CONVECTION AND MATTER TRANSPORT PROCESSES

REVIEW: CLOSED SYSTEM

Simple substance

i.e., no reacting components

internal energy

U = U(S,V,m)

constant mass makes this a two-port capacitor

— one port for each variable argument of the energy function

displacements:

S, -V

flows:

dS/dt, –dV/dt

efforts:

total differential of internal energy:

dU = (∂U/∂S)dS + (∂U/∂V)dV = TdS – PdV.

from this we identify efforts on the two ports as T, P

OPEN SYSTEM:

Mass may vary.

Simple substance

internal energy

$U = U(S,V,m)$

For convenience, work with molar units for mass.

Rewrite in terms of moles using m = M N where

N is number of moles

(units of N: e.g. Kg-moles, pound-moles)

M is molecular weight

(for a non-reacting mixture like air, M is an equivalent molecular weight)

Internal energy now has three variable arguments.

$U = U(S,V,N)$

Variable mass makes this a three-port capacitor.

Generalized displacement associated with mass "port":

number of moles, N

corresponding flow variable:

mass flow rate $dN/dt = \dot{N}$

Corresponding effort variable:

evaluate total differential of internal energy:

$dU = (\partial U/\partial S)dS + (\partial U/\partial V)dV + (\partial U/\partial N)dN$

$dU = TdS - PdV + \mu dN$

effort on the mass flow port (a definition):

$$\mu \triangleq \left.\frac{\partial U}{\partial N}\right|_{S,V}$$

$$\frac{T\square}{\dot{S}\square} \quad \mathbf{C} \quad \frac{P}{\dot{V}}$$
$$\mu \;\Big|\; \dot{N}\square$$

WHAT IS THIS "EFFORT" μ?

Form the Gibbs free energy function.

A Legendre transform of internal energy with respect to both the temperature-entropy and pressure-volume ports.

$G = U - TS + PV = G(P,T,N)$

$dG = dU - TdS - SdT + PdV + VdP$

substitute:

$dG = TdS - PdV + \mu dN - TdS - SdT + PdV + VdP$

$dG = \mu dN - SdT + VdP$

$$\mu \triangleq \left.\frac{\partial G}{\partial N}\right|_{P,T}$$

Thus μ has the same units as chemical potential.

Gibbs free energy per mole at constant temperature and pressure.

Because we dealing here with a single species and no reactions, μ has been termed a "matter potential".

Aside:

Note that $\left.\dfrac{\partial G}{\partial N}\right|_{P,T} = \left.\dfrac{\partial U}{\partial N}\right|_{S,V}$

TRANSPORT PROCESSES:

That's a strange-looking "effort" -- can we make sense of it?

How do we account for the power flow associated with mass transport?

Consider power flow past a given cross section.

There are two components:

"flow work rate"

"energy convection (transport) rate"

Neglecting kinetic energy:

convected energy rate: u $\dot{N}$

(rate of energy "carried with" the flow)

flow work rate = PQ = $\dfrac{P}{\rho}$ ρQ = Pv $\dot{N}$

(rate of work done in moving the fluid)

Net power flow

$$P_{net} = (Pv + u)\,\dot{N} \quad = h\,\dot{N}$$

h: molar specific enthalpy.

From this it appears that the appropriate effort is (molar) specific enthalpy.

Aside:

The above considered only convected internal energy. A similar argument may be applied to include other convected quantities.

μ or h?

How can we reconcile this apparent contradiction?

Consider the Legendre transforms which define the Gibbs function and the enthalpy:

$G = U + PV - TS$

$H = U + PV$

$\therefore\ H - TS = G$

That is, Gibbs free energy is a Legendre transform of enthalpy with respect to the temperature-entropy port.

or

$G + TS = H$

per unit mass (in moles):

$\mu + Ts = h$

KEY POINT: MASS FLOW AND ENTROPY FLOW ARE FUNDAMENTALLY COUPLED

The effort, μ, associated with accumulation of mass in the three-port capacitor does not fully account for the total energy added.

Energy "convection" fundamentally requires "entropy" convection.

Physically, there is a single "port" for mass flow.

Conceptually, the mass flow ($\mu\dot{N}$) port is fundamentally coupled to the thermal ($T\dot{S}$) port.

HOW MAY WE DEPICT THIS COUPLING?

One way: using a modulated transformer as follows:
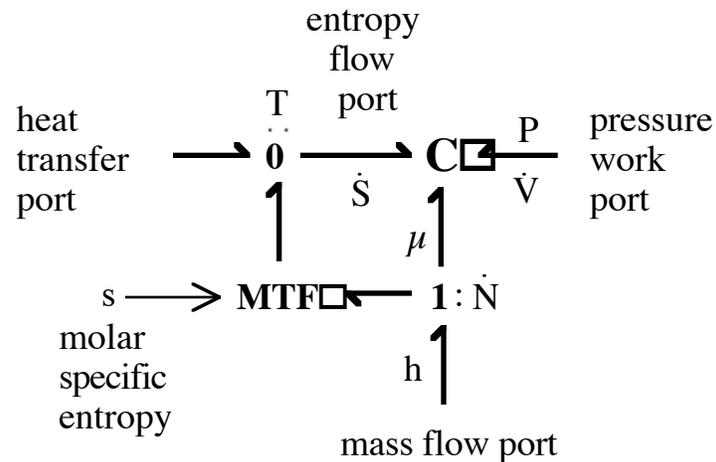
Note that the heat transfer port is NOT identical to the entropy flow port.

Adiabatic conditions are equivalent to closing the heat transfer port.

That does NOT prevent entropy flow.

  adiabatic ≠ isentropic

Entropy flow (and entropy production) does NOT require heat transfer.