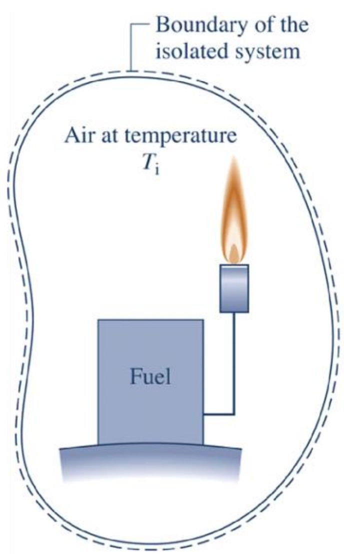
Fuel-air combination



Warm air mixture

Energy Balance in Isolated Systems

- Energy is always conserved. Energy cannot be destroyed nor created. Energy can only be transformed.
- Energy change = 0



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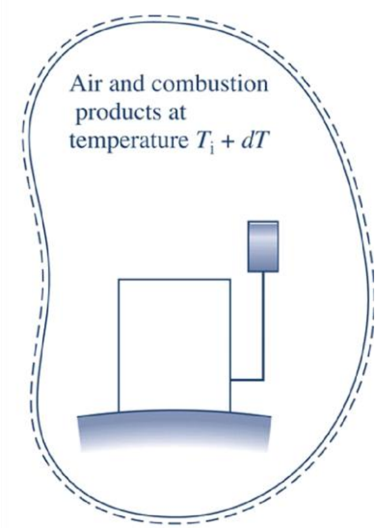
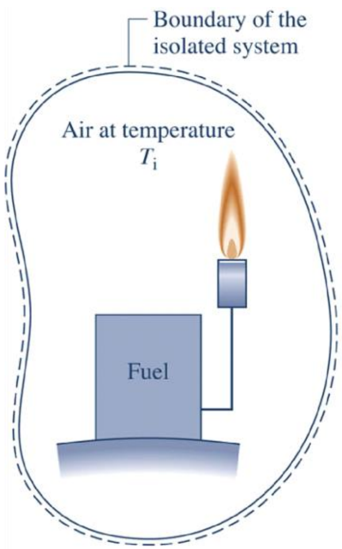


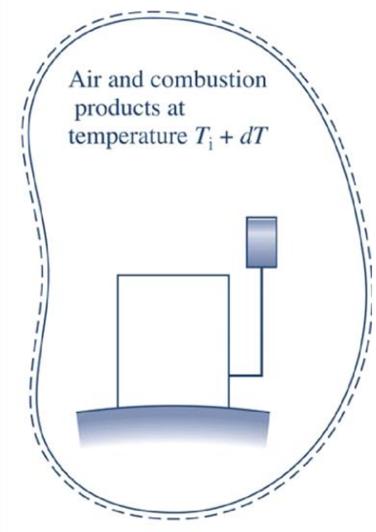
Warm air mixture

First Law of Thermodynamics

- Energy alone is not enough to distinguish two different states in this system



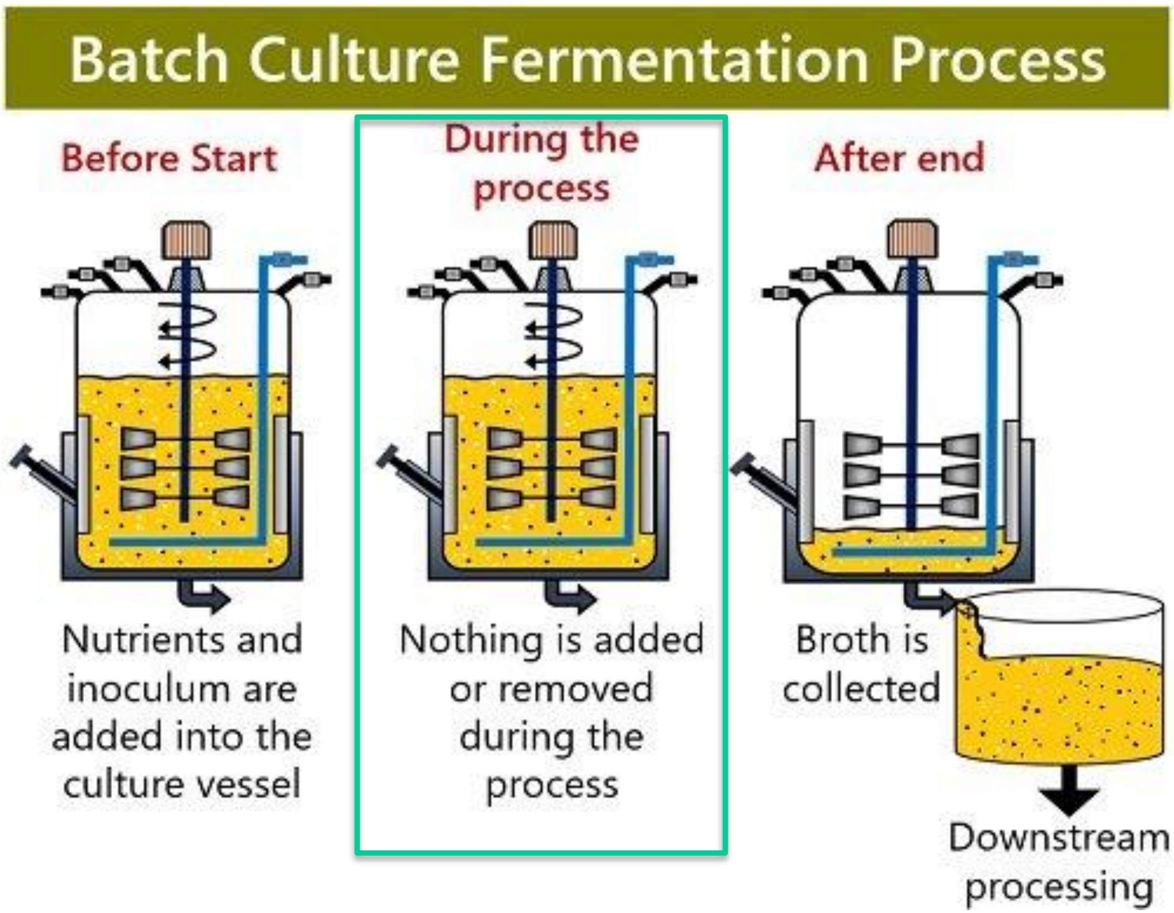
Fuel-air combination



Warm air mixture

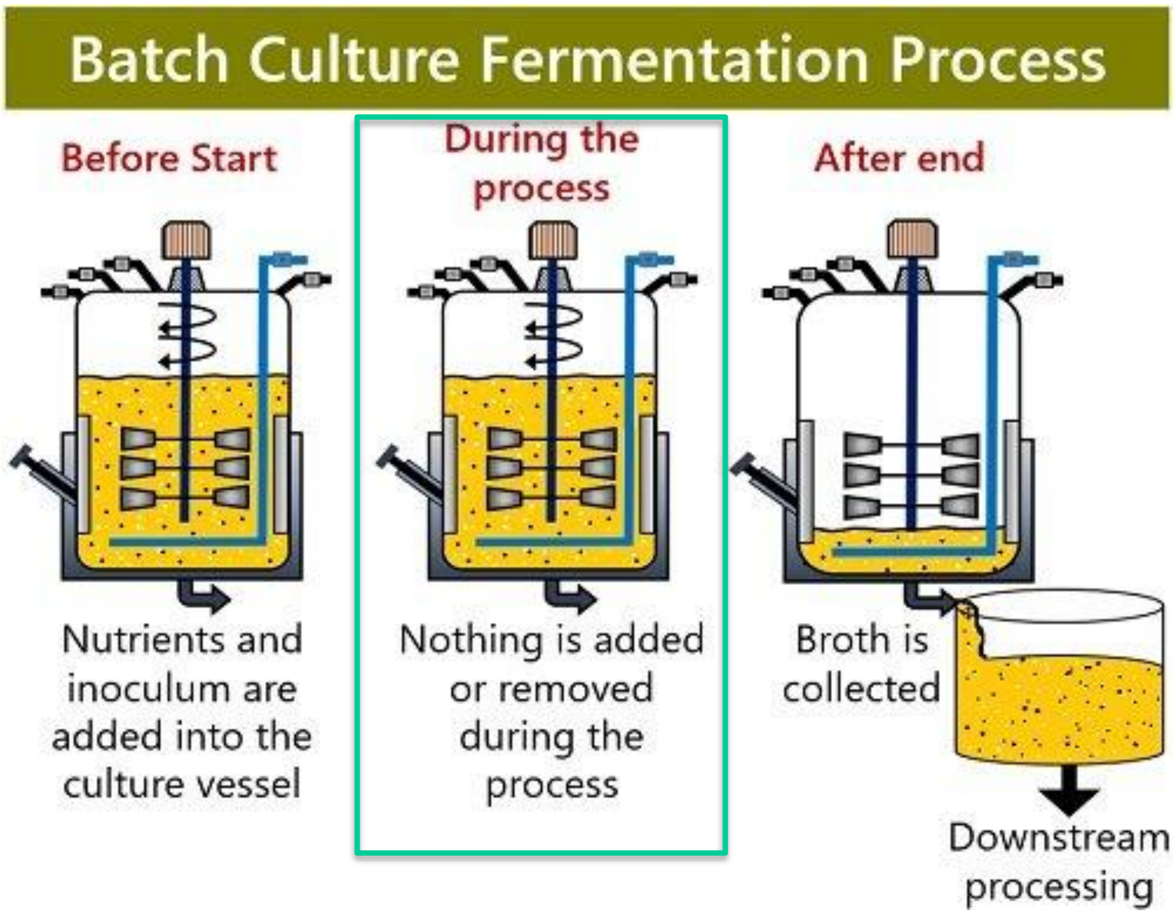
Energy Balance in Closed Systems

- Energy change?



Energy Balance in Closed Systems

- Energy change = Heat + Work



Energy Balance in Closed Systems

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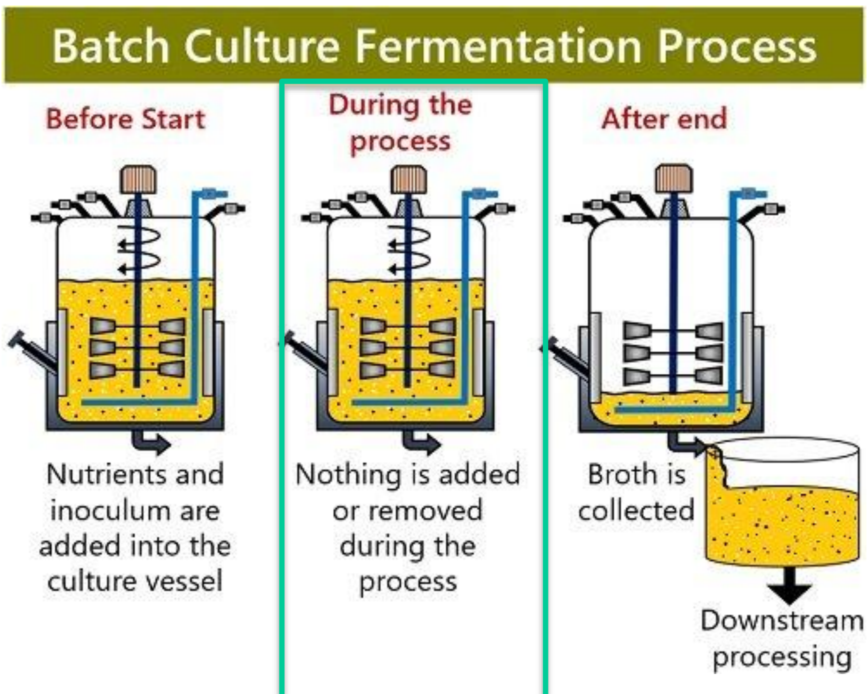
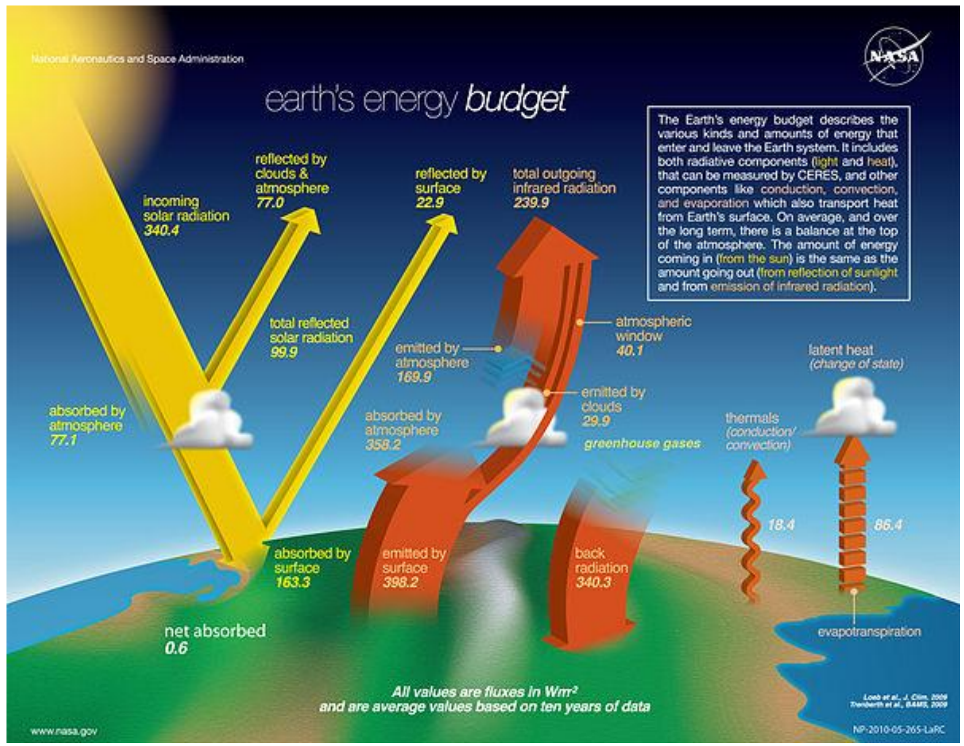


$$\Delta E = \Delta\left(U + E_p + E_c\right) = Q + W$$

- **1st Law: Energy Conservation**
- Forms of E: U, E_c and E_p
- Energy transfer by Q and W
- Sign of heat and work fluxes
- Steady state vs. Transient

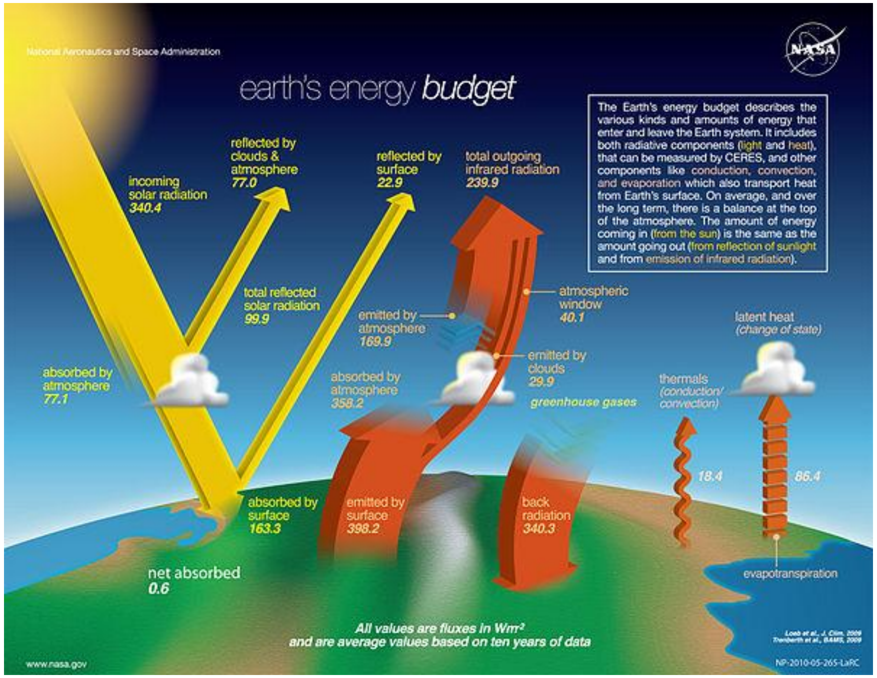
Energy Balance in Closed Systems

- Energy balance?



Energy Balance in Closed Systems

- Energy change = heat_in + heat_out ≈ 0



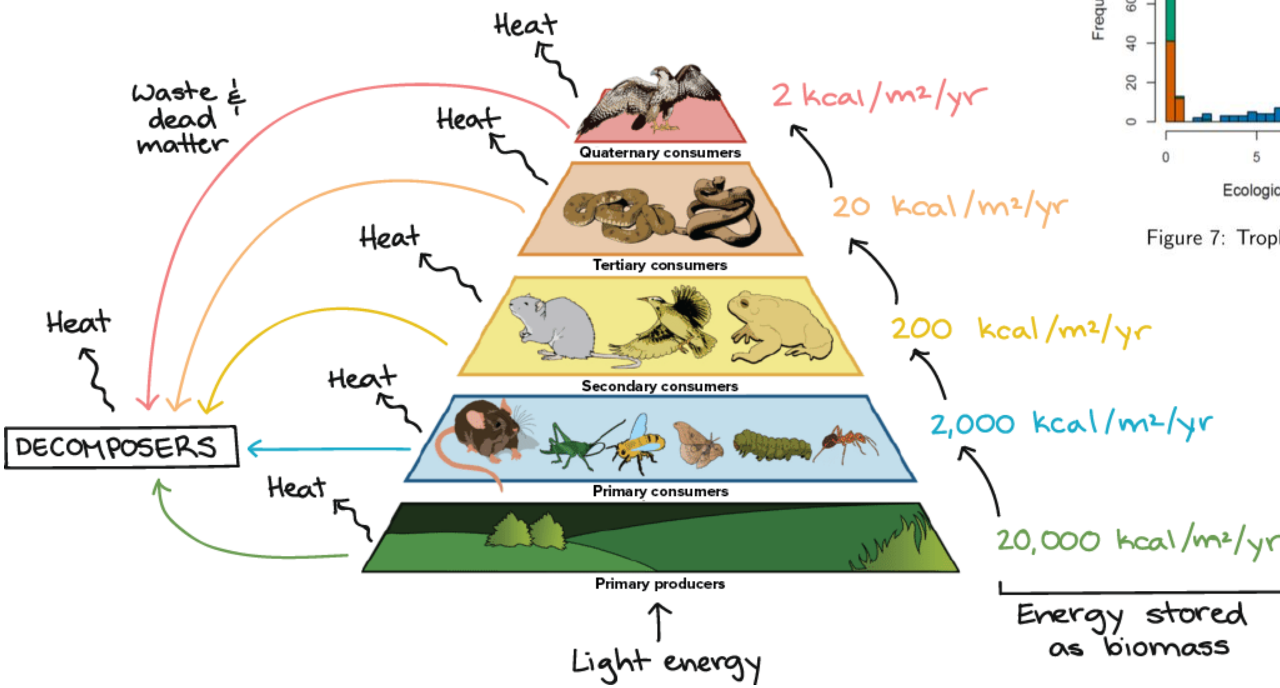
T_Sun = 5778 K; Radius_Sun = 696 340 km
Distance_Sun_Earth = 151 000 000 km; Albedo =30%
T_Earth = 255 K

Second Law of Thermodynamics

- Not all energy forms are the same. Some are better than others ☺

Second Law of Thermodynamics

- Energy is degraded in any real transformation process.



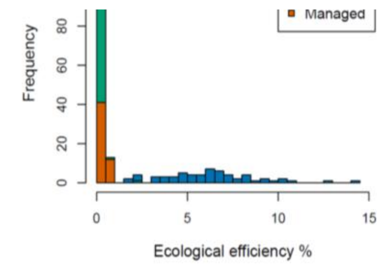
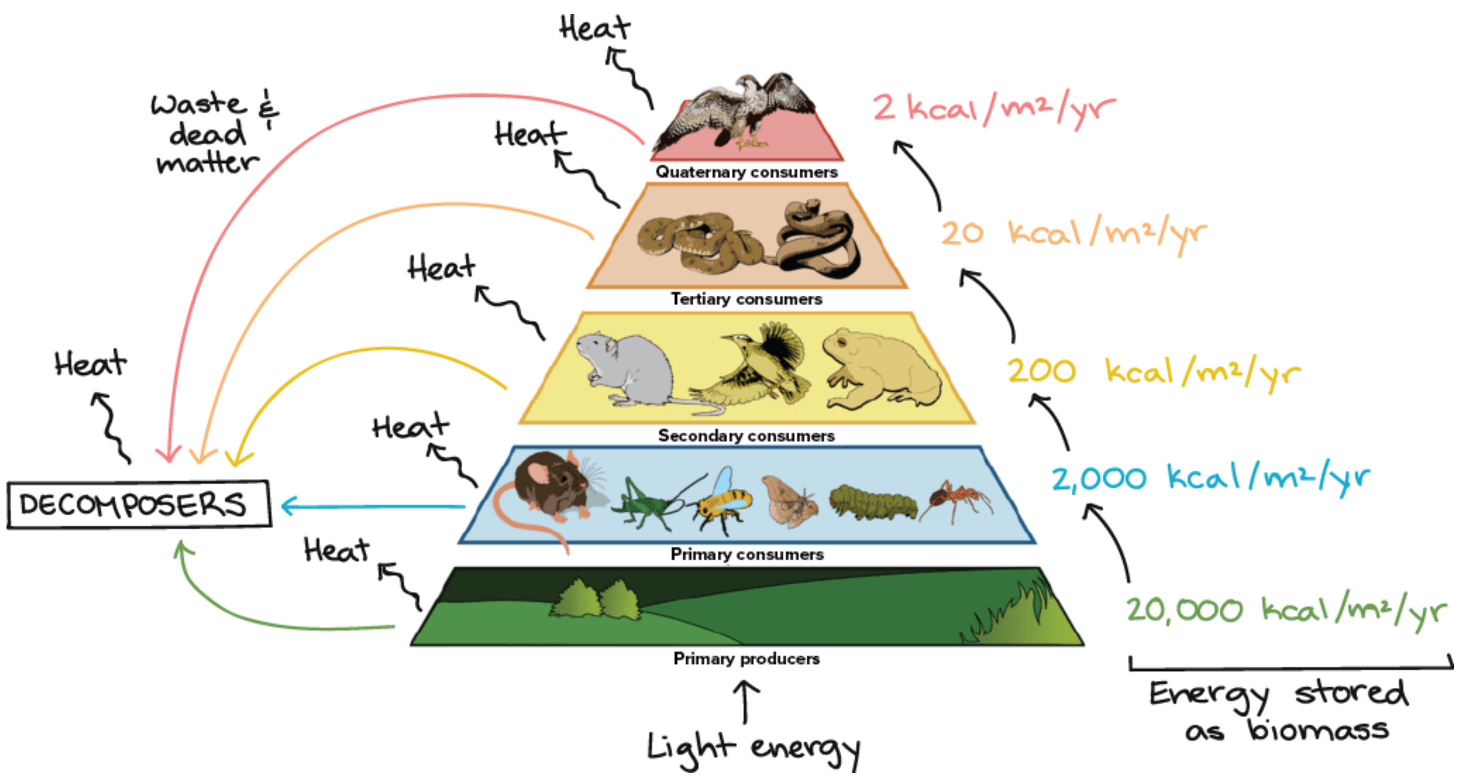


Figure 7: Trophic efficiency.

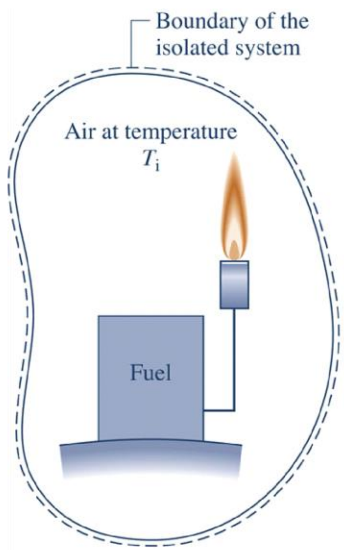
Second Law of Thermodynamics

- Entropy measures energy degradation. <u>Entropy cannot be destroyed; it can only be created.</u>

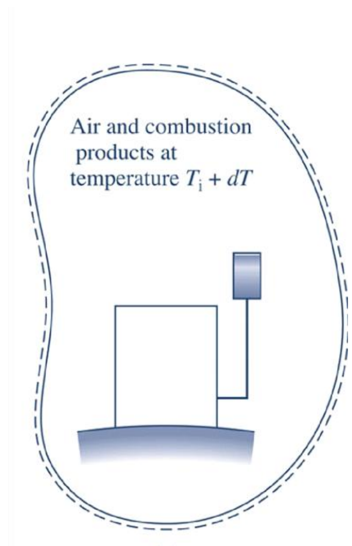


Entropy Balance in Isolated Systems

- Entropy cannot be destroyed; it can only be created.
- Entropy change?



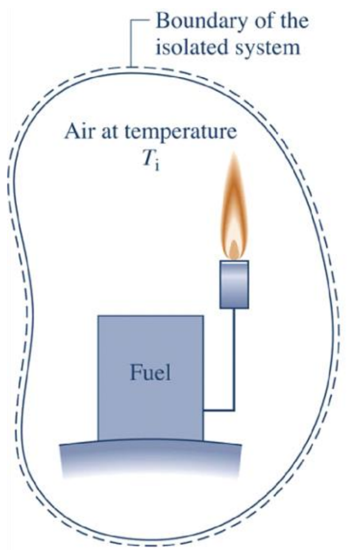
Fuel-air combination



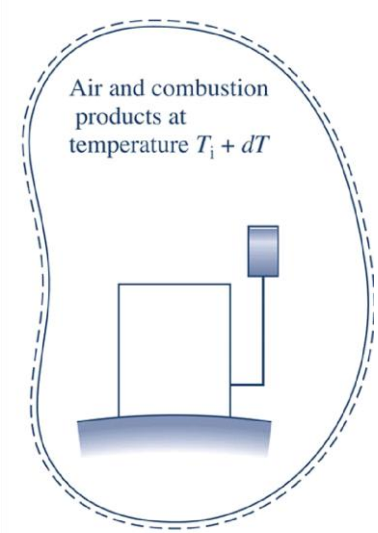
Warm air mixture

Entropy Balance in isolated Systems

- Entropy cannot be destroyed; it can only be created.
- Entropy change = entropy production > = 0



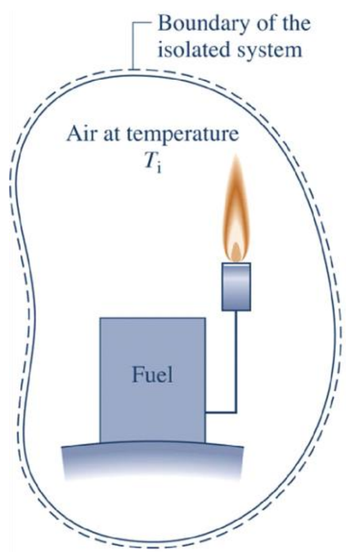
Fuel-air combination



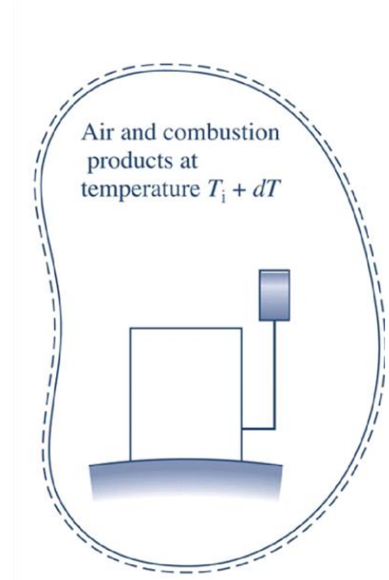
Warm air mixture

Second Law of Thermodynamics

- Entropy (not energy) distinguishes these two states of the system



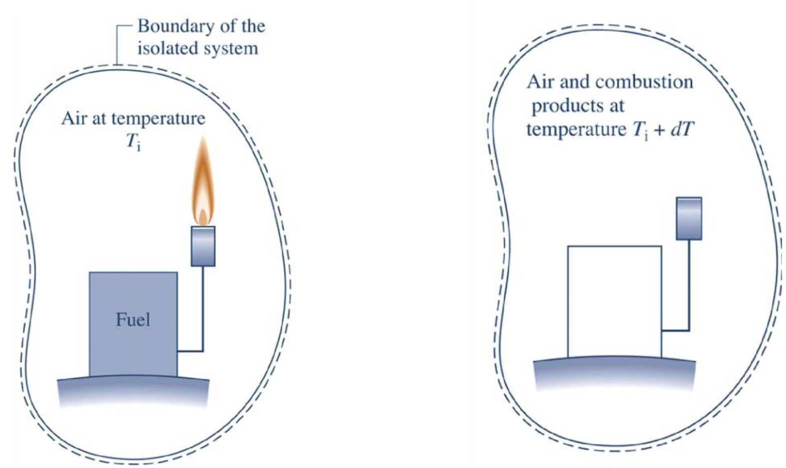
Fuel-air combination



Warm air mixture

Entropy Balance in isolated Systems

- Entropy cannot be destroyed; it can only be created.
- Entropy change = entropy production > = 0
- <u>Processes that occur naturally in isolated systems move the system to equilibrium</u>



Fuel-air combination　　Warm air mixture

Spontaneous Processes

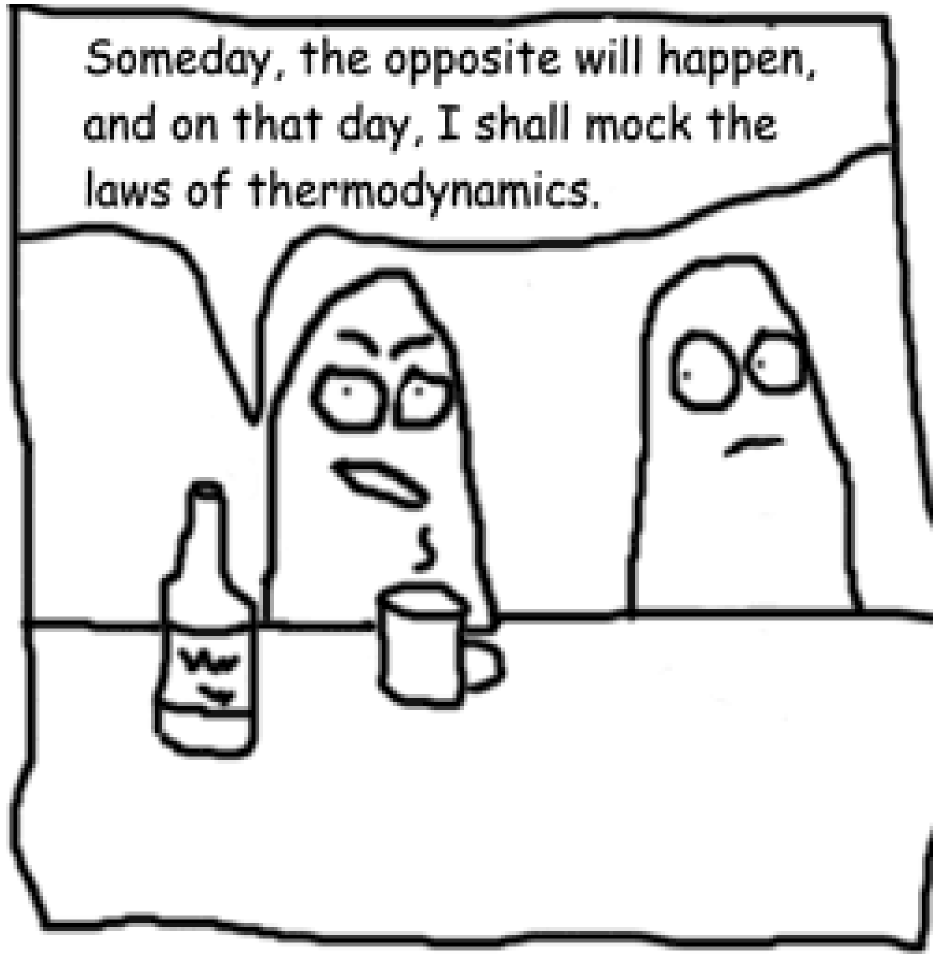
- **Spontaneous process** - a process that occurs "naturally" in isolated systems

- Hot coffee in a cold room gets colder and not hotter

- Ice on top of a boiling pan melts; it does not get cooler


I have a bottle of beer next to a mug of coffee.

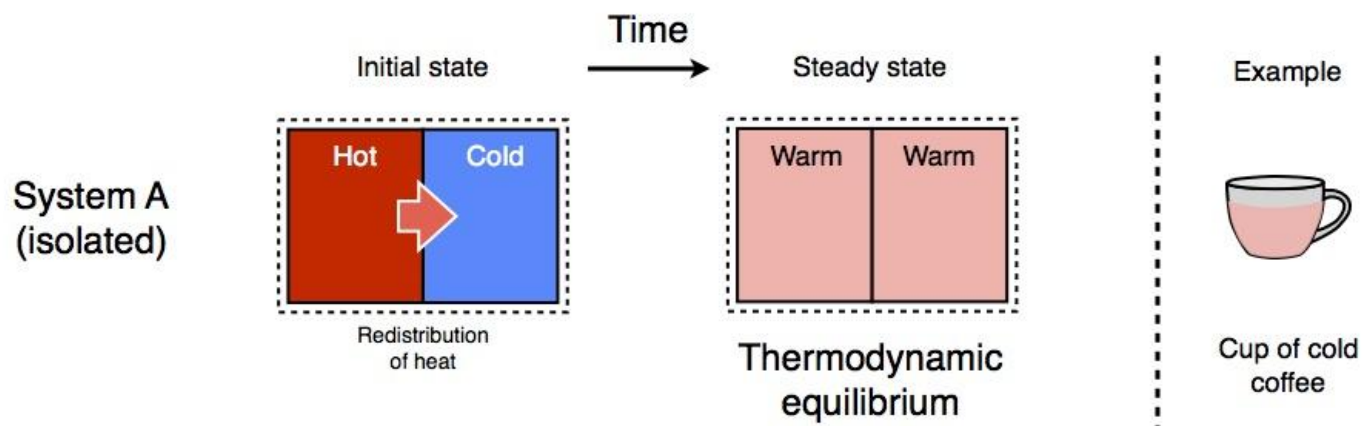

The beer is getting warmer, and the coffee is getting colder.


Someday, the opposite will happen, and on that day, I shall mock the laws of thermodynamics.


No, not today.
Not Today?

Second Law of Thermodynamics

- The entropy of an isolated system increases as it tends to equilibrium, where it achieves its maximum value



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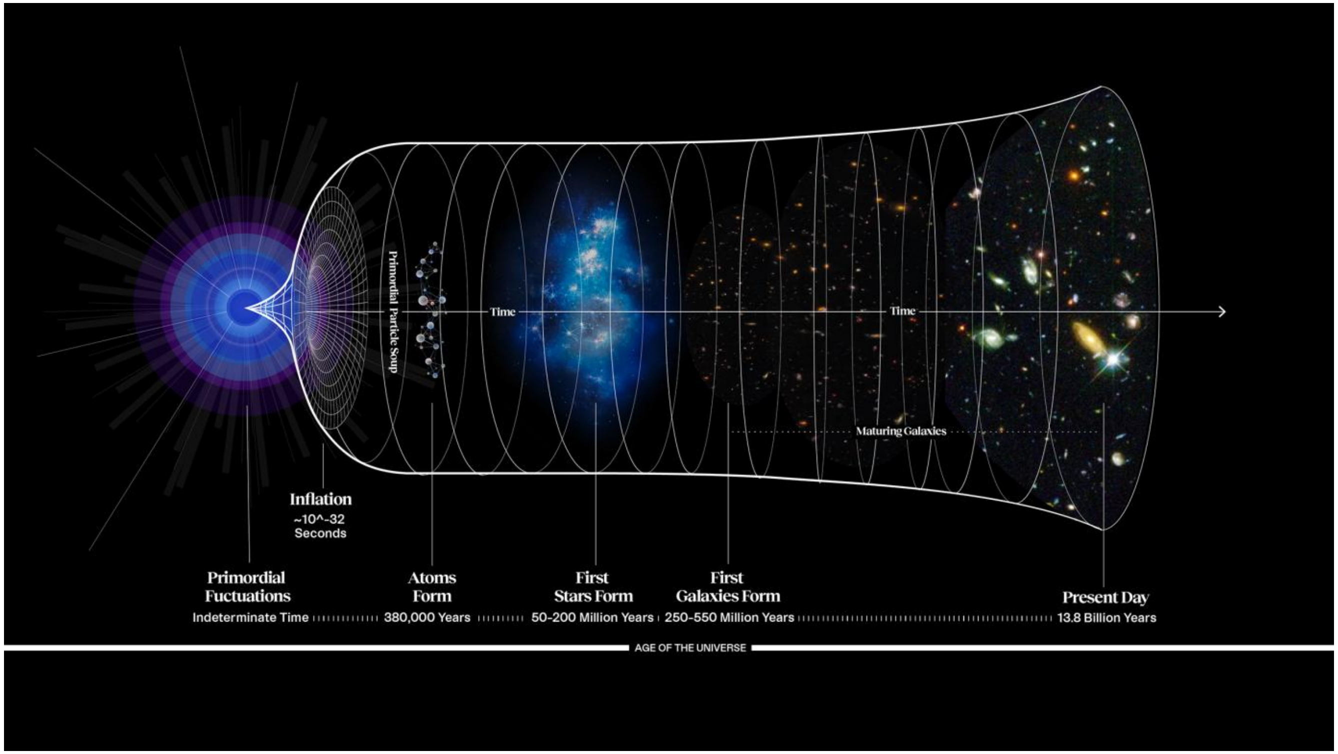
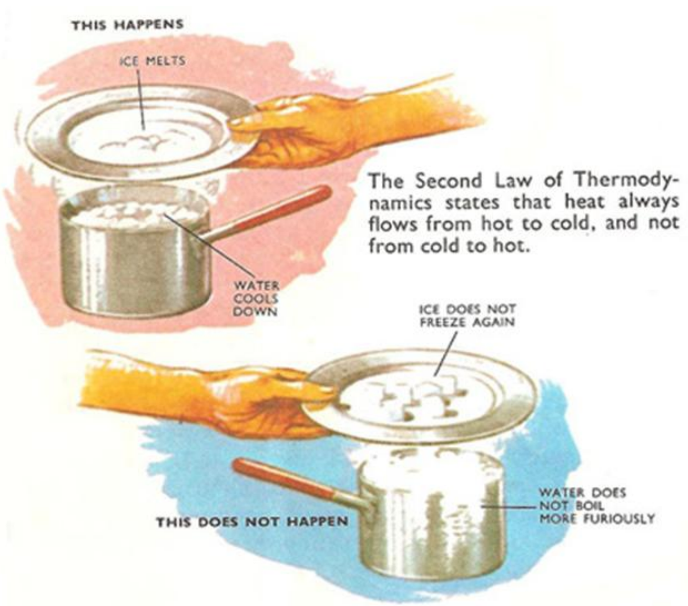
Second Law of Thermodynamics



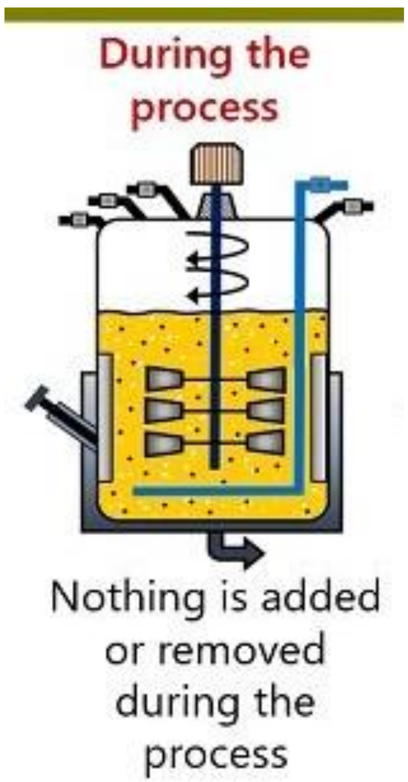
The state variable: Entropy

- Entropy is the state variable that gives unidirectionality to time in physical processes ocurring in isolated & adiabatic systems.



Entropy Balance in Closed Systems

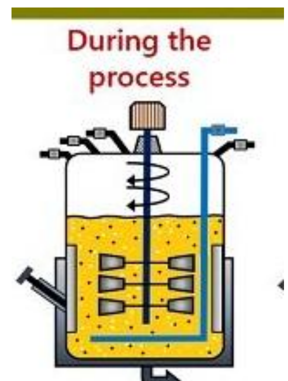
- Entropy change = Entropy transfer in the form of heat + entropy production

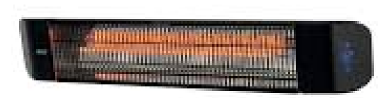


Entropy Balance in Closed Systems

- Entropy change = Entropy transfer in the form of heat + entropy production

$$\Delta S = \frac{Q}{T} + \sigma$$



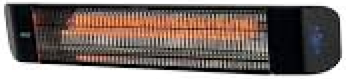


- The entropy of the heat flow decreases with increasing temperature
- <u>Entropy flows with heat but not with work</u>

Entropy Balance in Closed Systems

- Entropy change = Entropy transfer in the form of heat + entropy production

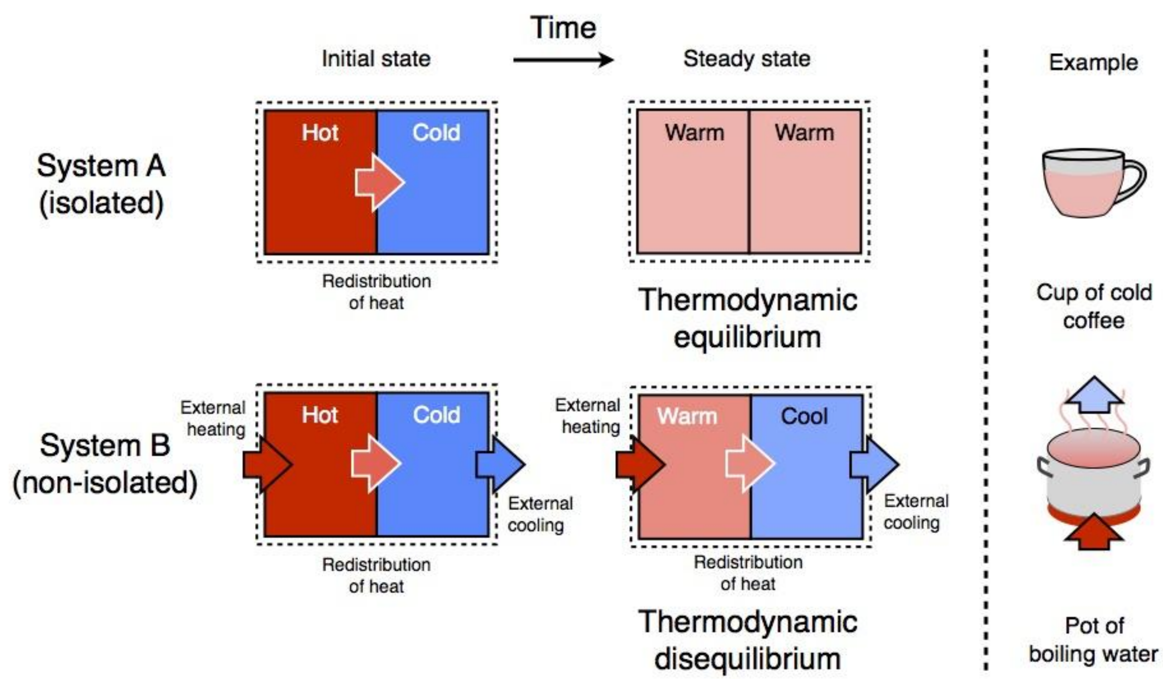
$$\Delta S = \frac{Q}{T} + \sigma$$



- **2nd Law: Energy Degradation**
- Entropy transfer by Q
- Sign of entropy flows
- Steady state vs. Transient

Second Law of Thermodynamics

- <u>The entropy of a closed system can stay constant – a closed system can remain in non-equilibrium</u>



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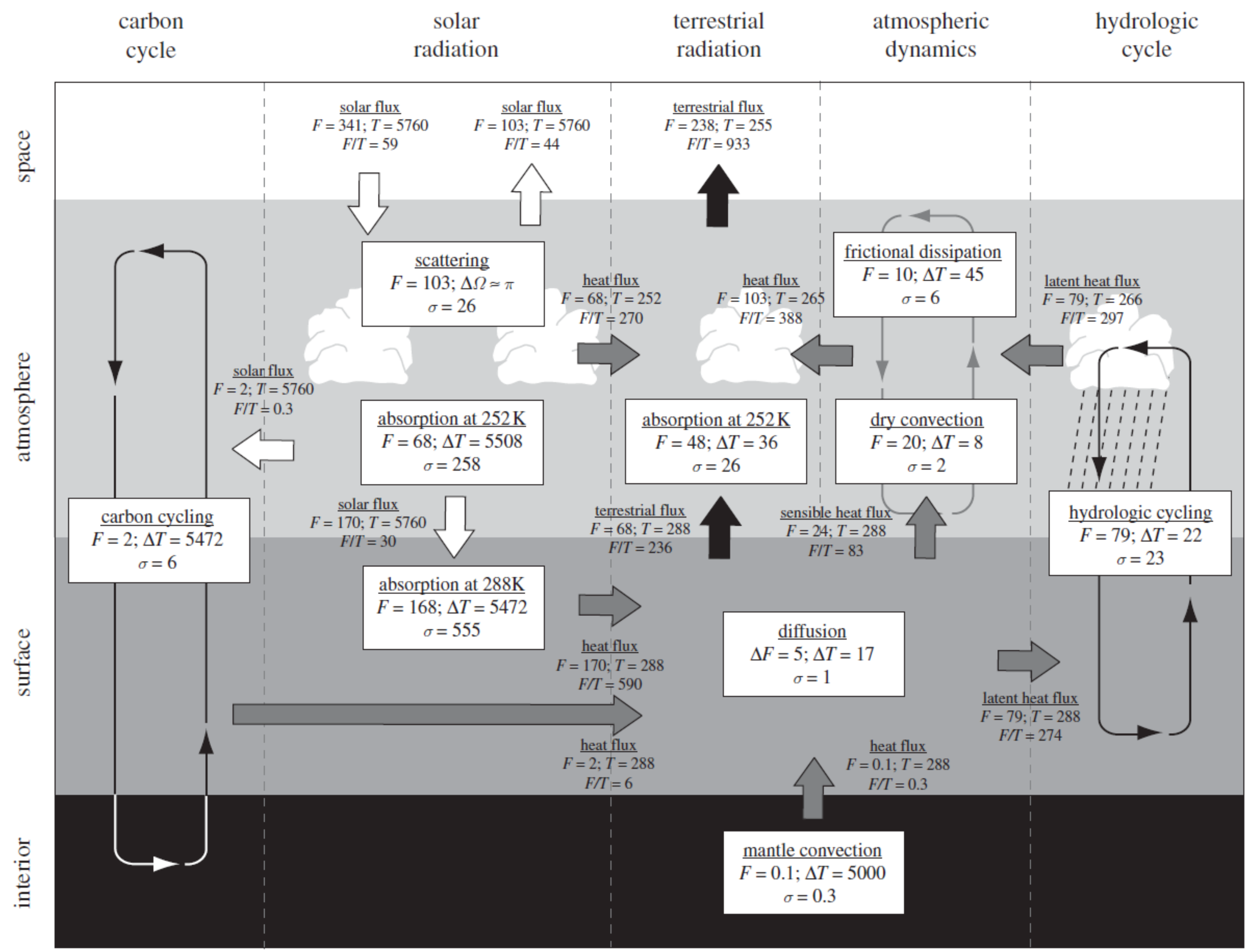
Second Law of Thermodynamics

- Why is Life possible in a closed system in steady-state?

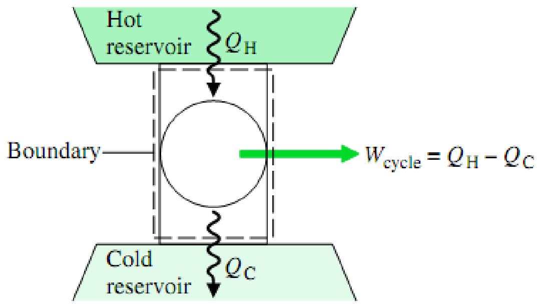
Second Law of Thermodynamics

- Entropy Change = Heat_in/T_sun + Heat_out/T_Earth + entropy production ≈ 0
- T_Sun = 5778 K; T_Earth = 255 K

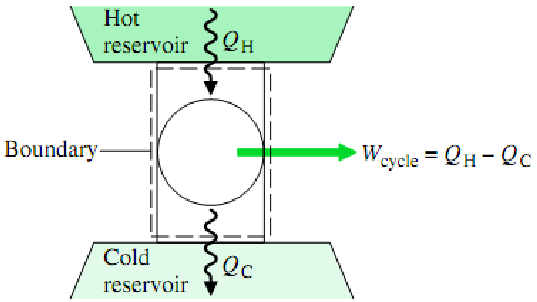
Entropy Production on Earth



Closed System – Power Cycle

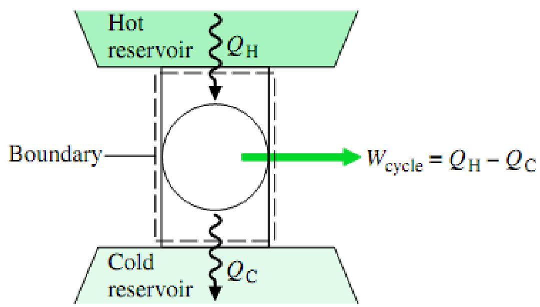


Closed System – Power Cycle



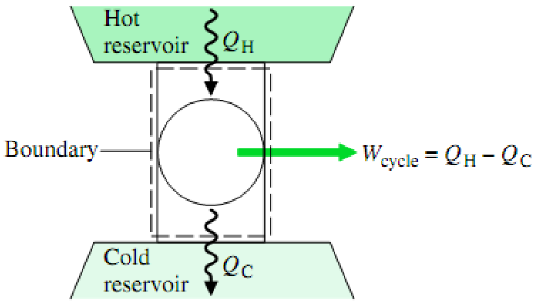
- First law?

Closed System – Power Cycle



- First law: $\Delta E = Q_H - Q_C - W_{cycle} = 0 \Rightarrow W_{cycle} = Q_H - Q_C$

Closed System – Power Cycle



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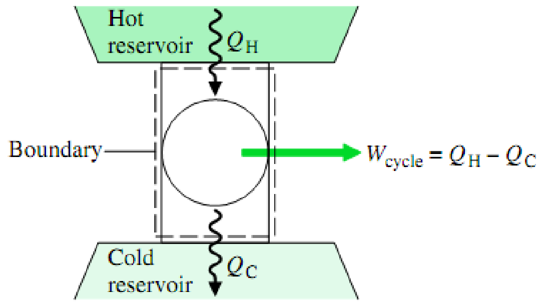
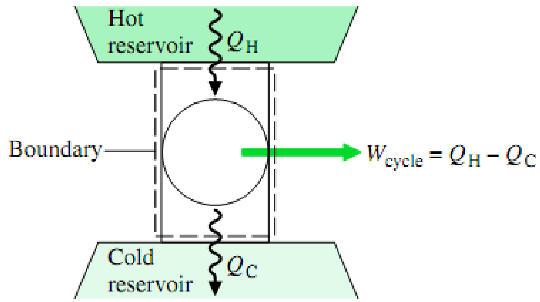
- Second law?

Closed System – Power Cycle



- First law: $\Delta E = Q_H - Q_C - W_{cycle} = 0 \Rightarrow W_{cycle} = Q_H - Q_C$
- Second law: $\Delta S = \dfrac{Q_H}{T_H} - \dfrac{Q_C}{T_C} + \sigma = 0 \Rightarrow Q_C \neq 0$

Closed System – Power Cycle



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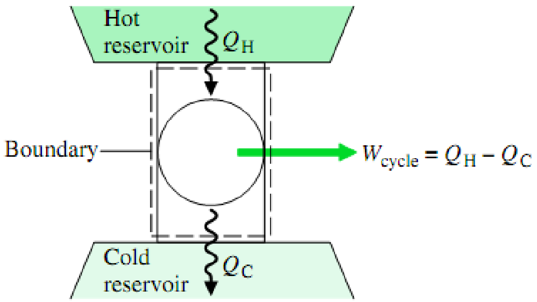
- <u>Not all available energy can be used to produce work</u>

Closed System – Power Cycle



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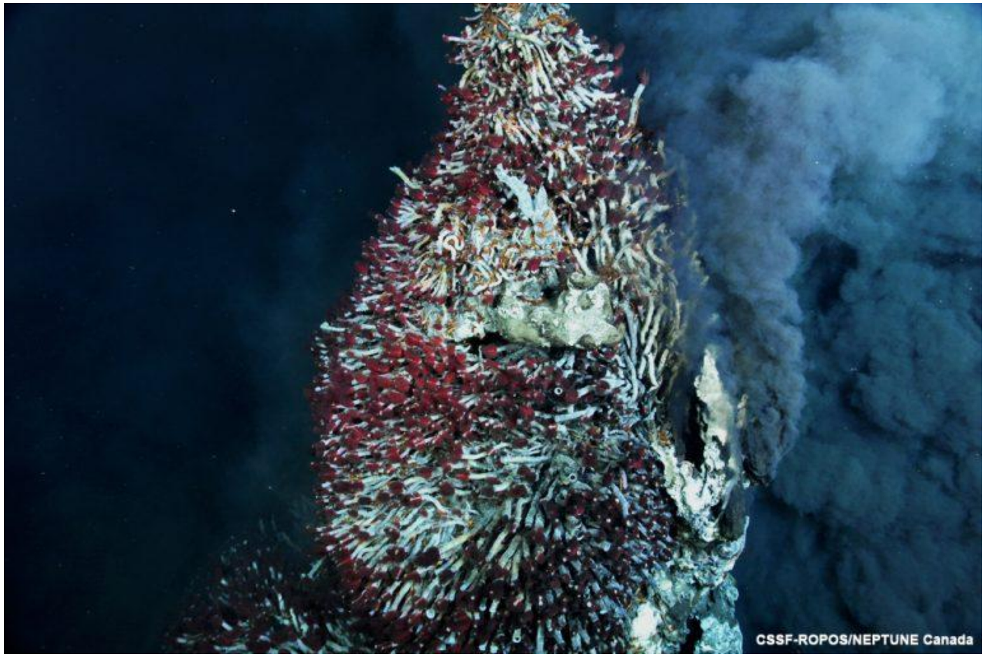
- Second law: $\Delta S = \dfrac{Q_H}{T_H} - \dfrac{Q_C}{T_C} + \sigma = 0 \Rightarrow Q_C \neq 0$

- <u>Not all available energy can be used to produce work</u>
- <u>Amount of work decreases with entropy production</u>

Temperature gradients in Life



- Giant tube worms in a hydrotermal vent (temperatures in water can range from 350ºC to 2ºC)
- Organisms do not have the apparatus to convert heat into work as closed systems

Thermodynamics in Open Systems

- First Law of Thermodynamics
  Mass and energy are conserved

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Mass Balance in Open Systems

Mass Change = Σ Mass Flows

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Mass Balance in DEB Organisms

$$M_V \dot{J}_V + M_E \dot{J}_E = M_X \dot{J}_X - M_P \dot{J}_P + M_O \dot{J}_O - M_C \dot{J}_C - M_H \dot{J}_H - M_N \dot{J}_N$$

- Conservation of mass (and number of moles) of carbon, oxygen, hydrogen and nitrogen

$$0 = \boldsymbol{n}_{\mathcal{M}} \dot{\boldsymbol{J}}_{\mathcal{M}} + \boldsymbol{n}_{\mathcal{O}} \dot{\boldsymbol{J}}_{\mathcal{O}}$$

- Strong homeostasis?

Mass Balance in DEB Organisms

$$M_V\dot{J}_V + M_E\dot{J}_E = M_X\dot{J}_X - M_P\dot{J}_P + M_O\dot{J}_O - M_C\dot{J}_C - M_H\dot{J}_H - M_N\dot{J}_N$$

- Conservation of mass (and number of moles) of carbon, oxygen, hydrogen and nitrogen

$$0 = \boldsymbol{n}_{\mathcal{M}}\dot{\boldsymbol{J}}_{\mathcal{M}} + \boldsymbol{n}_{\mathcal{O}}\dot{\boldsymbol{J}}_{\mathcal{O}}$$

- Strong homeostasis: chemical compositions are constant

Mass Balance in DEB Organisms

$$M_V \dot{J}_V + M_E \dot{J}_E = M_X \dot{J}_X - M_P \dot{J}_P + M_O \dot{J}_O - M_C \dot{J}_C - M_H \dot{J}_H - M_N \dot{J}_N$$

- Conservation of mass (and number of moles) of carbon, oxygen, hydrogen and nitrogen

$$0 = \boldsymbol{n}_{\mathcal{M}} \dot{\boldsymbol{J}}_{\mathcal{M}} + \boldsymbol{n}_{\mathcal{O}} \dot{\boldsymbol{J}}_{\mathcal{O}}$$

- Do mass balances completely specify aggregated chemical reactions?

Mass Balance in DEB Organisms

$$M_V \dot{J}_V + M_E \dot{J}_E = M_X \dot{J}_X - M_P \dot{J}_P + M_O \dot{J}_O - M_C \dot{J}_C - M_H \dot{J}_H - M_N \dot{J}_N$$

- Conservation of mass (and number of moles) of carbon, oxygen, hydrogen and nitrogen

$$0 = \boldsymbol{n}_{\mathcal{M}} \dot{\boldsymbol{J}}_{\mathcal{M}} + \boldsymbol{n}_{\mathcal{O}} \dot{\boldsymbol{J}}_{\mathcal{O}}$$

- Degrees of freedom – yEX, yVE and yPX.

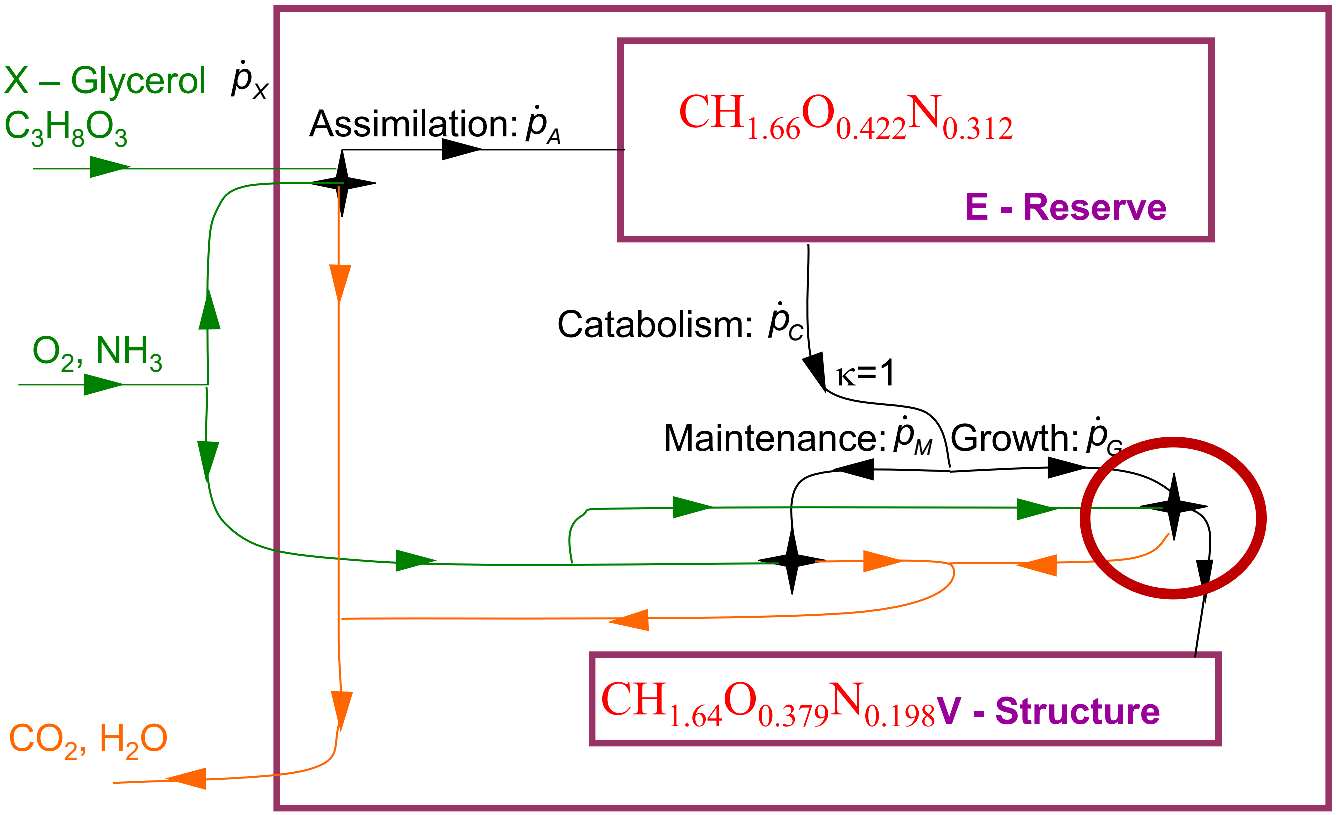
Mass Balance in DEB Organisms

$$0 = M_X \dot{J}_X - M_P \dot{J}_P + M_O \dot{J}_O - M_C \dot{J}_C - M_H \dot{J}_H - M_N \dot{J}_N$$

- Steady-state

Assimilation, Dissipation and Growth

Mass Change = Σ Mass Flows = 0



T=35ºC
pH: 6.8

- Klebsiella Aerogenes (V1-morph)

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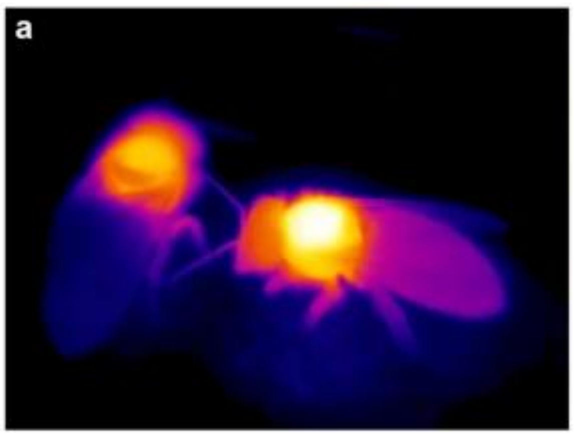
Energy Balance in Open Systems

Energy Change = Heat + Work + Energy in Mass Flow

$$\frac{dE}{dt} = \frac{d(U + KE + PE)}{dt} = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$



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- Internal energy
  - State variable
  - Extensive variable

Energy Balance in Open Systems

Energy Change = Heat + Work + Energy in Mass Flow

$$\frac{dE}{dt} = \frac{d(U + KE + PE)}{dt} = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$

- Kinetic and potential energy

Energy Balance in Open Systems

Energy Change = **Heat** + Work + Energy in Mass Flow

$$\frac{dE}{dt} = \frac{d(U+KE+PE)}{dt} = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$

- Heat (signs)

Energy Balance in Open Systems

Energy Change = Heat + **Work** + Energy in Mass Flow

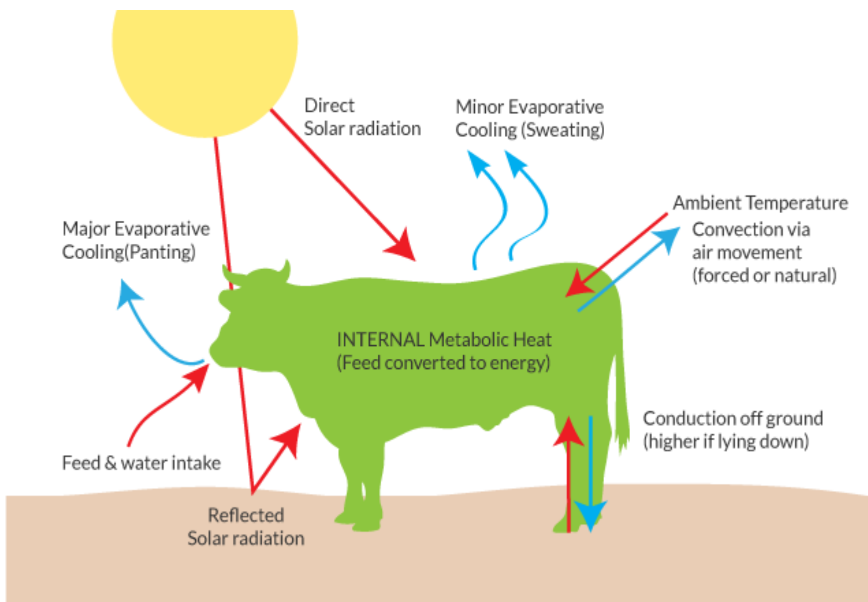
$$\frac{dE}{dt} = \frac{d(U + KE + PE)}{dt} = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$

- Work (signs)

Energy Balance in Open Systems

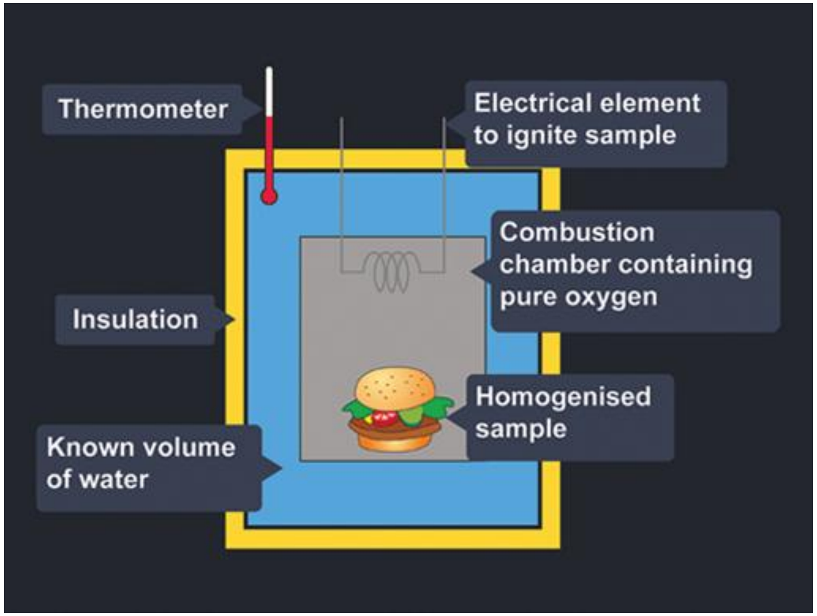
Energy Change = Heat + Work + Energy in Mass Flow

$$\frac{dE}{dt} = \frac{d(U + KE + PE)}{dt} = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$



- Enthalpy $h_i = u_i + p_i v_i$

Heating values



- Amount of heat released in complete combustion

Energy Balance in DEB organisms

$$\bar{h}_V \dot{J}_V + \bar{h}_E \dot{J}_E = \dot{Q} + \dot{W} + \bar{h}_X \dot{J}_X - \bar{h}_P \dot{J}_P + \bar{h}_O \dot{J}_O - \bar{h}_C \dot{J}_C - \bar{h}_H \dot{J}_H - \bar{h}_N \dot{J}_N$$

- Strong homeostasis: specific enthalpies are constant at constant T

Energy Balance in DEB organisms

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$$0 = \dot{Q} + \dot{W} + \bar{h}_X \dot{J}_X - \bar{h}_P \dot{J}_P + \bar{h}_O \dot{J}_O - \bar{h}_C \dot{J}_C - \bar{h}_H \dot{J}_H - \bar{h}_N \dot{J}_N$$

- Strong homeostasis: specific enthalpies are constant at constant T
- Steady-state

Structure and Reserve Enthalpies

- The energy balance equation applied to the chemostat to many steady-states:

$$0 = \overline{\boldsymbol{h}}_{\mathcal{M}}^T \dot{\boldsymbol{J}}_{\mathcal{M}} + \overline{\boldsymbol{h}}_{\mathcal{O}}^T \dot{\boldsymbol{J}}_{\mathcal{O}} + \dot{P}_{T+}. \quad \mathcal{M} : CO_2, H_2O, O_2, NH_3$$

$$\mathcal{O} : X, E, V$$

- The formation enthalpies (at 35ºC) are:

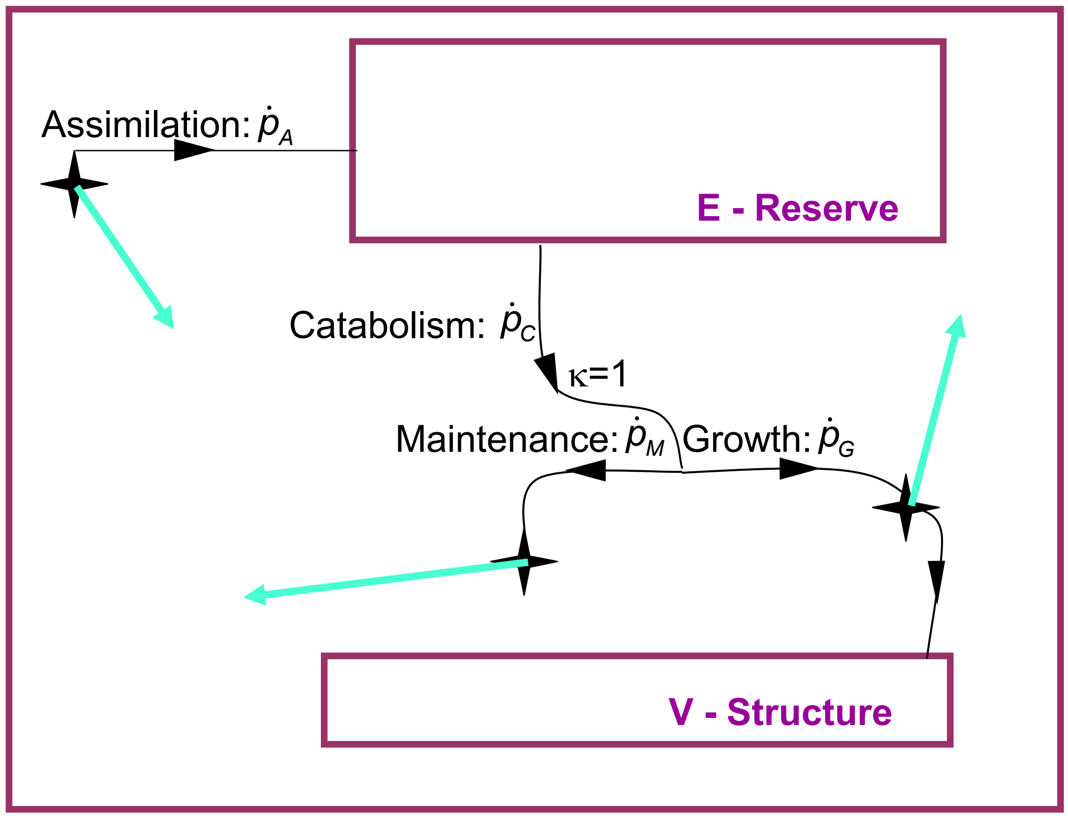
$\overline{h}_V = -107 kJ.C - mol^{-1}$ (structure)

$\overline{h}_E = -33 kJ.C - mol^{-1}$ (reserve)

- The formation enthalpy of biomass (at 35ºC) varies from: -76 kJ.C-mol to –105 kJ C-mol

Assimilation, Dissipation and Growth

$$0 = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$

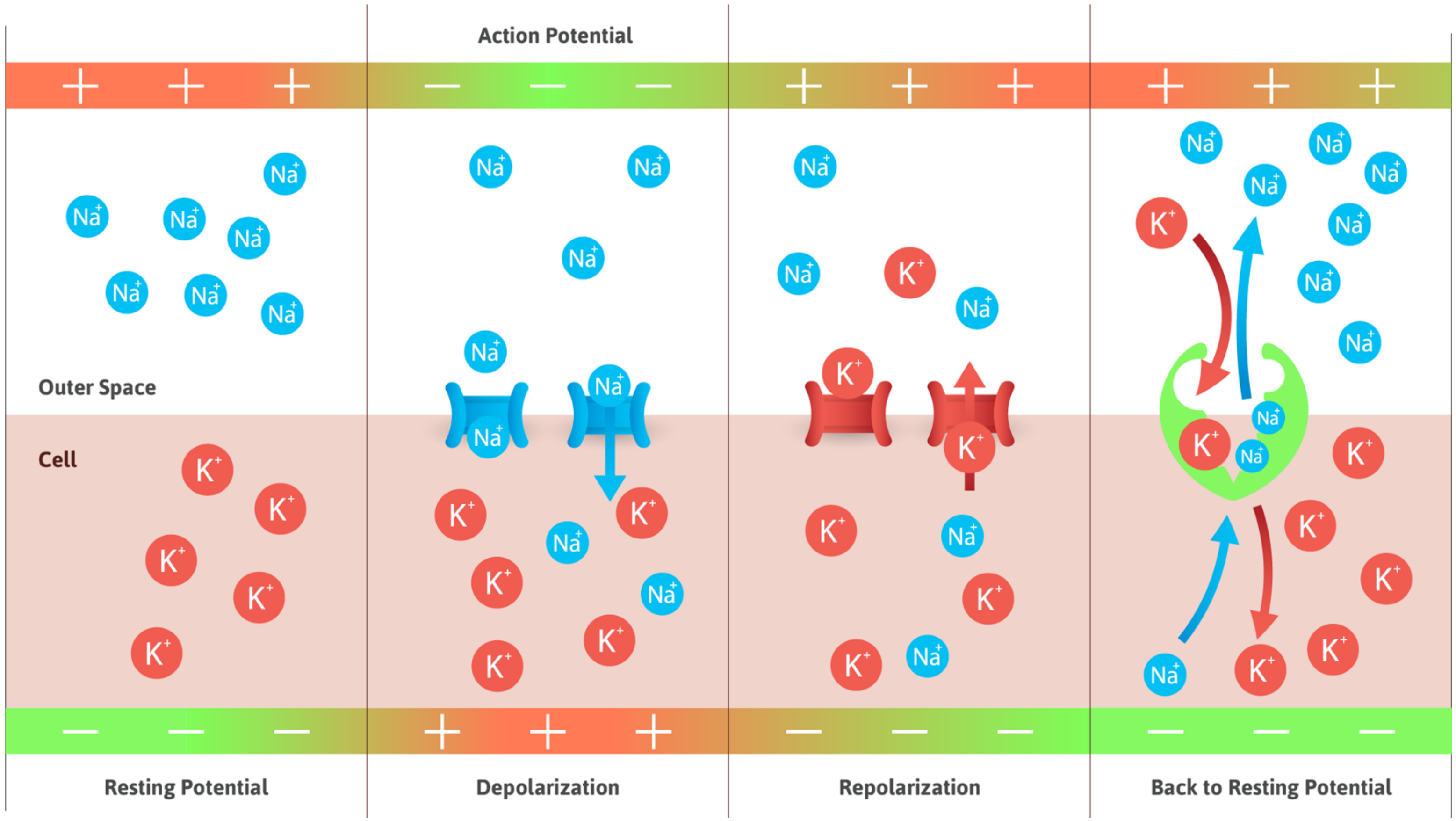


T=35ºC
pH: 6.8

Internal Work

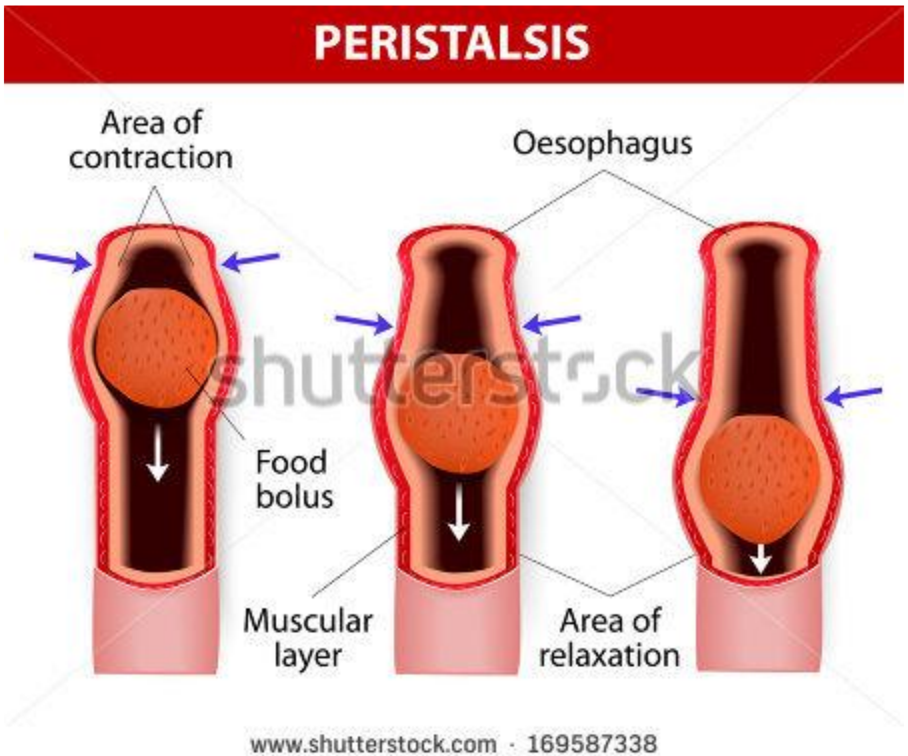
Internal Chemical Work

- Mantaining concentration gradients across membranes



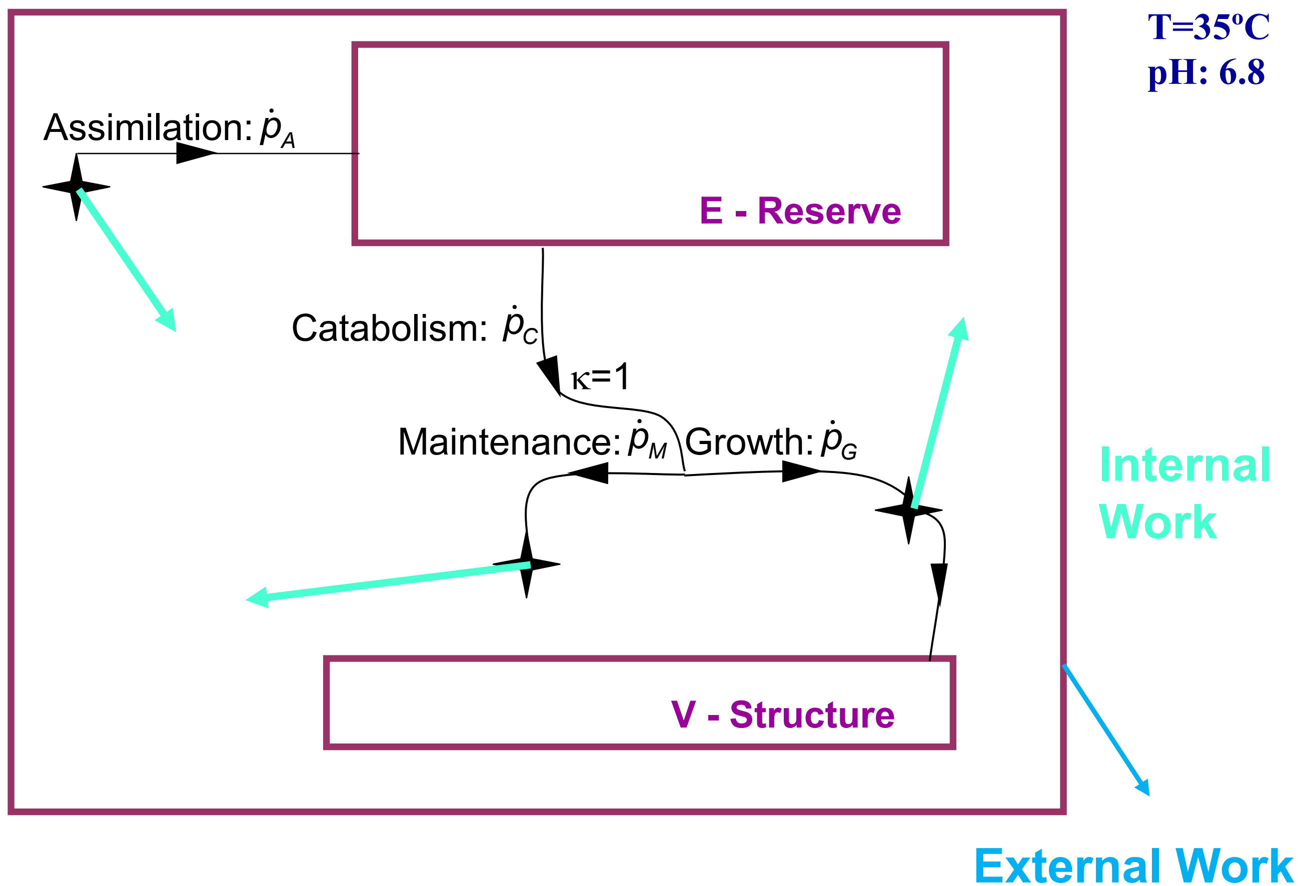
Internal Muscle Work

- Peristaltic movements by the oesophagus



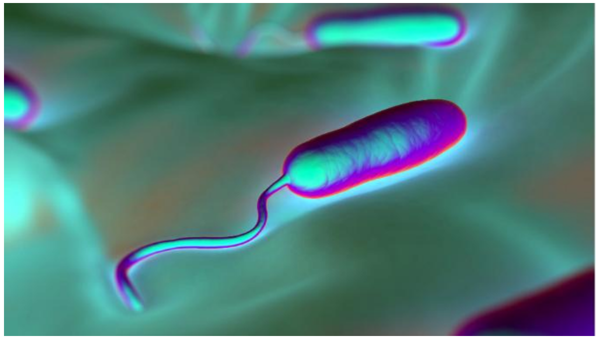
Energy Balance in DEB Organisms

$$\frac{dE}{dt} = \frac{d(U + KE + PE)}{dt} = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$



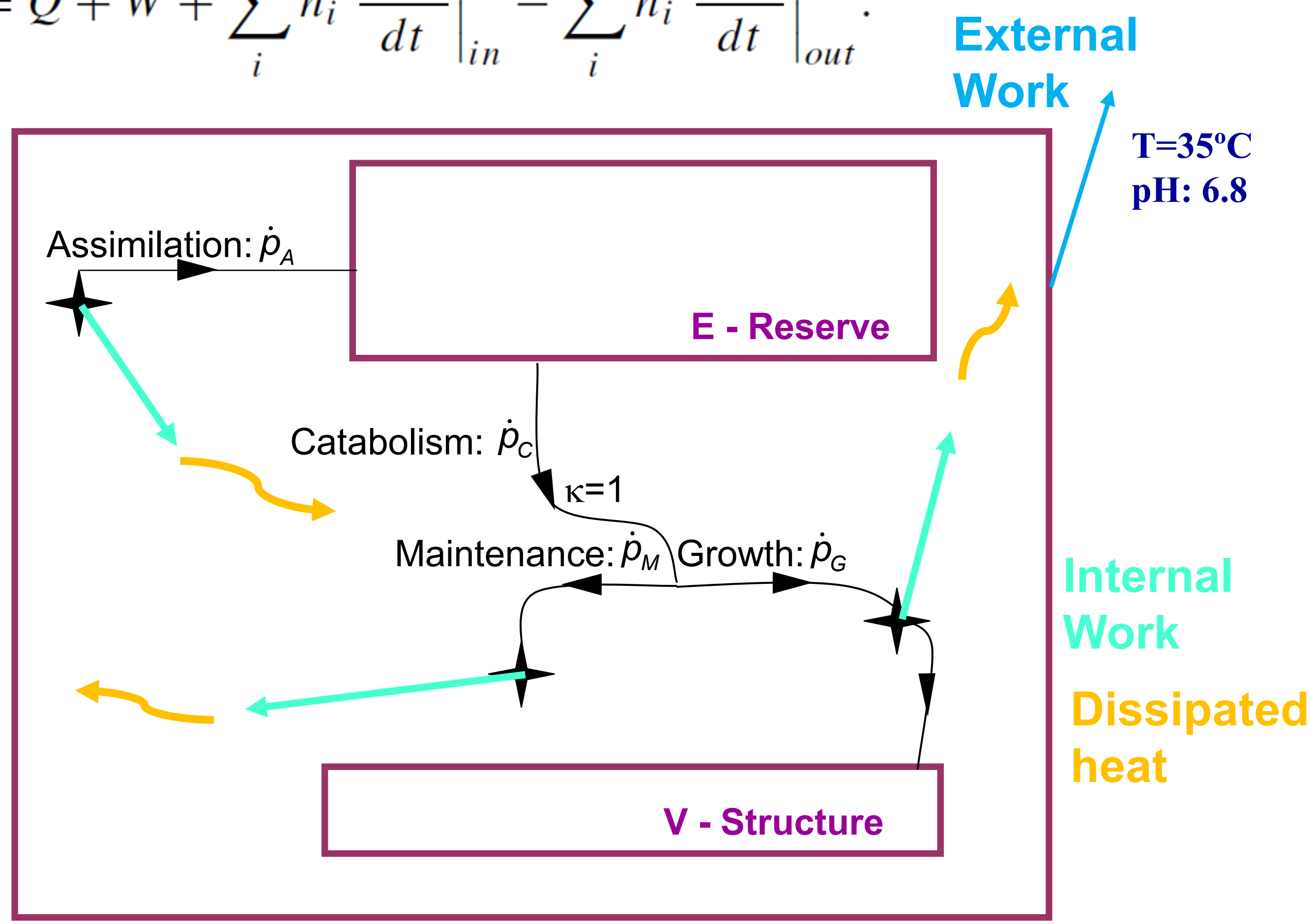
External Work

- Movement



Assimilation, Dissipation and Growth

$$0 = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$

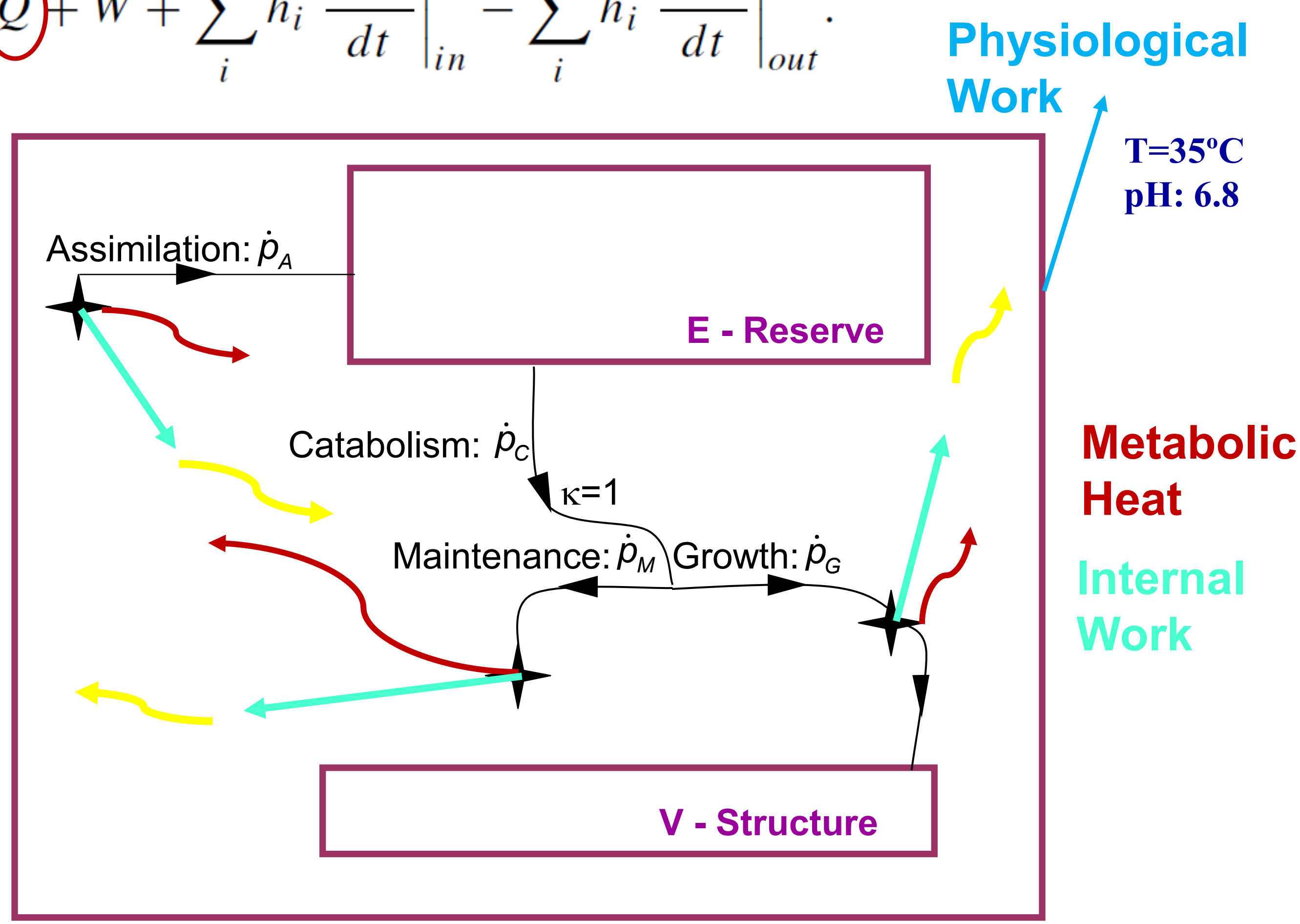


- Internal work ≠ external work!!

Internal Work dissipated as heat

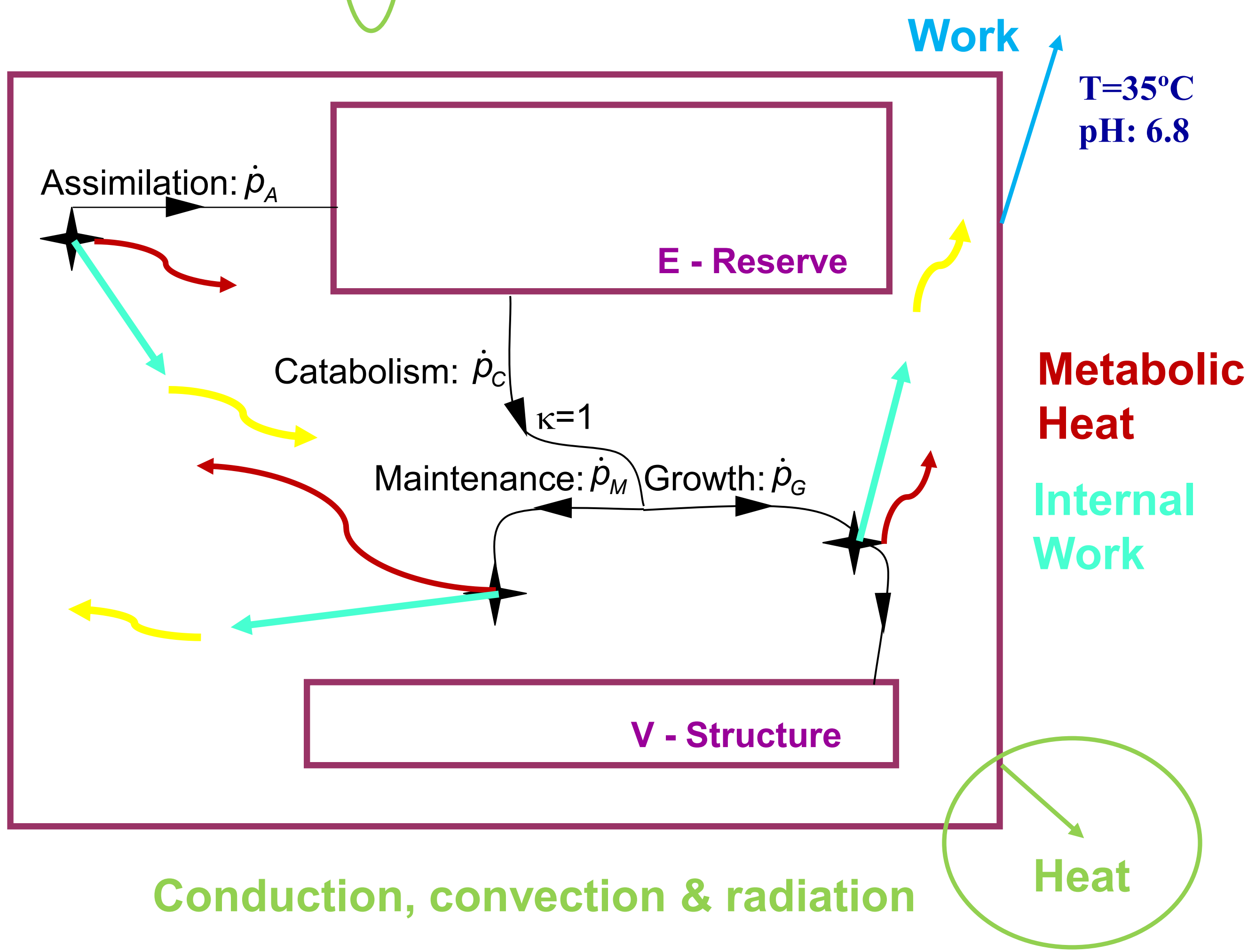
Assimilation, Dissipation and Growth

$$0 = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$



Energy Balance in DEB Organisms

$$\frac{dE}{dt} = \frac{d(U + KE + PE)}{dt} = \dot{Q} + \dot{W} + \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{h}_i \left.\frac{dM_i}{dt}\right|_{out}.$$



Endotherms

- Thermal homeostasis
- Somatic maintenance needs (p_T)
- Behaviour
- Insulation

Poikilotherms

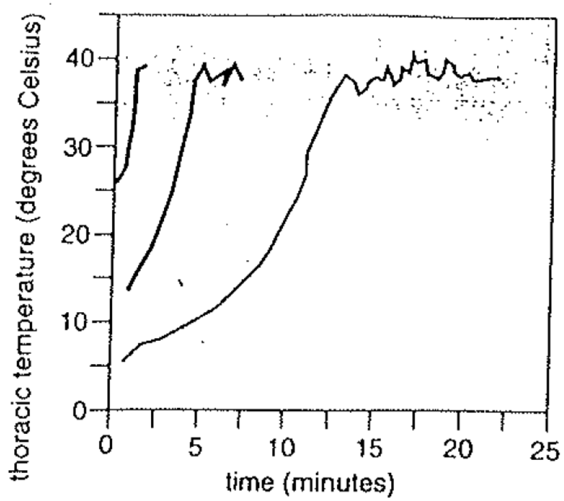


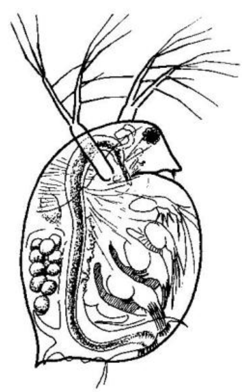
Figure 2. Bee warms up by contracting its flight muscles. A bumblebee in an ambient temperature of 24 *(blue)*, 13 *(red)* or 7 *(yellow)* degrees Celsius can quickly increase its thoracic temperature to a flight-ready level near 40 degrees. Warm-up may take several minutes in cold temperatures.

Metabolic rates: the effect of temperature

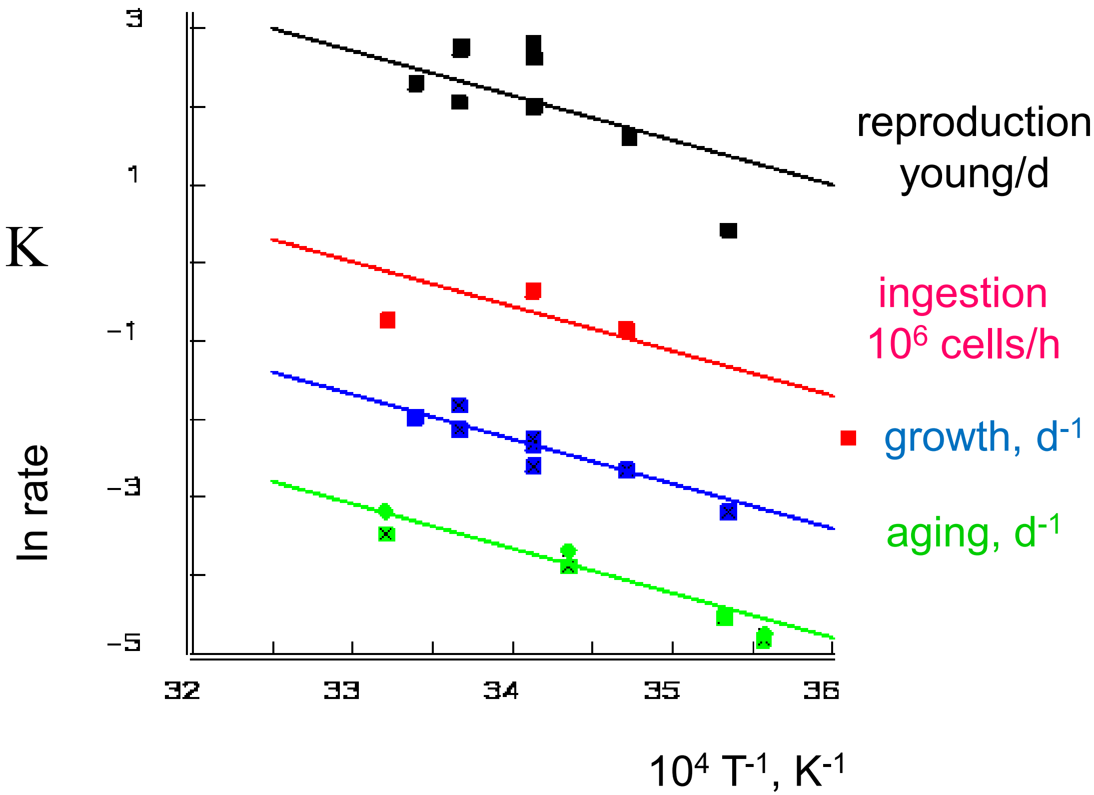
Arrhenius relationship

$$\ln k(T) = \ln k_1 + \frac{T_A}{T_1} - \frac{T_A}{T}$$

$$T_A = 6400\ \mathrm{K}; \quad T_1 = 293\ \mathrm{K}$$



Daphnia magna



Entropy Balance in Open Systems

Entropy Change = S in heat + S production+S in Mass Flow

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{\sigma} + \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{out}$$

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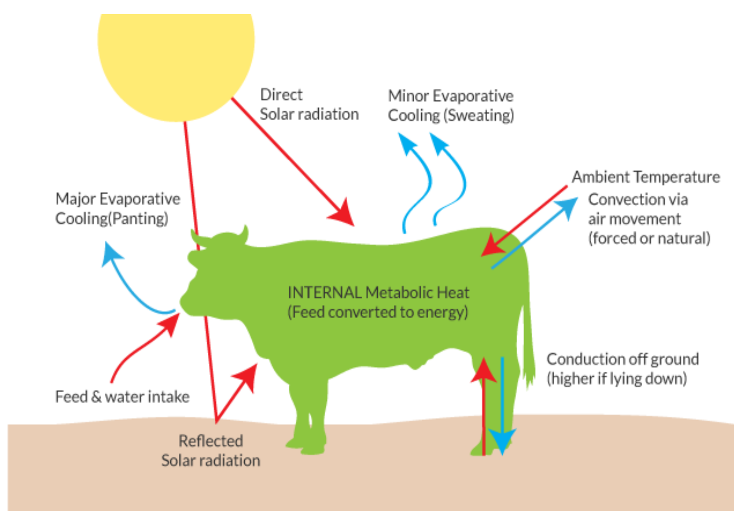
- Entropy
  - Extensive variable
  - State-variable

Entropy Balance in Open Systems

Entropy Change = S in heat + S production + S in Mass Flow

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{\sigma} + \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{out}$$

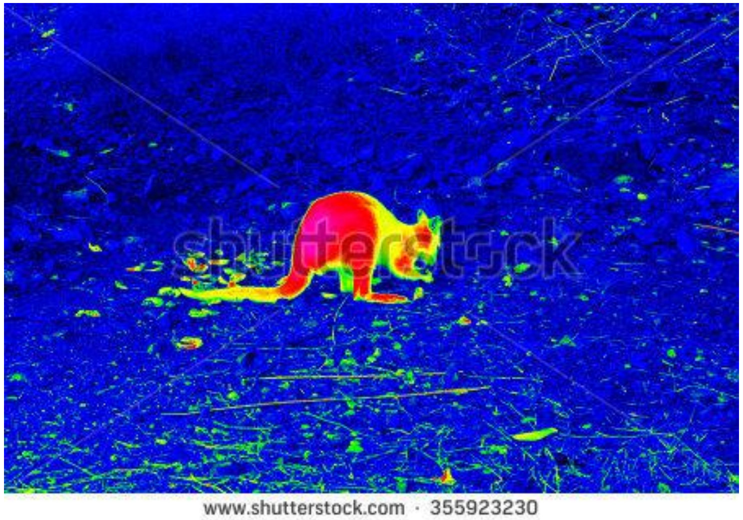
- "Organisms feed on negentropy" (Shrondinger)

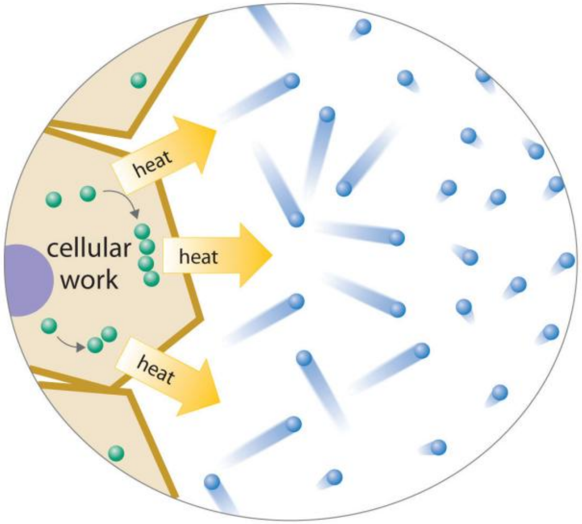


Entropy Balance in Open Systems

Entropy Change = S in heat + S production+S in Mass Flow

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{\sigma} + \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{out}$$





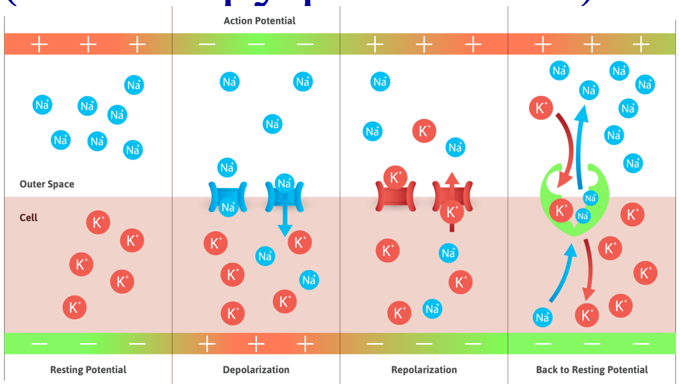
- Entropy flows with heat (but not with work)

Entropy Balance in Open Systems

Entropy Change = S in heat + S production + S in Mass Flow

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{\sigma} + \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{out}$$

- Energy and mass conversion leads to dissipation (or entropy production) $\dot{\sigma} \geq 0$



- For fully-grown aerobic organisms in steady-state entropy production is exported in the form of heat

Entropy Balance in DEB organisms

$$\bar{s}_V \dot{J}_V + \bar{s}_E \dot{J}_E = \frac{\dot{Q}}{T} + \dot{\sigma} + \bar{s}_X \dot{J}_X + \bar{s}_O \dot{J}_O - \bar{s}_P \dot{J}_P - \bar{s}_C \dot{J}_C - \bar{s}_H \dot{J}_H - \bar{s}_N \dot{J}_N .$$

- Strong homeostasis: specific entropies are constant at constant T

Entropy Balance in DEB organisms

$$0 = \frac{\dot{Q}}{T} + \dot{\sigma} + \bar{s}_X \dot{J}_X + \bar{s}_O \dot{J}_O - \bar{s}_P \dot{J}_P - \bar{s}_C \dot{J}_C - \bar{s}_H \dot{J}_H - \bar{s}_N \dot{J}_N .$$

- Steady-state

Structure and Reserve Entropies

- The entropy balance equation applied to the chemostat to many dilution rates:

$$\underbrace{0 = \bar{\boldsymbol{s}}_{\mathcal{M}}^T \dot{\boldsymbol{J}}_{\mathcal{M}} + \bar{\boldsymbol{s}}_{\mathcal{O}}^T \dot{\boldsymbol{J}}_{\mathcal{O}}}$$

$$\mathcal{M} : CO_2, H_2O, O_2, NH_3$$

$$\mathcal{O} : X, E, V$$

Valid for an aerobic, ectothermic organism because $\Delta\bar{g} = \Delta\bar{h} - T\Delta\bar{s} \simeq \Delta\bar{h}$

Unknowns: s_V, s_E

- The entropies are:

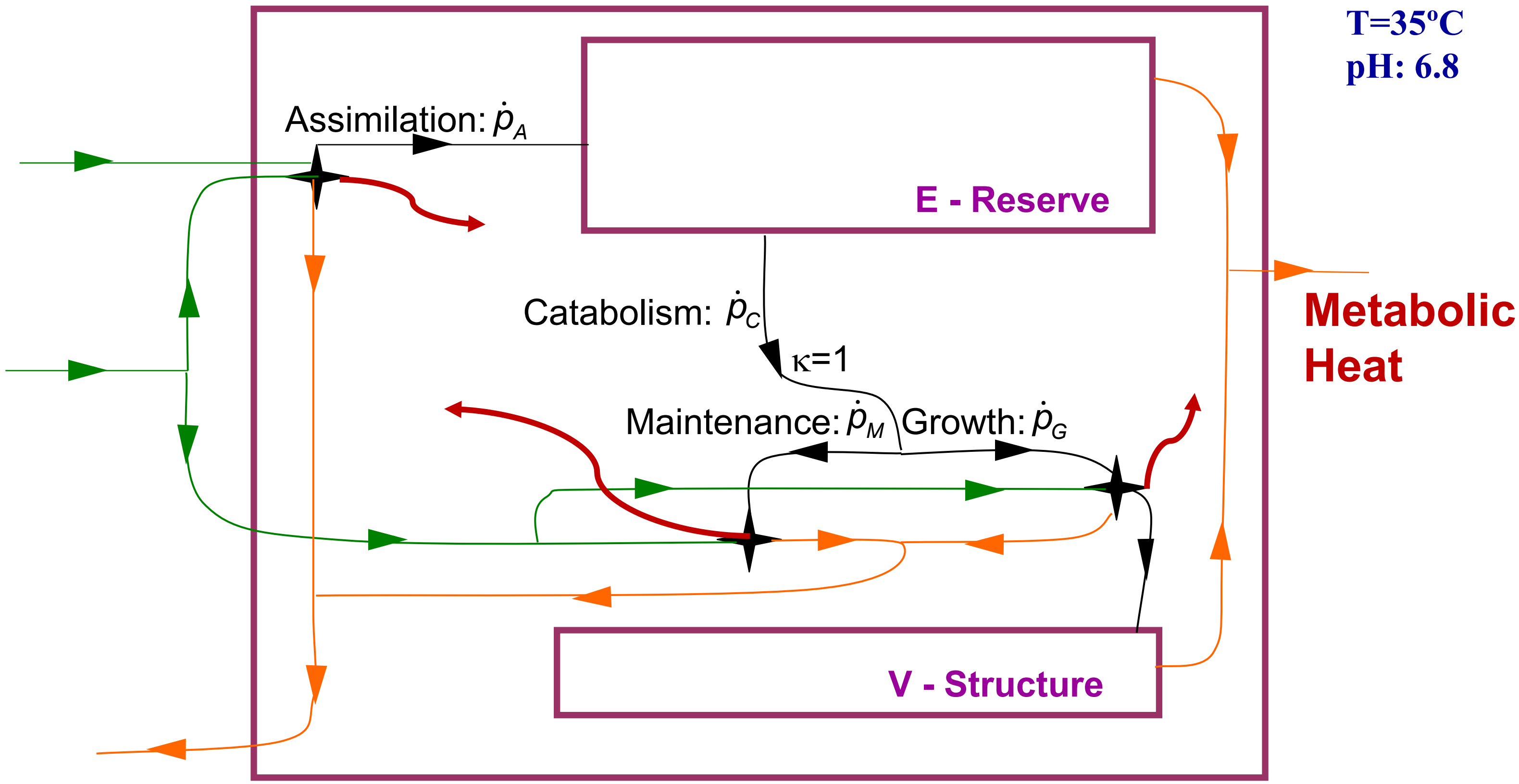
$$\bar{s}_V = 52.0 J.C-mol^{-1}.K^{-1} \quad \text{(structure)}$$

$$\bar{s}_E = 74.8 J.C-mol^{-1}.K^{-1} \quad \text{(reserve)}$$

- The entropy of biomass varies from: 52.4 J.C-mol to 61.4 J C-mol
- It is different from the entropy of organic compounds with the same chemical composition

Assimilation, Dissipation and Growth

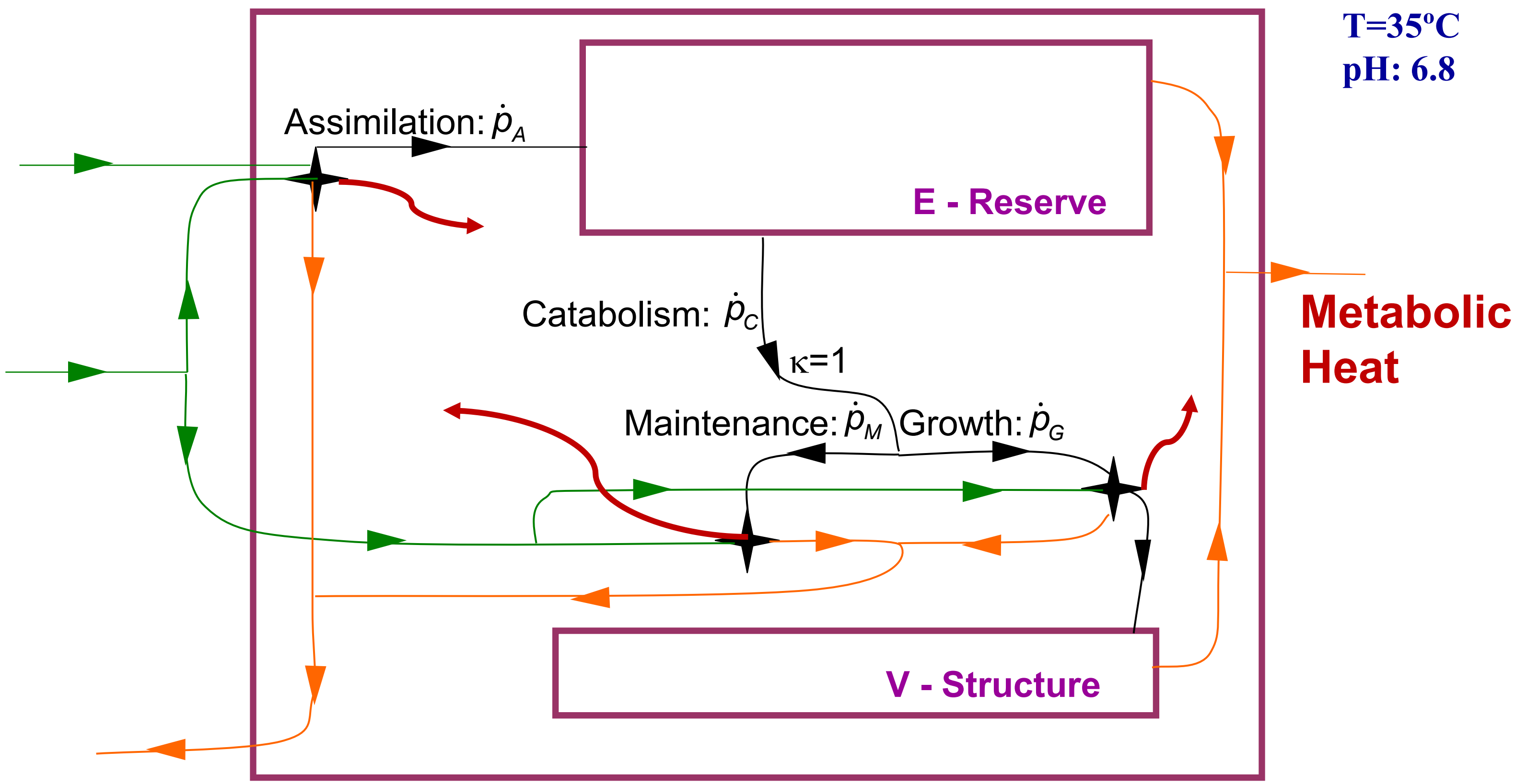
$$0 = \frac{\dot{Q}}{T} + \dot{\sigma} + \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{out}$$



T=35ºC
pH: 6.8

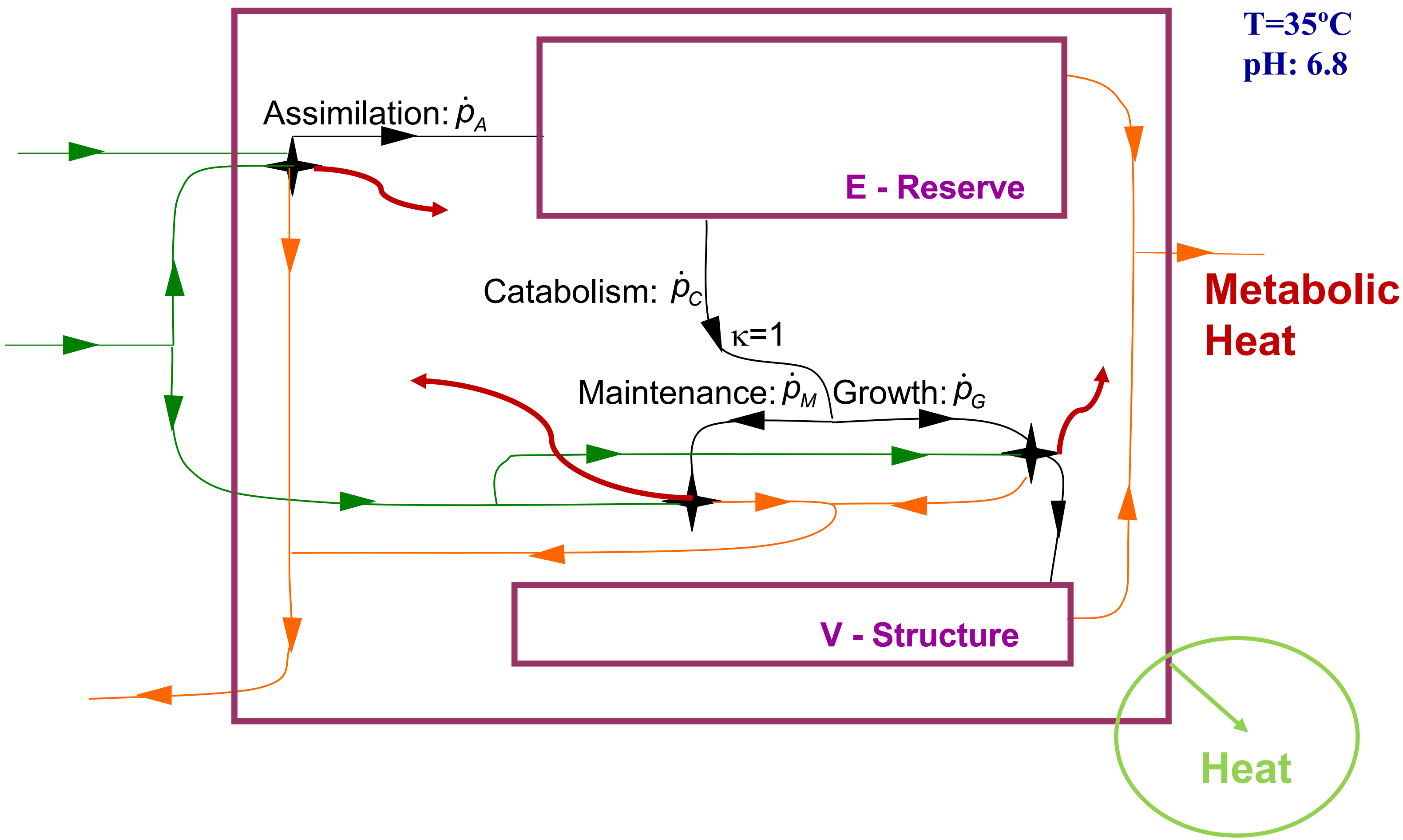
Assimilation, Dissipation and Growth

$$0 = \frac{\dot{Q}}{T} + \dot{\sigma} + \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{out}$$



Entropy Balance in DEB Organisms

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{\sigma} + \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{in} - \sum_i \bar{s}_i \left.\frac{dM_i}{dt}\right|_{out}$$

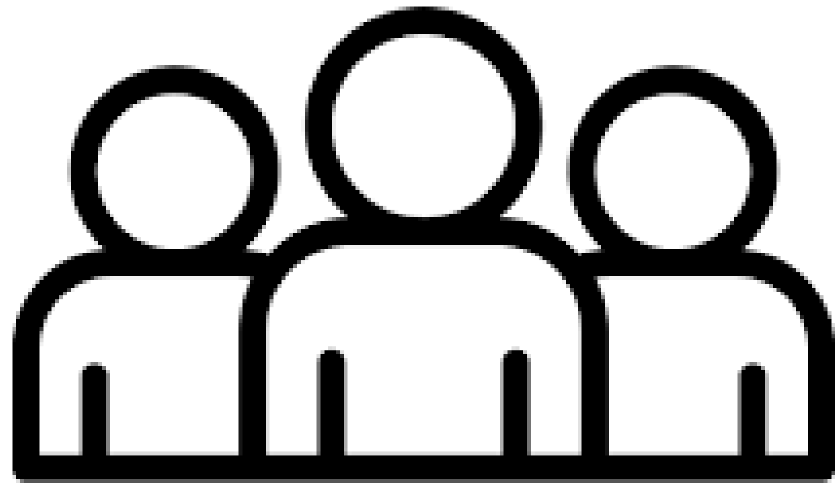


Activity Thermodynamics of Life

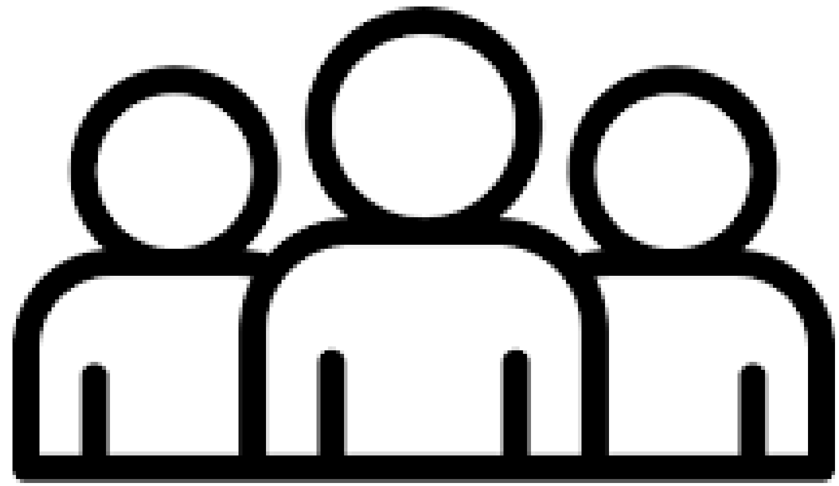
Activity Thermodynamics of Life

- **What?** Answer some questions for your pet
- **Who?** Groups of three students

Please create groups of three students



Please create groups of three students



02:00

Activity Thermodynamics of Life

What?	Answer some questions for your pet
Who?	Groups of three students
How?	Using what you learned here 😊
When?	During 15 minutes
Where?	Google slides

Activity Thermodynamics of Life

What?	Answer some questions for your pet
Who?	Groups of three students
How?	Using what you learned here 😊
When?	During 15:00
Where?	https://tinyurl.com/thermodynamicslife