WORK-TO-HEAT TRANSDUCTION IN THERMO-FLUID SYSTEMS

ENERGY-BASED MODELING IS BUILT ON THERMODYNAMICS
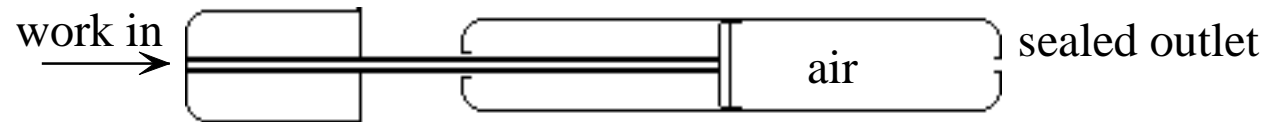
— the fundamental science of physical processes.

THERMODYNAMICS IS TO PHYSICAL SYSTEM DYNAMICS WHAT GEOMETRY IS TO MECHANICS.

WHY SHOULD WE CARE ABOUT THERMAL PHENOMENA?

— they can profoundly influence dynamic behavior.

EXAMPLE: A CLOSED BICYCLE PUMP

COMPRESSIBLE GAS (AIR) IN A CLOSED CONTAINER WITH VARIABLE VOLUME

Compress the gas and it gets hot.

When the gas is hotter than its surroundings the temperature gradient induces heat flow.

THIS IS ANOTHER FORM OF ENERGY TRANSDUCTION

— mechanical work to compress the gas is converted to heat.

— governed by the first law.

ENERGY TRANSDUCTION IS BILATERAL (IT WORKS BOTH WAYS)

Heat the gas and its pressure increases.

If the pressure moves the piston (to increase gas volume) mechanical work is done.

QUESTION:

If you do work on the gas, can you get all of it back?

(Answer: No — due to the second law.)

Under what conditions is this energy "loss" significant?

How do we integrate this behavior with our previous models?

AT LEAST TWO DIFFERENT PHENOMENA ARE INVOLVED:

energy storage

power dissipation

ENERGY STORAGE IN A COMPRESSIBLE GAS

ENERGY IS ADDED TO (OR TAKEN FROM) THE GAS IN TWO FORMS

— mechanical work or heat

MODEL THIS AS A MULTIPORT ENERGY STORAGE ELEMENT

— but of what kind?

A RELEVANT STATEMENT OF THE FIRST LAW:

U = Q – W

    U: internal energy of the gas

    Q: heat added to the gas

    W: work done by expansion of the gas

    (Notation and sign convention are standard for engineering thermodynamics.)

APPLY THIS ON AN INSTANT-BY-INSTANT BASIS USING ITS DIFFERENTIAL FORM.

    dU = dQ – dW

ON THE MECHANICAL SIDE:

dW = PdV

P: pressure

V: volume

THE GAS BEHAVES AS A CAPACITOR ON THE MECHANICAL SIDE

work is a form of energy

pressure is an effort

volume is a displacement

A COMMENT ON SIGN CONVENTION

POSITIVE WORK *COMPRESSES* THE GAS

— a negative volume change, $-dV$.

$dW = P(-dV)$

POSITIVE WORK INCREASES GAS INTERNAL ENERGY

$dU_{dQ=0} = dW = -PdV$

consistent with the usual convention.

ON THE THERMAL SIDE:

GIBBS' RELATION

(i.e., the relevant part of it)

dU = TdS – PdV

T: absolute temperature

S: entropy

THE GAS BEHAVES AS A CAPACITOR ON THE THERMAL SIDE ALSO.

heat is a form of energy

temperature behaves as an effort variable

e.g., temperature gradient induces heat flow
electric potential gradient induces charge motion
force induces mechanical motion

entropy behaves as a displacement variable

A COMMENT ON ENTROPY

A CLASSICAL DEFINITION OF ENTROPY IS

$$dS = dQ/T$$

REARRANGING YIELDS

$$dQ = TdS$$

ON THE THERMAL SIDE, HEAT ADDED IS

$$Q_1 = \int_{S_0}^{S_1} TdS + Q_0$$

Thus

$$dU_{dW = 0} = TdS$$

consistent with Gibbs' relation.

DRAWBACK

This suggests that entropy production requires heat transfer.

NOT SO

— adiabatic processes may generate entropy.
(adiabatic: no heat transfer)

THIS CLASSICAL DEFINITION IS NOT ESSENTIAL FOR OUR TREATMENT.

MULTIPORT CAPACITOR MODEL

$$\xrightarrow[\text{- dV/dt}]{\text{P}} C \xleftarrow[\text{dS/dt}]{\text{T}}$$
$$\substack{:: \\ U(S,V)}$$

ENERGY STORED IN A VARIABLE VOLUME OF COMPRESSIBLE GAS

IS A FUNCTION OF VOLUME AND ENTROPY.

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

INTERNAL ENERGY ALSO DEPENDS ON THE MASS OF GAS.

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

AS WE ASSUME A CLOSED CONTAINER, THE MASS IS CONSTANT.

— for now, mass, m, is a parameter.

(Later we will allow mass to vary, thereby adding a third port to the capacitor.)

MATHEMATICAL PROPERTIES:

Internal energy is a scalar.

U(S,V) is a scalar potential function (or field) defined on the space of displacements spanned by S and V.

$$\mathbf{q} = \begin{bmatrix} S \\ -V \end{bmatrix}$$

$U = U(\mathbf{q})$

Efforts in the two domains (thermal and mechanical) may be defined as the gradients of this potential with respect to the two displacements.

$$\mathbf{e} = \begin{bmatrix} T \\ P \end{bmatrix}$$

$$\mathbf{e} = \nabla U = \begin{bmatrix} \partial U/\partial S \\ \partial U/\partial(-V) \end{bmatrix}$$

IN TERMS OF COMPONENTS:

$$T = \nabla_S U(S, V)$$

(gradient "in the direction of" S)

$$T = \partial U / \partial S_{(V = \text{constant})}$$

$$P = \nabla_{-V} U(S, V)$$

(gradient "in the direction of" –V)

$$P = \partial U / \partial (-V) = -\partial U / \partial V_{(S = \text{constant})}$$

USING THE CHAIN RULE,

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

$$dU = TdS - PdV$$

which recapitulates Gibbs' relation.

NOTE:

A TWO-PORT CAPACITOR REQUIRES TWO CONSTITUTIVE EQUATIONS, ONE FOR EACH PORT.

$$T = T(S,V)$$

$$P = P(S,V)$$

HOWEVER, BOTH MAY BE DERIVED AS GRADIENTS OF A SINGLE ENERGY FUNCTION.

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

SYMMETRY:

THE CURL OF THE GRADIENT OF A POTENTIAL FUNCTION IS ZERO.

$$\nabla \times \nabla U(S, V) = 0$$

IN TERMS OF COMPONENTS:

$$\partial^2 U / \partial S \partial(-V) = \partial^2 U / \partial(-V) \partial S$$

(the order of differentiation doesn't matter)

REGROUPING

$$\partial(\partial U / \partial S) / \partial(-V) = \partial(\partial U / \partial(-V)) / \partial S$$

$$-\partial T / \partial V_{(S = constant)} = \partial P / \partial S_{(V = constant)}$$

— Maxwell's "reciprocity" condition.

INTRINSIC STABILITY:

DEFINE INVERSE CAPACITANCE

$$C^{-1} = \left[\frac{\partial \mathbf{e}}{\partial \mathbf{q}}\right] = \left[\frac{\partial^2 U}{\partial q_i \partial q_j}\right] = \begin{bmatrix} \partial T/\partial S & \partial T/\partial(-V) \\ \partial P/\partial S & \partial P/\partial(-V) \end{bmatrix}$$

Maxwell's reciprocity means this is a symmetric matrix.

STABILITY

determinant $C^{-1} > 0$

— a sufficient condition

ALTERNATIVE CAUSAL ASSIGNMENTS

CLASSICAL THERMODYNAMICS IDENTIFIES SEVERAL DIFFERENT FUNCTIONS RELATED TO ENERGY:
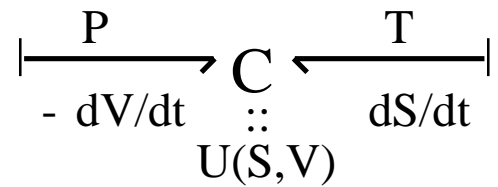
enthalpy

Helmholtz free energy

Gibbs free energy

THESE ARE NOTHING MORE THAN THE CO-ENERGY FUNCTIONS ASSOCIATED WITH DIFFERENT CAUSAL ASSIGNMENTS FOR THE TWO-PORT CAPACITOR.

INTERNAL ENERGY CORRESPONDS TO INTEGRAL CAUSALITY ON BOTH PORTS.

$$\overset{P}{\underset{-\ dV/dt}{\longrightarrow}} \quad \underset{\underset{U(S,V)}{::}}{C} \quad \overset{T}{\underset{dS/dt}{\longleftarrow}}$$

flow variable input on each port

time-integrate to find displacement

constitutive equations define output effort variables

ENTHALPY IS A LEGENDRE TRANSFORMATION OF ENERGY WITH RESPECT TO VOLUME.

$$L\{U(S,V)\} = U(S,V) - \left(\frac{\partial U}{\partial V}\right)V = H(S,P)$$

   i.e.,

$$H = U + PV$$

ALTERNATIVELY, DIFFERENTIATE THE DEFINITION OF ENTHALPY:

$$dH = dU + PdV + VdP$$
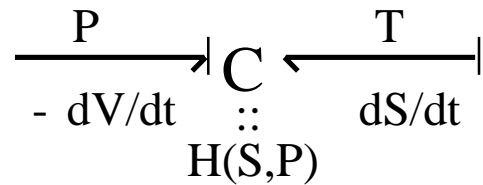
SUBSTITUTING FOR THE DIFFERENTIAL OF INTERNAL ENERGY:

$$dH = TdS - PdV + P\,dV + VdP = TdS + VdP$$

INTEGRATING YIELDS

$$H = H(S,P)$$

   as before.

ENTHALPY IS A CO-ENERGY FUNCTION CORRESPONDING TO DIFFERENTIAL CAUSALITY ON THE MECHANICAL PORT.

$$\xrightarrow[\text{- dV/dt}]{P} \;|C\; \xleftarrow[\text{dS/dt}]{T}|$$

$$\underset{H(S,P)}{::}$$

NOTE THAT

$$\partial H/\partial S_{(P\,=\,\text{constant})} = T$$

and

$$\partial H/\partial P_{(S\,=\,\text{constant})} = V$$

BECAUSE ENTHALPY IS A SCALAR FUNCTION OF S AND P, WE OBTAIN THE SYMMETRY RELATION

$$\partial T/\partial P = \partial V/\partial S$$

HELMHOLTZ FREE ENERGY IS A LEGENDRE TRANSFORMATION OF INTERNAL ENERGY WITH RESPECT TO ENTROPY.

$$L\{U(S,V)\} = U(S,V) - \left(\frac{\partial U}{\partial S}\right)S = F(T,V)$$

i.e.,

$$F = U - TS$$

AGAIN, AN ALTERNATIVE IS TO DIFFERENTIATE THE DEFINITION OF HELMHOLTZ FREE ENERGY:
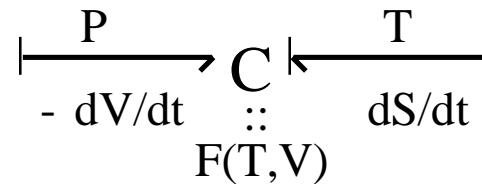
$$dF = dU - TdS - SdT$$

SUBSTITUTING FOR INTERNAL ENERGY:

$$dF = TdS - PdV - TdS - SdT = -SdT - PdV$$

INTEGRATING YIELDS

$$F = F(T,V)$$

HELMHOLTZ FREE ENERGY IS A CO-ENERGY FUNCTION CORRESPONDING TO DIFFERENTIAL CAUSALITY ON THE THERMAL PORT.

$$\begin{array}{ccc} \xrightarrow{\quad P \quad} & C & \xleftarrow{\quad T \quad} \\ -\,dV/dt & :: & dS/dt \\ & F(T,V) & \end{array}$$

NOTE THAT

$$\partial F/\partial T_{(V = \text{constant})} = -S$$

   and

$$\partial F/\partial V_{(T = \text{constant})} = -P$$

BECAUSE HELMHOLTZ FREE ENERGY IS A SCALAR FUNCTION OF T AND V, WE OBTAIN THE SYMMETRY RELATION

$$\partial S/\partial V = \partial P/\partial T$$

GIBBS FREE ENERGY IS A LEGENDRE TRANSFORMATION OF INTERNAL ENERGY WITH RESPECT TO BOTH ENTROPY AND VOLUME.

$$L\{U(S,V)\} = U(S,V) - \left(\frac{\partial U}{\partial S}\right)S - \left(\frac{\partial U}{\partial V}\right)V = G(T,P)$$

i.e.,

GIBBS FREE ENERGY

$$G = U - TS + PV$$

AGAIN, AN ALTERNATIVE IS TO DIFFERENTIATE THE DEFINITION OF GIBBS FREE ENERGY:
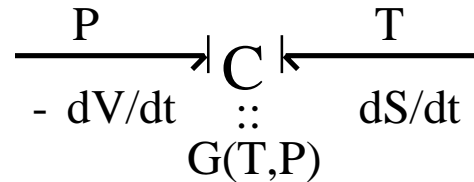
$$dG = dU - TdS - SdT + PdV + VdP$$

SUBSTITUTING FOR THE INTERNAL ENERGY:

$$dG = VdP - SdT$$

INTEGRATING YIELDS

$$G = G(T,P)$$

GIBBS FREE ENERGY CORRESPONDS TO DIFFERENTIAL CAUSALITY ON BOTH PORTS.

$$\begin{array}{ccc} P & & T \\ \xrightarrow{\hspace{2cm}} & C & \xleftarrow{\hspace{2cm}} \\ -\ dV/dt & \underset{::}{} & dS/dt \\ & G(T,P) & \end{array}$$

NOTE THAT

$$\partial G/\partial T = -S$$

and

$$\partial G/\partial P = V$$

BECAUSE GIBBS FREE ENERGY IS A SCALAR FUNCTION OF T AND P, WE OBTAIN THE SYMMETRY RELATION

$$\partial S/\partial P = -\partial V/\partial T$$

REMARKS

ONLY INTERNAL ENERGY IS A TRUE ENERGY

— it's the only one that's guaranteed conserved.

— the others are co-energies.

CO-ENERGY FUNCTIONS CAN SIMPLIFY PRACTICAL PROBLEMS

— they are widely used in classical thermodynamics.

(MORE) REMARKS

WE IMPLICITLY ASSUMED A SIMPLE THERMODYNAMIC SUBSTANCE CONTAINING ONLY ONE CHEMICAL SPECIES.

GENERALIZING TO SYSTEMS CONTAINING MULTIPLE CHEMICAL SPECIES IS STRAIGHTFORWARD.

Internal energy becomes a function of the molar quantities, η_i, of the various species.

$U = U(S,V,\eta_1,\eta_2, \ldots)$.

Treating η_i as displacements, the corresponding gradients of internal energy define chemical potentials, μ_i.

AN EXTENSION OF MAXWELL'S RECIPROCITY CONDITIONS MUST BE TRUE:

The vector field relating efforts (temperature, pressure, chemical potentials) to displacements (entropy, volume, molar quantities) must have zero curl.

FROM THIS VIEWPOINT, MUCH OF CLASSICAL THERMODYNAMICS IS THE STUDY OF PARTICULAR MULTIPORT CAPACITORS.