

## EXAMPLE: IDEAL GAS

MANY LOW-DENSITY GASES AT MODERATE PRESSURES MAY BE ADEQUATELY MODELED AS IDEAL GASES.

Are the ideal gas model equations compatible with models of dynamics in other domains?

AN IDEAL GAS IS OFTEN CHARACTERIZED BY THE RELATION

$$PV = mRT$$

P: (absolute) pressure

V: volume

m: mass

R: gas constant

T: absolute temperature

IN THE FORM

$$PV = mRT$$

THE IDEAL GAS EQUATION IS A RELATION BETWEEN VARIABLES WITH NO CAUSAL MEANING.

Used as an assignment operator relating input to output

$$PV := mRT$$

it would imply that both effort,  $P$ , and displacement,  $V$ , on the mechanical power port are outputs.

That is physically meaningless.

Similarly, the form

$$T := PV/mR$$

would imply that both effort,  $P$ , and displacement,  $V$ , on the mechanical power port are inputs.

That is also physically meaningless.

THE IDEAL GAS EQUATION MAY BE RE-ARRANGED INTO TWO FORMS THAT ADMIT A MEANINGFUL CAUSAL INTERPRETATION.

ONE FORM IS COMPATIBLE WITH THE CAUSAL ASSIGNMENT ASSOCIATED WITH THE HELMHOLTZ FUNCTION.

the “Helmholtz form”

$$P := mRT/V$$

THE OTHER FORM IS COMPATIBLE WITH THE CAUSAL ASSIGNMENT ASSOCIATED WITH THE GIBBS FUNCTION.

the “Gibbs form”

$$V := mRT/P$$

## AN IMPORTANT POINT

THE RELATION  $PV = MRT$  DOES NOT COMPLETELY CHARACTERIZE THE GAS.

We model the interacting thermal and mechanical effects using a two-port capacitor.

A two-port capacitor needs two constitutive equations.

THE SECOND IS USUALLY OBTAINED BY ASSUMING A PARTICULAR RELATION BETWEEN INTERNAL ENERGY AND TEMPERATURE.

Common practice:

assume  $c_v$  is constant.

$c_v$ : specific heat at constant volume

WHAT'S "SPECIFIC HEAT"?

AND HOW DOES IT DETERMINE THE RELATION BETWEEN INTERNAL ENERGY AND TEMPERATURE?

"SPECIFIC" IN THIS CONTEXT MEANS "PER UNIT MASS".

## EXTENSIVE VARIABLES:

ALL QUANTITIES THAT VARY WITH THE AMOUNT (OR EXTENT) OF A SUBSTANCE (ALL OTHER FACTORS BEING EQUAL) ARE *EXTENSIVE VARIABLES* (OR PROPERTIES).

mass

volume

(total) entropy

(total) internal energy

(total) enthalpy

etc.

EVERY *EXTENSIVE* VARIABLE (PROPERTY) HAS A “SPECIFIC” COUNTERPART.

specific internal energy,  $u$

$$u = U/m$$

internal energy per unit mass

specific entropy,  $s$

$$s = S/m$$

entropy per unit mass

specific volume,  $v$

$$v = V/m$$

volume per unit mass

the inverse of density,  $\rho$

$$v = 1/\rho$$

(Note: “specific mass” -- mass per unit mass -- has dubious value and usually is not defined.)

## EXTENSIVE VS. INTENSIVE

INTENSIVE VARIABLES:

ALL QUANTITIES THAT DO NOT VARY WITH THE AMOUNT (OR EXTENT) OF A SUBSTANCE (ALL OTHER FACTORS BEING EQUAL) ARE *INTENSIVE* VARIABLES (OR PROPERTIES).

pressure

temperature

chemical potential

etc.

THUS WE DO NOT DEFINE “SPECIFIC” INTENSIVE VARIABLES.

– “temperature per unit mass” or “pressure per unit mass” would have no particular meaning.

THE GIBBS RELATION (A DIFFERENTIAL FORM OF THE FIRST LAW) MAY BE WRITTEN IN TERMS OF SPECIFIC VARIABLES.

$$dU = TdS - PdV$$

PER UNIT MASS:

$$du = Tds - Pdv$$

IF VOLUME REMAINS CONSTANT, (SPECIFIC) HEAT FLOW CHANGES (SPECIFIC) INTERNAL ENERGY.

$$dq = dQ/m$$

$$dq = Tds = du|_{dv=0}$$



DEFINE *SPECIFIC HEAT AT CONSTANT VOLUME*

$$c_v = \partial q / \partial T|_{dv=0}$$

THUS, AT CONSTANT VOLUME

$$dq|_{dv=0} = c_v dT = du|_{dv=0}$$

HENCE

$$c_v = \partial u / \partial T|_v$$

## THE OTHER IDEAL GAS EQUATION

IN GENERAL  $C_V$  MAY VARY WITH THE STATE OF THE GAS.

TO OBTAIN A SECOND CONSTITUTIVE EQUATION FOR THE IDEAL GAS WE FOLLOW COMMON PRACTICE

— ASSUME  $C_V$  IS CONSTANT.

Integrating yields (specific) internal energy as a function of temperature alone

$$u - u_o = c_v(T - T_o)$$

Subscript o denotes a reference state.

Usually,  $u_o = 0$ , i.e.,  $u = 0$  when  $T = T_o$ .

GIVEN THIS RELATION BETWEEN SPECIFIC INTERNAL ENERGY AND TEMPERATURE, WE MAY RESTATE THE FIRST LAW AS

$$c_v dT = T ds - P dv$$

Rearranging

$$ds = c_v dT/T + P dv/T$$

USING SPECIFIC QUANTITIES THE IDEAL GAS EQUATION IS

$$Pv = RT$$

Substituting

$$ds = c_v dT/T + R dv/v$$

$$ds = c_v d \ln(T) + R d \ln(v)$$

Integrating

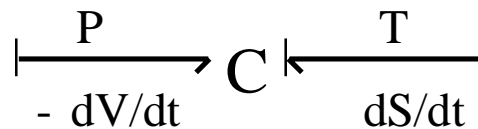
$$s - s_0 = c_v \ln T/T_0 + R \ln v/v_0$$

THIS IS THE SECOND CONSTITUTIVE EQUATION FOR THE IDEAL GAS.

THIS EQUATION IS IN THE CAUSAL FORM ASSOCIATED WITH THE HELMHOLTZ FUNCTION,  
 $s := s(T, V)$

THE CORRESPONDING CAUSAL FORM FOR THE OTHER CONSTITUTIVE EQUATION IS  $P := P(T, V)$

The Helmholtz function is the co-energy corresponding to integral causality on the mechanical port and differential causality on the thermal port.



CAUTION!

**Total** power flow requires **total** entropy and volume, **not** specific entropy and volume (except in the unlikely case where we have unit mass of gas.)

Thus one causal form of the two constitutive equations for the two-port capacitor model of the ideal gas is

$$S := mc_v \ln T/T_0 + mR \ln V/V_0 + S_0$$

$$P := mRT/V$$

THE FORM CORRESPONDING TO INTEGRAL CAUSALITY ON BOTH PORTS REQUIRES PRESSURE, TEMPERATURE AND INTERNAL ENERGY AS FUNCTIONS OF ENTROPY AND VOLUME.

IT COULD BE OBTAINED BY MANIPULATING  $S = S(T, V)$  ABOVE INTO THE FORM  $T = T(S, V)$ , SUBSTITUTING TO FIND  $P = P(S, V)$  AND INTEGRATING TO FIND  $U = U(S, V)$ .

IT MAY ALSO BE FOUND AS FOLLOWS, STARTING FROM THE FIRST LAW.

$$du = Tds - Pdv$$

ASSUME  $c_v$  IS CONSTANT AND USE THE IDEAL GAS EQUATION.

$$c_v dT = Tds - (RT/v)dv$$

REARRANGE WITH ENTROPY AND VOLUME ON THE “INPUT” SIDE.

$$\frac{dT}{T} = \frac{ds}{c_v} - \frac{R}{c_v} \frac{dv}{v}$$

$$d \ln(T) = \frac{ds}{c_v} - \frac{R}{c_v} d \ln(v)$$

Integrate

$$\ln\left(\frac{T}{T_0}\right) = \frac{s - s_0}{c_v} - \frac{R}{c_v} \ln\left(\frac{v}{v_0}\right)$$

EXPONENTIATE

$$\left(\frac{T}{T_0}\right) = \left(\frac{v}{v_0}\right)^{-\frac{R}{c_v}} \exp\left(\frac{s - s_0}{c_v}\right)$$

This is in the required form  $T = T(s,v)$ .

TO FIND THE PRESSURE EQUATION, USE THE IDEAL GAS EQUATION

$$\frac{P}{P_0} = \frac{T}{T_0} \frac{v_0}{v}$$

Substitute

$$\left(\frac{P}{P_0}\right) = \left(\frac{v}{v_0}\right)^{-\left(\frac{R}{c_v} + 1\right)} \exp\left(\frac{s - s_0}{c_v}\right)$$

This is in the required form  $P = P(s,v)$ .

TO FIND  $u = u(S, v)$  REARRANGE THE EXPRESSION FOR INTERNAL ENERGY

$$u - u_0 = c_v(T - T_0)$$

$$u = c_v T_0 \left( \frac{T}{T_0} - 1 \right) + u_0$$

and substitute

$$u = c_v T_0 \left[ \left( \frac{v}{v_0} \right)^{-\frac{R}{c_v}} \exp\left( \frac{s - s_0}{c_v} \right) - 1 \right] + u_0$$



GIVEN THE COMPLEXITY OF THESE EQUATIONS IT IS WISE TO CHECK IF THEY ARE CONSISTENT.

$$T = \frac{\partial u}{\partial s} = c_v T_o \left( \frac{v}{v_o} \right)^{-\frac{R}{c_v}} \exp\left( \frac{s - s_o}{c_v} \right) \frac{1}{c_v}$$

–OK

$$-P = \frac{\partial u}{\partial v} = c_v T_o \left[ -\frac{R}{c_v} \frac{1}{v_o} \left( \frac{v}{v_o} \right)^{-\left( \frac{R}{c_v} + 1 \right)} \exp\left( \frac{s - s_o}{c_v} \right) \right]$$

substitute  $RT_o = P_o v_o$

$$P = P_o \left( \frac{v}{v_o} \right)^{-\left( \frac{R}{c_v} + 1 \right)} \exp\left( \frac{s - s_o}{c_v} \right)$$

–OK

WE MAY ALSO CHECK FOR SYMMETRY, I.E. THAT MAXWELL'S RECIPROCITY CONDITION IS SATISFIED.

$$\frac{\partial P}{\partial s} = P_0 \left( \frac{v}{v_0} \right)^{-\left( \frac{R}{c_v} + 1 \right)} \exp\left( \frac{s - s_0}{c_v} \right) \frac{1}{c_v}$$

$$\frac{\partial T}{\partial(-v)} = T_0 \exp\left( \frac{s - s_0}{c_v} \right) \left( \frac{v}{v_0} \right)^{-\left( \frac{R}{c_v} + 1 \right)} \frac{R}{c_v} \frac{1}{v_0}$$

Rearranging and using  $RT_0 = P_0 v_0$  we see that

$$\frac{\partial P}{\partial s} = \frac{\partial T}{\partial(-v)}$$

as required.

WE MAY FURTHER CHECK FOR INTRINSIC STABILITY

– compute the inverse capacitance.

$$C^{-1} = \begin{bmatrix} \partial T / \partial S & \partial T / \partial (-V) \\ \partial P / \partial S & \partial P / \partial (-V) \end{bmatrix}$$

The off-diagonal terms were computed above. The diagonal terms are

$$\frac{\partial T}{\partial S} = T_0 \left( \frac{v}{v_0} \right)^{-\frac{R}{c_v}} \exp\left( \frac{s - s_0}{c_v} \right) \frac{1}{c_v}$$

$$\frac{\partial P}{\partial (-v)} = - \left[ - \left( \frac{R}{c_v} + 1 \right) \left( \frac{v}{v_0} \right)^{-\left( \frac{R}{c_v} + 2 \right)} \frac{1}{v_0} P_0 \exp\left( \frac{s - s_0}{c_v} \right) \right]$$

Using  $RT_0 = P_0 v_0$  to identify factors common to all terms yields

$$C^{-1} = \frac{R T_0}{c_v} \left( \frac{v}{v_0} \right)^{-\frac{R}{c_v}} \exp\left( \frac{s - s_0}{c_v} \right) \begin{bmatrix} 1/R & 1/v \\ 1/v & \frac{R + c_v}{v^2} \end{bmatrix}$$

INTRINSIC STABILITY IS ESTABLISHED IF THE DETERMINANT OF  $C^{-1}$  IS POSITIVE.

The common factor is always positive.

The determinant is also always positive.

$$\frac{R + c_v}{R v^2} - \frac{1}{v^2} = \frac{c_v}{R v^2} > 0$$

THUS THE IDEAL GAS MODEL IS INTRINSICALLY STABLE

– which makes physical sense.

FINALLY, REMEMBER THAT TOTAL POWER FLOW REQUIRES EQUATIONS IN TERMS OF TOTAL ENTROPY, VOLUME AND INTERNAL ENERGY.

$$\left(\frac{T}{T_0}\right) = \left(\frac{V}{V_0}\right)^{-\frac{R}{c_v}} \exp\left(\frac{S - S_0}{mc_v}\right)$$

$$\left(\frac{P}{P_0}\right) = \left(\frac{V}{V_0}\right)^{-\left(\frac{R}{c_v} + 1\right)} \exp\left(\frac{S - S_0}{mc_v}\right)$$

$$U = mc_v T_0 \left[ \left(\frac{V}{V_0}\right)^{-\frac{R}{c_v}} \exp\left(\frac{S - S_0}{mc_v}\right) - 1 \right] + U_0$$

$$\begin{array}{c} \overline{\text{P}} \\ \leftarrow \text{C} \rightarrow \\ \text{- dV/dt} \quad \text{dS/dt} \end{array}$$

## DISCUSSION

TWO SIMPLE EQUATIONS CHARACTERIZE THE IDEAL GAS:

$$Pv = RT$$

$$c_v = \text{constant}$$

THE END RESULT OF OUR TEDIOUS MANIPULATIONS SEEMS MERELY TO CONVERT THEM INTO THE COMPLICATED EXPRESSIONS ABOVE.

Why bother?

What have we gained?

Why does it matter what causal form we use for the ideal gas equations?

THE DISARMING SIMPLICITY OF  $Pv = RT$  HIDES AN ASSUMPTION THAT TEMPERATURE IS AN INPUT VARIABLE.

The meaningful causal forms of this equation are

$$P := RT/v$$

$$v := RT/P$$

This *implicit* assumption about the thermal boundary conditions may not always be applicable.

It is not compatible with the typical situation involving work-to-heat transduction.

For example, in a bicycle-pump the trapped air temperature varies in response to mechanical work done on the gas.

Heat transfer occurs when trapped air temperature differs from environmental temperature.

Trapped air temperature is not determined by the environmental temperature.

THE FIRST REASON TO MANIPULATE THE IDEAL GAS EQUATIONS IS BECAUSE A COMPUTABLE STATE-DETERMINED REPRESENTATION MAY *REQUIRE* THESE PARTICULAR FORMS.

A well-posed computational model requires equations structured so that each of its elements has properly-defined inputs and outputs.

These computational constraints depend upon interactions between connected elements.

They are revealed by causal analysis.

A SECOND REASON IS THAT WE MAY GAIN INSIGHT — THE MAIN PURPOSE OF MODELING.

For example, the van der Waals equation is another common model of simple gases.

Analysis similar to the above reveals a constraint on the model parameter values to ensure intrinsic stability.



CHANGING THE BOUNDARY ON ONE PORT OF A TWO-PORT ELEMENT MAY CHANGE THE APPARENT BEHAVIOR ON THE OTHER PORT.

If a compressible gas is maintained at constant volume it has a heat capacity characterized by  $c_v$ , the specific heat at constant volume.

If pressure is maintained constant, (specific) heat flow may change both (specific) internal energy and (specific) volume.

DEFINE *SPECIFIC HEAT AT CONSTANT PRESSURE*

$$c_p = \partial q / \partial T |_{dP=0}$$

thus

$$dq|_{dP=0} = c_p dT$$

FROM GIBBS' RELATION

$$dq = Tds = du + Pdv$$

USING

$$d(Pv) = Pdv + vdP$$

$$\text{at constant pressure } d(Pv)|_{dP=0} = Pdv$$

$$\text{and } dq = Tds = du|_{dP=0} + d(Pv)|_{dP=0} = dh|_{dP=0}$$

where  $h = u + Pv$  is specific enthalpy

HENCE

$$c_p = \partial h / \partial T|_P$$

USING THE IDEAL GAS EQUATION  $Pv = RT$  AND ASSUMING CONSTANT PRESSURE

$$Pv - Pv_0 = RT - RT_0$$

Assuming constant  $c_v$  as above

$$u - u_0 = c_v T - c_v T_0$$

Combining

$$h - h_0 = (u + Pv) - (u_0 + Pv_0) = c_v T - c_v T_0 + RT - RT_0$$

$$h - h_0 = (c_v + R)(T - T_0)$$

Thus

$$c_p = c_v + R$$

HENCE

$c_p$  is also constant for an ideal gas.

enthalpy, like internal energy, depends only on temperature.

The apparent heat capacity at constant pressure is always greater than at constant volume.

THIS MAKES PHYSICAL SENSE:

more heat is required to expand the gas against the constant pressure as well as raise its temperature.