

Thermodynamic Property Relations

Reading Material: Moran & Shapiro, Chapter 11, Bejan, pp 171-188.

Introduction

- In Thermodynamics I & II, we discussed the meaning of various fluid properties and how to use them in solving thermodynamics problems. Some properties (T, P, V, m) can be measured directly, but others (u, h, s) must be derived. The purpose of this chapter is to develop the tools necessary to derive the unknown quantities from the measureable ones—i.e. thermodynamic property relations.

Mathematical Representation

- The states of simple compressible substances are normally specified by two independent variables, and other properties are written as a function of those two. In other words, for three properties x, y, and z, we can write

$$z = f(x, y)$$

- From calculus, we know that we can write a change in the variable z as

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad 2.2.1$$

where the subscripts denote variables held constant, or

$$dz = M dx + N dy \quad 2.2.2$$

where $M = \left(\frac{\partial z}{\partial x} \right)_y$, and $N = \left(\frac{\partial z}{\partial y} \right)_x$. In thermodynamics, the derivatives M and N represent properties of the substance which can be measured or derived.

- If we are evaluating a process where x=constant, then

$$dz = N dy$$

- For example, if we choose to express pressure as $P = P(T, v)$ then we have

$$dP = \left(\frac{\partial P}{\partial T} \right)_v dT + \left(\frac{\partial P}{\partial v} \right)_T dv$$

and if we evaluate the change in pressure during a constant temperature process, then we have

$$dP = \left(\frac{\partial P}{\partial v} \right)_T dv$$

EXAMPLE: Internal Energy

- Let $z=u$, $x=s$, and $y=v$. With these choices, we have

$$du = \left(\frac{\partial u}{\partial s} \right)_v ds + \left(\frac{\partial u}{\partial v} \right)_s dv$$

which gives changes in internal energy with changes in entropy (heat transfer), and changes in volume (work).

- Note that if we compare this to the equation

$$du = T ds - P dv$$

we can observe that

$$\left(\frac{\partial u}{\partial s} \right)_v = T \quad 2.2.3$$

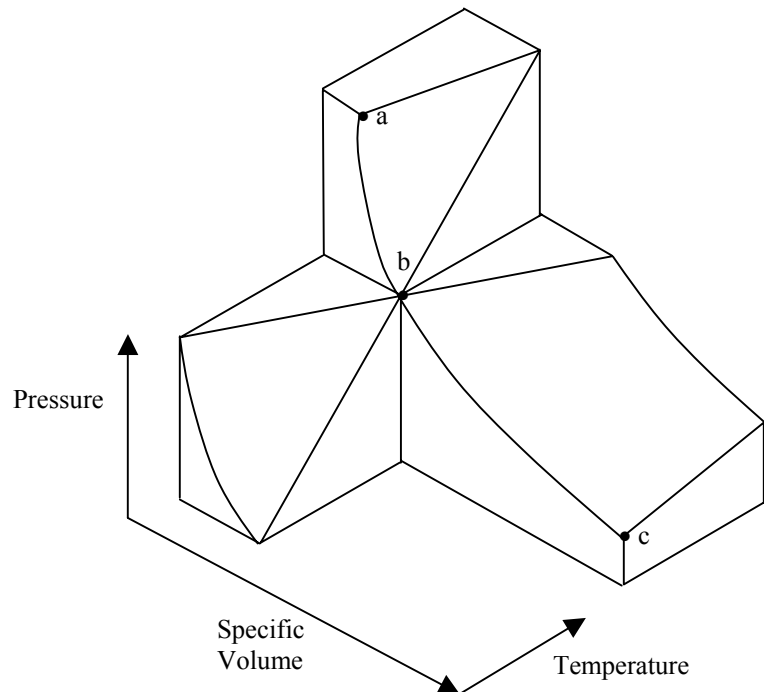
and

$$\left(\frac{\partial u}{\partial v} \right)_s = -P \quad 2.2.4$$

- These relations will prove to be useful later when we need to condense expressions involving derivatives to known properties.

We can represent the relationship between properties $z = f(x, y)$ graphically as well as mathematically. If we choose $P = P(T, v)$, for example, then we have a diagram as shown. In this figure, the $P = P(T, v)$ surface has been "cut" by several constant P , T , and v planes. The property derivatives are represented by the slopes of the surface in various directions. For example, the curve abc represents an isotherm, and at the point 'b', we define $\left(\frac{\partial P}{\partial v} \right)_T$ as the slope

$\frac{\partial P}{\partial v}$ along the isotherm.



Some Mathematical Theorems

- If we write $dz = Mdx + Ndy$, then the following important relations can be derived (see homework problem):

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

- The two relations above were based on $z = f(x, y)$, which represents a dependence of one variable on two others. We can also derive some useful relations among groups of four variables, with two still being independent (e.g. P, v, T, and s). Let w, x, y, and z be our variables, and start with the relations $x = f(w, y)$, and $y = f(w, z)$.

Writing the differentials, we have

$$dx = \left(\frac{\partial x}{\partial w}\right)_y dw + \left(\frac{\partial x}{\partial y}\right)_w dy \quad dy = \left(\frac{\partial y}{\partial w}\right)_z dw + \left(\frac{\partial y}{\partial z}\right)_w dz$$

Now, substitute dy from the second equation into the first,

$$dx = \left[\left(\frac{\partial x}{\partial w}\right)_y + \left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial w}\right)_z \right] dw + \left[\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w \right] dz$$

Compare this to the the differential for $x = f(w, z)$:

$$dx = \left(\frac{\partial x}{\partial w}\right)_z dw + \left(\frac{\partial x}{\partial z}\right)_w dz$$

Equating the coefficients on dw yields:

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial w}\right)_y + \left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial w}\right)_z$$

and equating the coefficients on dz gives

$$\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w \left(\frac{\partial z}{\partial x}\right)_w = 1$$

Now we have four general equations relating derivatives of thermodynamic properties:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad 2.3.1$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad 2.3.2$$

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial w}\right)_y + \left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial w}\right)_z \quad 2.3.3$$

$$\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w \left(\frac{\partial z}{\partial x}\right)_w = 1 \quad 2.3.4$$

EXAMPLE: Sound Speed

- By definition, $c^2 = \left(\frac{\partial P}{\partial \rho}\right)_s$. Let's write it in terms of P , ρ , and u instead. Using equation 2.3.3 above and letting $x=P$, $w=\rho$, $z=s$, and $y=u$, we have

$$\left(\frac{\partial P}{\partial \rho}\right)_s = \left(\frac{\partial P}{\partial \rho}\right)_u + \left(\frac{\partial P}{\partial u}\right)_\rho \left(\frac{\partial u}{\partial \rho}\right)_s$$

Also,

$$\left(\frac{\partial u}{\partial \rho}\right)_s = \left(\frac{\partial u}{\partial v}\right)_s \left(\frac{\partial v}{\partial \rho}\right)_s = \left(\frac{\partial u}{\partial v}\right)_s \left(\frac{-1}{\rho^2}\right)$$

- Using the relation $\left(\frac{\partial u}{\partial v}\right)_s = -P$, (2.2.4), we have

$$\left(\frac{\partial u}{\partial \rho}\right)_s = \frac{P}{\rho^2}$$

and finally,

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_u + \frac{P}{\rho^2} \left(\frac{\partial P}{\partial u}\right)_\rho$$

Special Case: Ideal Gas

- For an ideal gas, $P = \rho RT$. If the specific heats are constant, then we also have $du = C_v dT$. With these relations, we have

$$\begin{aligned}
c^2 &= \left(\frac{\partial P}{\partial \rho} \right)_u + \frac{P}{\rho^2} \left(\frac{\partial P}{\partial u} \right)_\rho \\
&= \left(\frac{\partial P}{\partial \rho} \right)_T + \frac{P}{\rho^2 C_V} \left(\frac{\partial P}{\partial T} \right)_\rho \\
&= RT + \frac{RP}{\rho C_V} = RT \left(1 + \frac{R}{C_V} \right)
\end{aligned}$$

- Using $R = C_p - C_V$, and $\gamma \equiv \frac{C_p}{C_V}$, we have

$$\boxed{c^2 = \gamma RT}$$

Maxwell's Relations

- Pressure, volume, temperature, and entropy could be considered the four most basic thermodynamic state parameters, in the sense that work interactions are related to pressure and volume ($\delta w_{rev} = Pdv$), and heat interactions are related to temperature and entropy ($\delta q_{rev} = Tds$). Also, all four can be fixed experimentally. Using a set of isobars, isochors, isotherms and adiabats on a Pv diagram, James Clerk Maxwell (1831-1879) derived a set of equations relating derivatives of these four properties. Among other things, these useful relations can be used to relate changes in entropy to measurable properties.
- Maxwell's relations can be derived using calculus and the four energy functions internal energy (u), enthalpy ($h \equiv u + Pv$), Helmholtz free energy ($f \equiv u - Ts$), and Gibbs free energy ($g \equiv h - Ts$), as follows:

→ An energy balance for a simple, compressible substance can be written

$$du = Tds - Pdv$$

Combining this equation with the definitions of h, f, and g, yields:

$$dh = Tds + vdP$$

$$df = -Pdv - sdT$$

$$dg = vdP - sdT$$

Now we have four equations in the form of $dz = Mdx + Ndy$, and we can use 2.3.1 to relate derivatives of M and N:

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \quad \text{MR \#1}$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \quad \text{MR \#2}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad \text{MR \#3}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \quad \text{MR \#4}$$

Keypoints:

- P, T, and v can be measured, and s can be derived from the Maxwell Relations.
- The LHS of #3 and #4 come directly from measurements, and could also be calculated given an equation of state.

EXAMPLE: Evaluation of Entropy

- Let's take a closer look at how the Maxwell Relations help in the evaluation of entropy. In other words, let's express changes in entropy in terms of the measurable properties P, v, and T. (We will also need C_p and C_v .) We have three possible pairs of independent variables to choose from: (P,v), (P,T), and (v,T). Each pair has two partial derivatives of s associated with it, for a total of six:

$$\left(\frac{\partial s}{\partial P}\right)_v, \left(\frac{\partial s}{\partial v}\right)_P, \left(\frac{\partial s}{\partial P}\right)_T, \left(\frac{\partial s}{\partial T}\right)_P, \left(\frac{\partial s}{\partial v}\right)_T, \left(\frac{\partial s}{\partial T}\right)_v$$

- If we can express each of these derivatives in terms of P, v, T, and other measurable properties, we will have complete information on the entropy of a pure substance.
- The 3rd and 5th come directly from MR #4 and MR #3:

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

- The 6th and 4th can be evaluated using 2.2.3 and 2.2.4:

$$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v \left(\frac{\partial T}{\partial s}\right)_v = C_V \left(\frac{\partial T}{\partial s}\right)_v$$

$$\left(\frac{\partial u}{\partial s}\right)_v = T$$

$$\left(\frac{\partial T}{\partial s}\right)_v = \frac{T}{C_V}$$

Similarly, using enthalpy,

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_P}{T}$$

- The two remaining derivatives can be evaluated using the previous two relations:

$$\left(\frac{\partial s}{\partial P}\right)_v = \left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial T}{\partial P}\right)_v = \frac{C_V}{T} \left(\frac{\partial T}{\partial P}\right)_v$$

$$\left(\frac{\partial s}{\partial v}\right)_P = \left(\frac{\partial s}{\partial T}\right)_P \left(\frac{\partial T}{\partial v}\right)_P = \frac{C_P}{T} \left(\frac{\partial T}{\partial v}\right)_P$$

Keypoints:

- All partial derivatives of entropy have been expressed in terms of P, T, v, and C_P, C_V.

EXAMPLE: Derivation of Joule's Law

- Previously, we discussed Joule's free-expansion experiment, concluding for an ideal gas:

$$u = u(T)$$

$$\left(\frac{\partial u}{\partial v}\right)_T = 0$$

- Now let's use what we have developed about thermodynamic properties to show this is true from a more fundamental approach. To do this, let's express

$$\left(\frac{\partial u}{\partial v}\right)_T$$

in terms of P, v, and T. Since we know an equation of state for ideal gasses (Pv=RT), we can also use derivatives among P, v, and T.

- Using 2.3.3 and selecting (v,T) as independent variables, and (u,s) as dependent, we have

$$\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial u}{\partial v}\right)_s + \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial v}\right)_T$$

- We can express the partials on the RHS as

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad (2.2.3)$$

$$\left(\frac{\partial u}{\partial v}\right)_s = -P \quad (2.2.4)$$

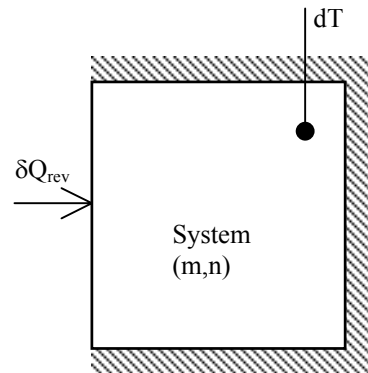
$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad (\text{MR \#3})$$

- Substituting these equations into the RHS,

$$\left(\frac{\partial u}{\partial v}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_v = -P + T \frac{R}{v} = -P + P = 0$$

Measurable Derivatives

- By conducting experiments in which some property is fixed (e.g. use a constant volume vessel, or an insulated container), and measuring the change in some other property (P, T, or v) as heat is added or work is done, one obtains values for certain derivatives. These properties, like Maxwell's relations, can be used to relate unknown properties to known properties.
- In the following, recall that we are taking all processes to be reversible. Also note that there is a summary of derivatives on page 24.



Constant Volume Heating (no work)

- Measure δQ and dT , and define

$$C_V = \frac{\delta Q}{m dT} \Big|_V$$

Since there is no work, $dU = \delta Q$. The definition of entropy gives $\delta Q_{\text{rev}} = T dS$, and we have

$$C_V = \left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$$

Special cases:

Often, $C_V = C_V(T)$ (e.g. ideal gas, incompressible substance), or $C_V = \text{constant}$. (perfect gas)

EXAMPLE: C_V for an Ideal Gas

- In general, for any pure substance, we can write u as a function of two independent properties, such as

$$u = u(T, v)$$

and it follows that

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

- Introducing our definition $C_V = \left(\frac{\partial u}{\partial T} \right)_v$ gives

$$du = C_V dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

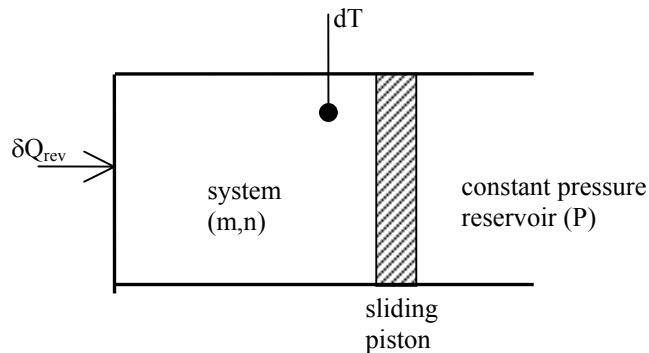
- In general, we must realize that $C_V = f(T, v)$. However, in the case of an ideal gas, we know from Joule's free expansion experiment that $\left(\frac{\partial u}{\partial v} \right)_T = 0$, so that

$$du = C_V dT$$

- Since u is a function only of temperature for an ideal gas, it follows that C_V also must be a function of temperature for an ideal gas:

$$C_V = C_V(T) \quad \text{for an ideal gas}$$

Constant Pressure Heating



Similar to C_V analysis, measure δQ and dT . Since a change in enthalpy at constant pressure is equal to the heat addition, we have, in an analogous manner to the C_V analysis,

$$C_P = \left(\frac{\partial h}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P$$

- In addition, since the fluid is now also expanding, this configuration yields the "volumetric expansivity", or "coefficient of thermal expansion", which is important in buoyancy-induced convection:

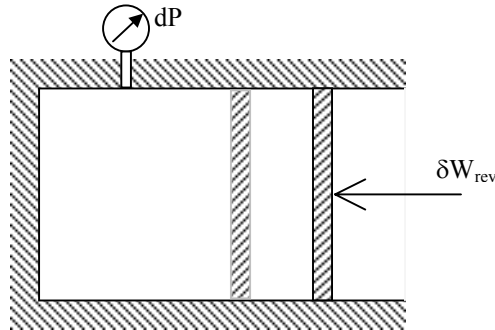
$$\beta \equiv \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$$

Special cases:

$$\beta = \frac{1}{T} \quad \text{Ideal gas}$$

$$\beta = 0 \quad \text{Incompressible substance}$$

Adiabatic Volume Change (no heat transfer)



- The "isentropic expansion coefficient" k relates pressure and volume during an adiabatic (and reversible) expansion, and is defined as

$$k \equiv -\frac{v}{P} \left(\frac{\partial P}{\partial v} \right)_s$$

This gives the fractional change in pressure for a fractional change in volume during an isentropic process, and is unitless.

- Note that we can use k to express the P - v path along an isentrope as follows:
- Let $s = s(P, v)$ and write

$$ds = \left(\frac{\partial s}{\partial P} \right)_v dP + \left(\frac{\partial s}{\partial v} \right)_P dv$$

- $ds = 0$, and Maxwell's relations can be used to convert the derivatives

$$0 = -\left(\frac{\partial v}{\partial T} \right)_s dP + \left(\frac{\partial P}{\partial T} \right)_s dv$$

- Rearranging,

$$0 = dP - \left(\frac{\partial P}{\partial T} \right)_s \left(\frac{\partial T}{\partial v} \right)_s dv$$

$$0 = dP - \left(\frac{\partial P}{\partial v} \right)_s dv$$

$$0 = \frac{dP}{P} - \frac{1}{P} \frac{v}{v} \left(\frac{\partial P}{\partial v} \right)_s dv$$

$$0 = \frac{dP}{P} + k \frac{dv}{v}$$

- In general, $k = k(T, P)$, but if we consider a region where k can be considered locally constant, then we have

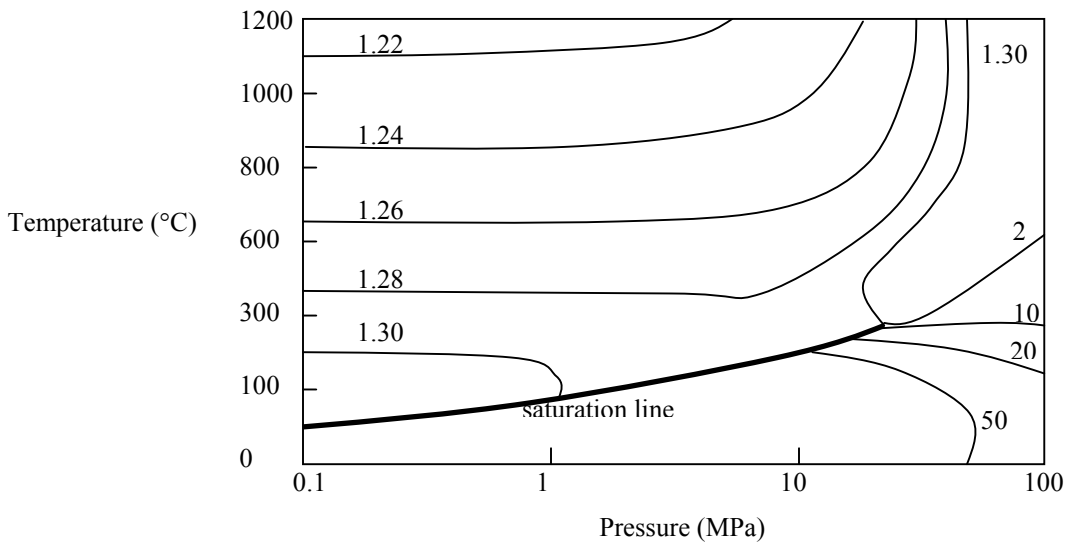
$$Pv^k = \text{constant}$$

- In Thermo I, we discussed a relation similar to this for isentropic processes of an ideal gas, where we used $k = \frac{C_P}{C_V}$. Now we see that the relationship is true in general for isentropic processes if k is the isentropic expansion coefficient. Furthermore, we can write (see homework problem):

$$k = -\frac{v}{P} \left(\frac{\partial P}{\partial v} \right)_T \frac{C_P}{C_V}$$

which is simply C_P/C_V for an ideal gas, showing that the more general case reduces to what we already know for an ideal gas.

- The following sketch shows values of k for steam in the liquid, vapor, and supercritical regions. Notice that in the ideal gas region (low pressures), k becomes a function only of temperature.



Special cases:

$$k = \frac{C_P}{C_V} \quad \text{Ideal gas}$$

$$k = \infty \quad \text{Incompressible substance}$$

EXAMPLE: Sound Velocity in H₂O

- By definition, $c^2 = \left. \frac{\partial P}{\partial \rho} \right|_s$
- We can rewrite this as

$$c^2 = \left. \frac{\partial P}{\partial \rho} \right|_s = \left. \frac{\partial P}{\partial v} \right|_s \left. \frac{\partial v}{\partial \rho} \right|_s = \left. \frac{\partial P}{\partial v} \right|_s \left. \frac{\partial (1/\rho)}{\partial \rho} \right|_s$$

$$= \left. \frac{\partial P}{\partial v} \right|_s \left\{ (-1) \frac{1}{\rho^2} \left. \frac{\partial \rho}{\partial \rho} \right|_s \right\}_s$$

or

$$c^2 = -v^2 \left. \frac{\partial P}{\partial v} \right|_s$$

- We can write this strictly in terms of properties as

$$c^2 = -v^2 \left. \frac{\partial P}{\partial v} \right|_s = vP \left(-\frac{v}{P} \left. \frac{\partial P}{\partial v} \right|_s \right)$$

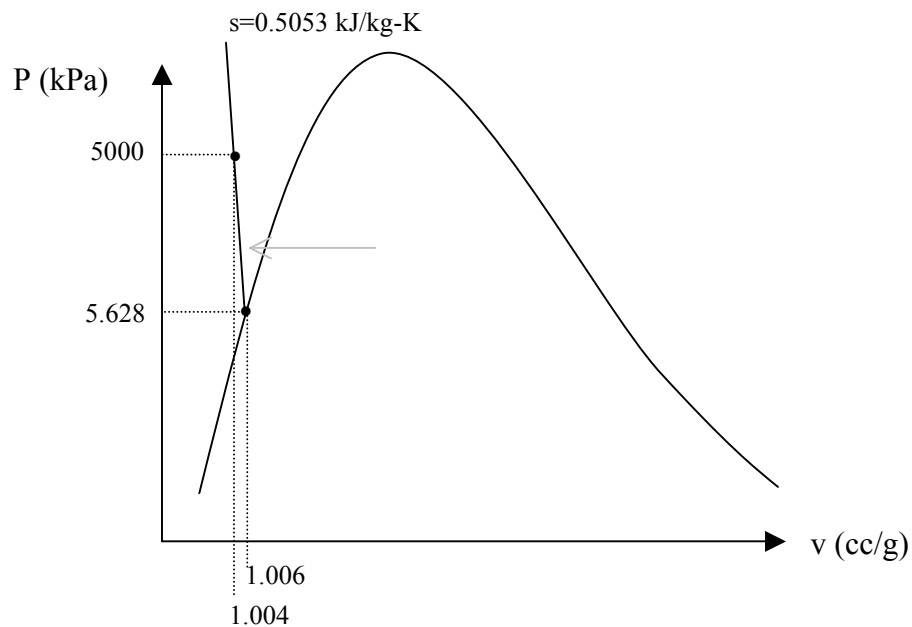
$$c^2 = vPk = vB_s = \frac{v}{\beta_s}$$

where

k = isentropic expansion coefficient

B_s = adiabatic bulk modulus

β_s = isentropic compressibility



- consider H₂O at 35°C:
- estimate β_s from steam table data...
First look up saturated liquid data at 35°C:
P=5.628kPa
s_f=0.5053 kJ/kg-K

$$v_f = 0.001006 \text{ m}^3/\text{kg}$$

Now look up compressed liquid at 5 MPa at the same entropy:

$$v = 0.001004$$

Thus

$$\beta_s = -\frac{1}{v} \frac{\partial v}{\partial P} \bigg|_s \approx -\frac{1}{v_{ave}} \frac{\Delta v}{\Delta P} \bigg|_s = 0.398 \times 10^{-3} (\text{MPa})^{-1}$$

- Finally

$$c = \sqrt{v/\beta_s} \approx 1588 \text{ m/s}$$

EXAMPLE: Sound Velocity in Ideal Gas

- Previously, we showed

$$c^2 = -v^2 \frac{\partial P}{\partial v} \bigg|_s = vPk$$

where

$$k = -\frac{v}{P} \frac{\partial P}{\partial v} \bigg|_s = -\frac{v}{P} \frac{\partial P}{\partial v} \bigg|_T \frac{C_p}{C_v}$$

- For an ideal gas,

$$k = \frac{C_p}{C_v} \equiv \gamma$$

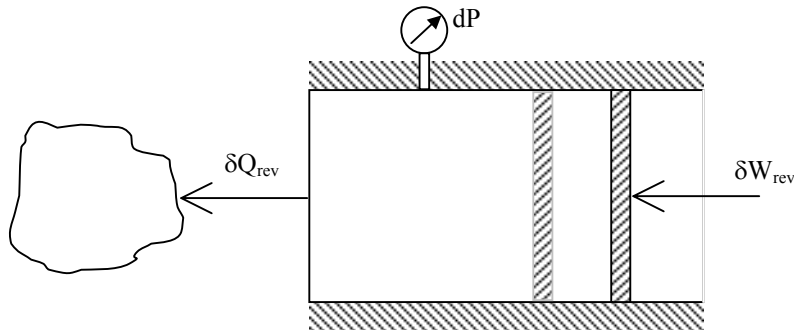
- Therefore, for an ideal gas,

$$c^2 = vP\gamma$$

or

$$c^2 = \gamma RT$$

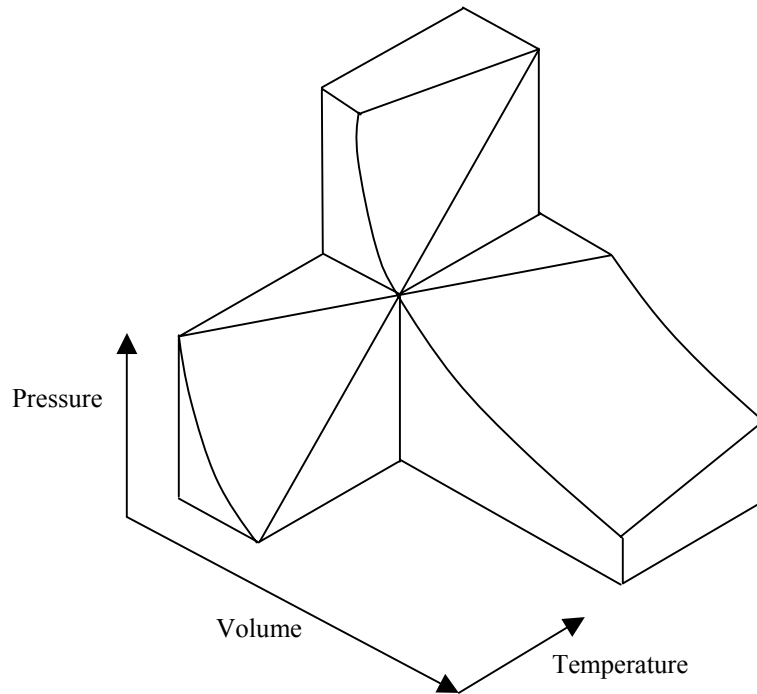
Isothermal Volume Change



- By measuring ΔP associated with Δv , we can define the *isothermal compressibility*:

$$K \equiv -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$$

- Like other properties, in general, $K = K(P, T)$
- Notice the relationship between K and $\beta \left(= \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \right)$. Both measure slopes of the $v=v(P, T)$ surface, K measuring along an isotherm, and β along an isobar:



Special cases:

$K=1/P$	Ideal gas
$K=0$	Incompressible substance

- Now let's return to Maxwell's Relations and express the derivatives as properties:

MR # 3:

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v = - \left(\frac{\partial v}{\partial T} \right)_P \left(\frac{\partial P}{\partial v} \right)_T \quad (\text{from the cyclic relationship})$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{\beta}{K}$$

MR #4:

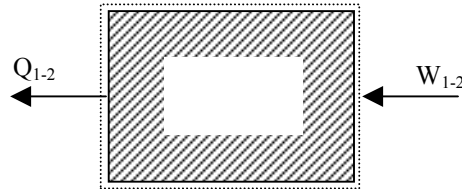
$$-\left(\frac{\partial s}{\partial P}\right)_T = \left(\frac{\partial v}{\partial T}\right)_P = \beta v$$

Keypoint:

- Entropy relations are now written in terms of easy to measure properties of the fluid.

EXAMPLE: Compression of Solid

- A 1kg block of copper is compressed in a reversible manner from 0.1 to 100 MPa while the temperature is held constant at 15°C. Determine the work done, entropy change, and heat transfer.



- Solution:
- Over the range of pressure considered here,

$$\text{volume expansivity } \beta = \frac{1}{v} \left. \frac{\partial v}{\partial T} \right|_P = 5 \times 10^{-5} \text{ K}^{-1}$$

$$\text{isothermal comp. } K = \frac{-1}{v} \left. \frac{\partial v}{\partial P} \right|_T = 8.6 \times 10^{-12} \text{ Pa}^{-1}$$

$$\text{specific volume } v \cong 1.14 \times 10^{-4} \text{ m}^3/\text{kg}$$

- Work during isothermal expansion:

$$W = \int_1^2 P dv$$

Rewriting isothermal compressibility,

$$vK dP_T = -dv_T \quad \left(\text{note } \left. \frac{\partial v}{\partial P} \right|_T = \left. \frac{dv}{dP} \right|_T \right)$$

Thus

$$W = -\int_1^2 P v K dP_T$$

Since K and v are nearly constant,

$$W = \frac{-vK}{2} (P_2^2 - P_1^2)$$

$$\boxed{W = -4.9 \text{ J/kg}}$$

(i.e. "on system")

- Entropy Change
- Start with Maxwell relation

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

and introduce the definition of volume expansivity to get

$$\left(\frac{\partial s}{\partial P}\right)_T = -v\beta$$

- Since our process is at constant temperature,

$$\left(\frac{\partial s}{\partial P}\right)_T = \frac{ds}{dP}\bigg|_T = -v\beta$$

or

$$ds_T = -v\beta dP_T$$

- Assuming v and β are nearly constant,

$$s_2 - s_1 = -v\beta(P_2 - P_1)$$

→

$$\boxed{s_2 - s_1 = -0.5694 \text{ J/kg-K}}$$

- Heat Transfer
- Since the process is reversible and isothermal,

$$q = T(s_2 - s_1)$$

→

$$\boxed{q = -164.1 \text{ J/kg}}$$

(i.e. "out of system")

- As we did for isentropic processes, we can also express the P-v path of an isothermal process using thermodynamic properties. To do this, let $T=T(P,v)$:

$$dT = \left(\frac{\partial T}{\partial P}\right)_v dP + \left(\frac{\partial T}{\partial v}\right)_P dv$$

Rearranging, we have

$$0 = \frac{dP}{P} + k_T \frac{dv}{v} \quad (\text{can you show this?})$$

where we have defined

$$\boxed{k_T \equiv \frac{v}{P} \left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial P}{\partial T}\right)_v}$$

as the *isothermal expansion coefficient*.

Special Cases:

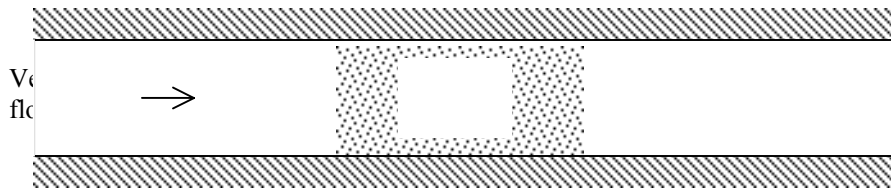
$$k_T = 1 \quad (\text{Ideal gas}), \quad k_T = \infty \quad (\text{Incompressible substance})$$

- In general, $k_T = k_T(P, T)$, but for a small departure from a given state, $k_T \approx \text{constant}$, and the equation above can be integrated to give

$$Pv^{k_T} = \text{constant}$$

- Also, after some manipulation, $k_T = \frac{1}{KP}$
- It can also be shown that $\frac{k}{k_T} = \frac{C_P}{C_V}$

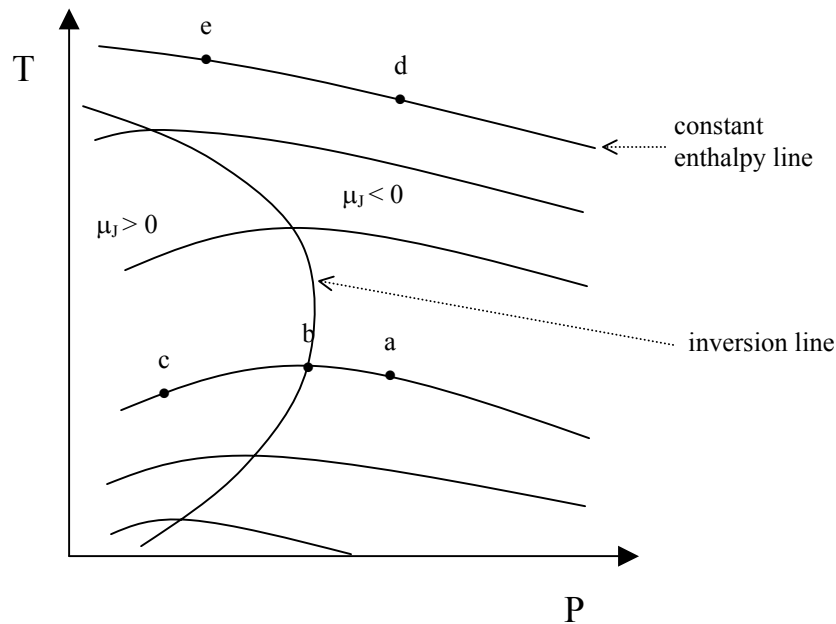
Constant Enthalpy Expansion



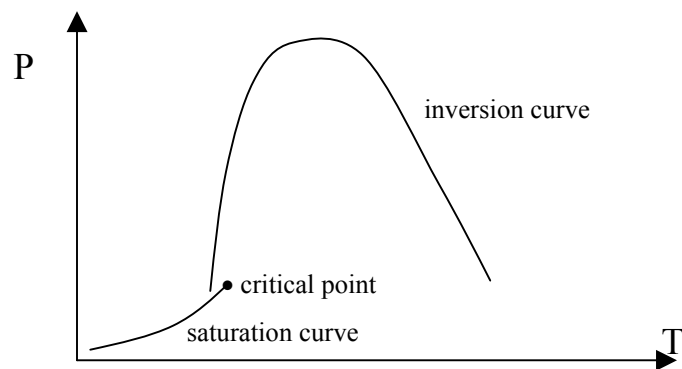
- One additional experimental configuration, important in refrigeration, is flow through a porous plug. This can be used to measure the *Joule-Thompson Coefficient*:

$$\mu_J \equiv \left(\frac{\partial T}{\partial P} \right)_h$$

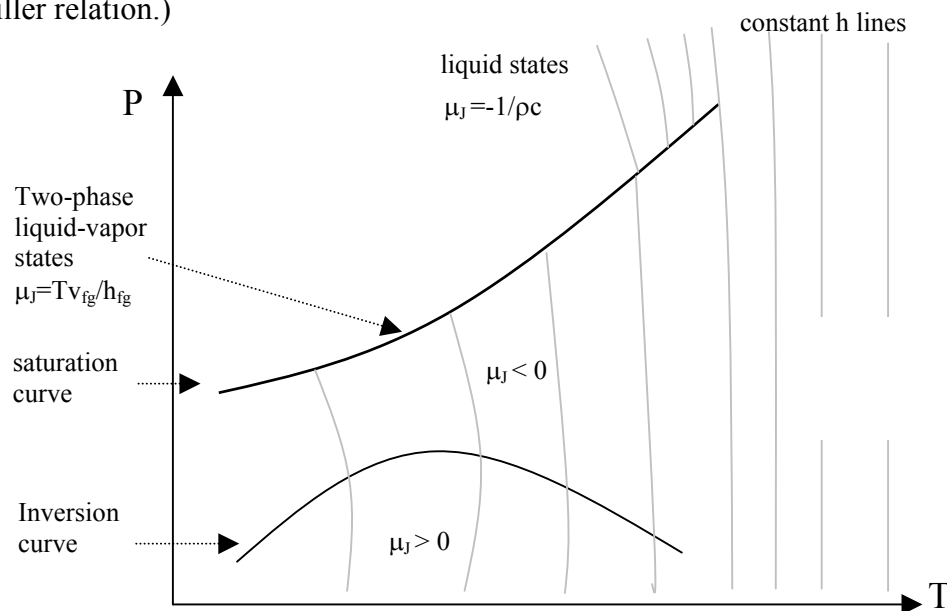
- If $\mu_J > 0$, then the fluid cools as it passes through the plug (i.e. $\Delta P < 0$ and $\Delta T < 0$), and it may be used as a refrigerant. If $\mu_J < 0$, then the fluid heats up as it passes through the plug and is unsuitable for refrigeration. In general, μ_J varies with pressure and temperature, and the dividing line between the region where $\mu_J > 0$ and $\mu_J < 0$ is called the “inversion line”.
- Consider the figure below. The expansion process proceeds from the right to the left. To the right of the inversion line (e.g. $a \rightarrow b$) the temperature increases during the expansion, and the fluid is not a candidate for a refrigerant in this region. To the left of the inversion line (e.g. $b \rightarrow c$), the temperature decreases during the expansion, and the fluid can be used for refrigeration. Above the inversion line (e.g. $d \rightarrow e$) expansion produces an increase in temperature regardless of how low the pressure drops.



- How does this look on an ordinary phase diagram? For a typical simple substance, (compare to the data for Helium and Nitrogen shown below)

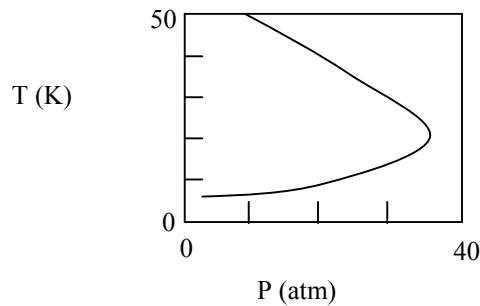


- This is not universally true, however. For example, *Thermodynamics: Foundations and Applications*, Gyftopoulos and Beretta, 1991, gives a figure such as this: (Note to future editor: I believe this figure is wrong and should be removed.)(Compare to Miller relation.)



- Notice that the inversion line passes through the points of maximum temperature on every h-line. Also, at low pressures (e.g. atmospheric) the inversion line approaches a maximum temperature, above which the fluid is entirely unusable. Some typical values of T_{\max} are:
- Plots of the inversion curve for two common cryogenic refrigerants are shown below:

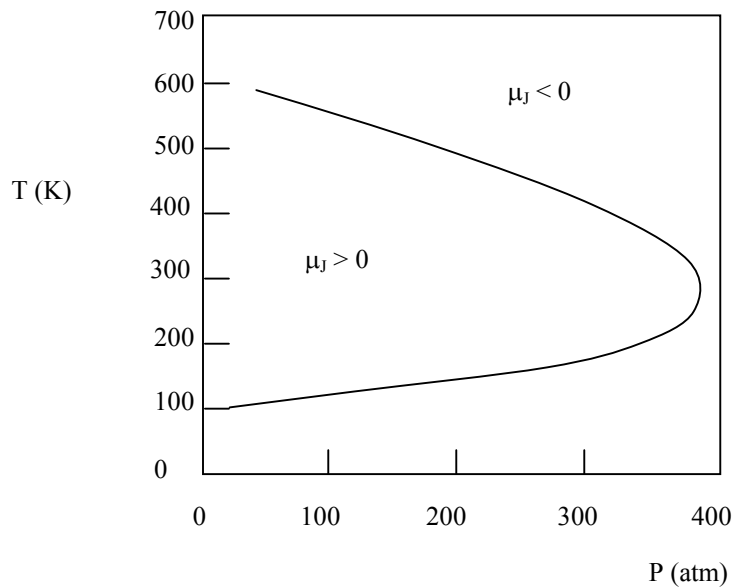
T_{\max}	Gas
205	H ₂
621	N ₂
659	Air
764	O ₂
780	Ar



Helium-4

($T_c = 5.2$ K)

($P_c = 2.3$ bar)



Nitrogen

($T_c = 126$ K)

($P_c = 33.9$ bar)

Keypoint:

- Joule-Thompson coefficient is a property that depends on the state (i.e. P , T)

EXAMPLE: Joule-Thompson coefficient related to PvT data

- By definition, $\mu = \left. \frac{\partial T}{\partial P} \right|_h$
- To evaluate this, let $T = T(h, P)$ and write

$$\begin{aligned}
 dT &= \left. \frac{\partial T}{\partial h} \right|_P dh + \left. \frac{\partial T}{\partial P} \right|_h dP \\
 &= \left. \frac{\partial T}{\partial h} \right|_P dh + \mu dP
 \end{aligned}
 \tag{a}$$

- Now, from the Tds relationship for enthalpy, we have

$$dh = Tds + v dP$$

- Let $s=s(P,T)$, write

$$ds = \left. \frac{\partial s}{\partial T} \right|_P dT + \left. \frac{\partial s}{\partial P} \right|_T dP,$$

and substitute into the expression for dh to give

$$dh = T \left. \frac{\partial s}{\partial T} \right|_P dT + \left[T \left. \frac{\partial s}{\partial P} \right|_T + v \right] dP$$

- We can substitute this into (a) to yield

$$\begin{aligned}
 dT &= \left. \frac{\partial T}{\partial h} \right|_P \left\{ T \left. \frac{\partial s}{\partial T} \right|_P dT + \left[T \left. \frac{\partial s}{\partial P} \right|_T + v \right] dP \right\} + \mu dP \\
 dT &= \left[T \left. \frac{\partial T}{\partial h} \right|_P \left. \frac{\partial s}{\partial T} \right|_P \right] dT + \left. \frac{\partial T}{\partial h} \right|_P \left[T \left. \frac{\partial s}{\partial P} \right|_T + v + \mu \right] dP
 \end{aligned}$$

or, since the second coefficient must equal zero,

$$\left. \frac{\partial T}{\partial h} \right|_P \left[-T \left. \frac{\partial s}{\partial P} \right|_T - v \right] = \mu$$

- From MR #4, we can write

$$\left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P$$

- Also, from the definition of C_P ,

$$C_P = \left(\frac{\partial h}{\partial T} \right)_P$$

- Thus we have

$$\mu = \frac{1}{C_P} \left[T \left. \frac{\partial v}{\partial T} \right|_P - v \right]$$

Keypoints:

- function of C_P , T , v , P
- if $Pv=RT$, $\mu=0$

- Note that the expression above can be used to measure C_P (indirectly) at high P .

- Required: 1) measure μ with valve expansion process
2) measure P, v, T data
3) compute $\left. \frac{\partial v}{\partial T} \right|_P$
4) compute C_P

EXAMPLE: Joule-Thompson coefficient for steam

- Consider steam expanding from 6 MPa, 400°C, to 2 MPa
- Steam is SHV, since $T_{\text{sat}}(6\text{MPa}) = 275^\circ\text{C}$
- If we assume ideal gas, then $\mu = 0$, $\Delta T = 0$. Otherwise, we can approximate

$$\mu = \left. \frac{\partial T}{\partial P} \right|_h \approx \left. \frac{\Delta T}{\Delta P} \right|_h$$

- At $P = 6$ MPa and $T = 400^\circ\text{C}$, $h = 3177.2$ kJ/kg
- At $P = 7$ MPa and $h = 3177.2$, $T = 407.4$
- At $P = 5$ MPa and $h = 3177.2$, $T = 392.7$
- Thus

$$\mu = \left. \frac{407.4^\circ\text{C} - 392.7^\circ\text{C}}{7\text{MPa} - 5\text{MPa}} \right|_{h=3177.2}$$

$$\boxed{\mu = 7.35 \frac{^\circ\text{C}}{\text{MPa}}}$$

- Thus T drops approximately 29°C in going from 6 MPa to 2 MPa

Summary of Measurable Thermodynamic Derivatives

- It is possible to express any arbitrary derivative as a function of (P, v, T) and these measurable parameters:

C_V	Specific heat at constant volume
C_P	Specific heat at constant pressure
β	Coefficient of thermal expansion
k	Isentropic expansion coefficient
K	Isothermal compressibility
k_T	Isothermal expansion coefficient
μ_J	Joule-Thompson coefficient

Property	Ideal Gas Limit	Incompressible Limit
$P = P(v, T)$	$Pv = RT$	$V = \text{constant}$
$C_V = \left(\frac{\partial u}{\partial T} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v$	$C_V(T)$	$C(T)$
$C_P = \left(\frac{\partial h}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P$	$C_P(T) = C_V + R$	$C(T)$
$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$	$\frac{1}{T}$	0
$k = -\frac{v}{P} \left(\frac{\partial P}{\partial v} \right)_s$	$\frac{C_P}{C_V}$	∞
$K = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$	$\frac{1}{P}$	0
$k_T = -\frac{v}{P} \left(\frac{\partial P}{\partial v} \right)_T$	1	∞
$\mu_J = \left(\frac{\partial T}{\partial P} \right)_h$	0	$-\frac{v}{C}$

Bridgman Jacobian

- In 1914, P. W. Bridgman expressed all partial derivatives of the most frequently used properties (P, T, v, s, u, h, f, and g) in terms of the measurable P-v-T relationship and the three easy to measure derivatives (C_P , β , and K). Using the shorthand notation

$$\left(\frac{\partial x}{\partial y} \right)_z = \frac{(\partial x)_z}{(\partial y)_z},$$

he summarized 336 possibilities in a 28 line table:

[P]	$(\partial T)_P = -(\partial P)_T = 1$
	$(\partial v)_P = -(\partial P)_v = \beta v$
	$(\partial s)_P = -(\partial P)_s = C_P/T$
	$(\partial u)_P = -(\partial P)_u = C_P - \beta P v$
	$(\partial h)_P = -(\partial P)_h = C_P$
	$(\partial f)_P = -(\partial P)_f = -s - \beta P v$
	$(\partial g)_P = -(\partial P)_g = -s$
[T]	$(\partial v)_T = -(\partial T)_v = \kappa v$
	$(\partial s)_T = -(\partial T)_s = \beta v$
	$(\partial u)_T = -(\partial T)_u = \beta T v - \kappa P v$
	$(\partial h)_T = -(\partial T)_h = -v + \beta T v$
	$(\partial f)_T = -(\partial T)_f = -\kappa P v$
	$(\partial g)_T = -(\partial T)_g = -v$
[v]	$(\partial s)_v = -(\partial v)_s = \beta^2 v^2 - \kappa v C_P/T$
	$(\partial u)_v = -(\partial v)_u = T \beta^2 v^2 - \kappa v C_P$
	$(\partial h)_v = -(\partial v)_h = T \beta^2 v^2 - \kappa v C_P - \beta v^2$
	$(\partial f)_v = -(\partial v)_f = \kappa v s$
	$(\partial g)_v = -(\partial v)_g = \kappa v s - \beta v^2$
[s]	$(\partial u)_s = -(\partial s)_u = \beta^2 v^2 P - \kappa v C_P P/T$
	$(\partial h)_s = -(\partial s)_h = -v C_P/T$
	$(\partial f)_s = -(\partial s)_f = \beta v s + \beta^2 v^2 P - \kappa v C_P P/T$
	$(\partial g)_s = -(\partial s)_g = \beta v s - v C_P/T$

EXAMPLE: Sound Velocity

By definition,

$$c^2 = \left. \frac{\partial P}{\partial \rho} \right|_s$$

$$c^2 = \frac{\partial P}{\partial v} \bigg|_s \frac{\partial v}{\partial \rho} \bigg|_s = \frac{\partial P}{\partial v} \bigg|_s \frac{\partial (\rho^{-1})}{\partial \rho} \bigg|_s$$

$$c^2 = \frac{\partial P}{\partial v} \bigg|_s (-1) \rho^{-2} \frac{\partial \rho}{\partial \rho} \bigg|_s$$

$$c^2 = -v^2 \frac{\partial P}{\partial v} \bigg|_s$$

- Now, from Bridgman table,

$$(dP)_s = \frac{-C_P}{T}$$

$$(dv)_s = - \left[\beta^2 v^2 - \frac{KvC_P}{T} \right] = - \left[\left(\frac{\partial v}{\partial T} \right)_P^2 + \frac{\partial v}{\partial P} \bigg|_T \frac{C_P}{T} \right]$$

- Thus

$$c^2 = -v^2 \frac{\partial P}{\partial v} \bigg|_s = -v^2 \frac{(\partial P)_s}{(\partial v)_s}$$

$$c^2 = \frac{-v^2}{\left[\frac{\partial v}{\partial P} \bigg|_T + \frac{T}{C_P} \left(\frac{\partial v}{\partial T} \right)_P^2 \right]}$$

or

$$c^2 = \frac{1}{\left[\frac{K}{v} - \frac{\beta^2 T}{C_P} \right]}$$

Ideal Gas Limit:

$$Pv = RT$$

$$\beta = \frac{1}{v} \frac{\partial v}{\partial T} \bigg|_P = \frac{1}{T}$$

$$K = \frac{-1}{v} \frac{\partial v}{\partial P} \bigg|_T = \frac{1}{P}$$

$$C_P - C_v = R$$

- Thus

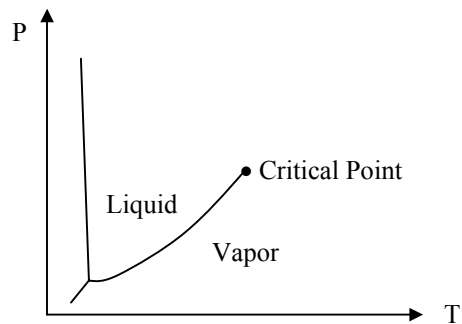
$$c^2 = \frac{C_P}{C_v} RT$$

EXAMPLES: Bridgman Table

Derivative	Derivative in terms of properties	Derivative evaluated by the Bridgman table
$\left. \frac{\partial u}{\partial s} \right _v$	T (2.2.3)	$\frac{(\partial u)_v}{(\partial s)_v} = \frac{T\beta^2 v^2 - K v C_P}{\beta^2 v^2 - K v C_P / T} = T$
$\left. \frac{\partial u}{\partial v} \right _s$	-P (2.2.4)	$\frac{(\partial u)_s}{(\partial v)_s} = \frac{\beta^2 v^2 P - K v C_P P / T}{-\beta^2 v^2 + K v C_P / T} = -P$
$\left. \frac{\partial T}{\partial P} \right _h = \mu$	$\frac{1}{C_P} \left[T \left. \frac{\partial v}{\partial T} \right _P - v \right]$	$\frac{(\partial T)_h}{(\partial P)_h} = \frac{v - \beta T v}{-C_P}$ $\frac{1}{C_P} \left[T \left. \frac{\partial v}{\partial T} \right _P - v \right]$
$\left. \frac{\partial u}{\partial T} \right _v$	C_v	$\frac{(\partial u)_v}{(\partial T)_v} = \frac{T\beta^2 v^2 - K v C_P}{-K v}$ $= C_P - \frac{T\beta^2 v}{K}$
$T \left. \frac{\partial s}{\partial T} \right _v$	C_v	$T \frac{(\partial s)_v}{(\partial T)_v} = T \frac{\beta^2 v^2 - K v C_P / T}{-K v}$ $= C_P - \frac{T\beta^2 v}{K}$

Clapeyron Equation

- Relates saturation properties



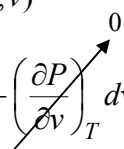
- Start with MR #3:

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

- During phase change, $T=\text{constant}$
- In general, during phase change $\left(\frac{\partial P}{\partial v}\right)_T = 0$. That is, v changes but P does not!

$$P = P(T, v)$$

$$dP = \left(\frac{\partial P}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial v}\right)_T dv$$



$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_v$$

- MR #3 thus becomes (after evaluating across phase change)

$$\left.\frac{dP}{dT}\right|_{sat} = \left(\frac{\partial s}{\partial v}\right)_T = \frac{(s_g - s_f)}{(v_g - v_f)} = \frac{s_{fg}}{v_{fg}}$$

- Since $Tds = dh - vdP$ and $dP=0$,

$$\Delta s = \frac{\Delta h}{T}$$

and

$$\boxed{\left.\frac{dP}{dT}\right|_{sat} = \frac{h_{fg}}{Tv_{fg}}} \quad \text{CLAPEYRON EQUATION}$$

- In general, we can replace 'f' and 'g' with any phase change (e.g. solid to liquid):

$$\boxed{\left.\frac{dP}{dT}\right|_{sat} = \frac{(h'' - h')}{T(v'' - v')}} \quad \text{CLAPEYRON EQUATION}$$

Keypoints: Clapeyron Equation

- 1 Important since it relates 3 measurable properties

- i) slope of $P_{\text{sat}}-T_{\text{sat}}$ line
 - ii) latent heat of phase transformation ($h''-h'$) from phase (') to phase ('')
 - iii) volume change during phase transformation
- 2 Can be used to calculate one of 3 properties from other 2
- 3 If phase ('') is vapor, at low pressure the equation can be simplified by assuming
- i) $v'' \gg v'$
 - ii) $v'' = RT/P$ (ideal gas)
- yielding

$$\left. \frac{dP}{dT} \right|_{\text{sat}} = \frac{h_g - h'}{T(RT/P)}$$

This can be integrated to get

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{h_g - h'}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

where we have assumed $h_g - h'$ is constant between states 1 and 2.

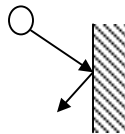
Kinetic Theory of Gases--State Equations and Specific Heats

- The ideal gas equation of state can be derived from the kinetic theory of gases
- It should be noted that such a derivation has no bearing on classical thermodynamics.
- Recall, classical thermodynamics
 - 1) does not depend on microscopic structure of matter
 - 2) does not predict anything about microscopic features
- Why study kinetic theory in a course that focuses more on classical thermodynamics?
 - 1) gives good physical understanding to concepts presented in classical thermodynamics (i.e. ideal gas assumption, definition of C_p).
 - 2) helps one understand why real gases behave differently from ideal gases.

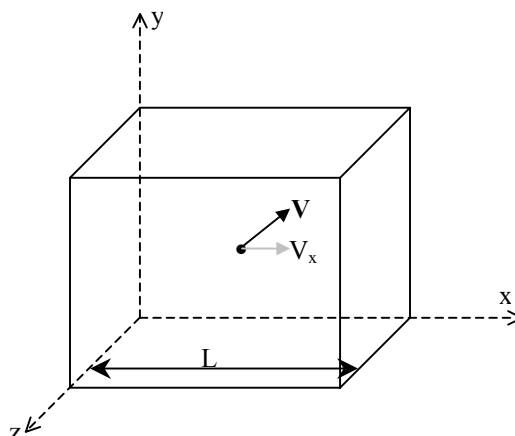
- Analysis: Let's consider a monatomic gas and make the following assumptions:

- 1) The gas consists of an enormous number of molecules. All of the molecules are identical (assuming a pure gas).
- 2) The molecules are very small relative to the average distance between them. The volume occupied by the molecules themselves is a tiny fraction of the volume of the container.
- 3) The molecules fly about randomly in all directions—there is no preferred direction.
- 4) The molecules do not interact except when they collide.
- 5) Collisions of the molecules with each other and with the walls of the container are perfectly elastic.
- 6) The laws of macroscopic mechanics (Newton's laws) apply to individual molecules.

- According to kinetic theory, the pressure exerted by an ideal gas on the walls of a container results from the action of a great number of molecules striking and rebounding.



- Let's first look at one molecule in a box, with mass m and velocity components V_x , V_y , and V_z .



- Consider a molecule striking the wall at $x=L$. When it rebounds, there is no change in V_y and V_z , but V_x changes to $-V_x$.
- The corresponding x-component of momentum changes from mV_x to $-mV_x$. Thus, the magnitude of momentum change is $2mV_x$.
- Also, the molecule travels the distance L in time L/V_x . Thus it could cross the chamber and return in time $\Delta t=2L/V_x$. The number of collisions per unit time (collision frequency) is

$$f = \frac{V_x}{2L}$$

- Now, the change in x-momentum per unit time is the product of the change per collision and the frequency of collision,

$$\frac{\Delta(x - \text{momentum})}{\text{time}} = 2mV_x \left(\frac{V_x}{2L} \right) = \frac{mV_x^2}{L}$$

- Thus, the force on the wall is

$$F_x = \frac{mV_x^2}{L} \quad (\text{one molecule})$$

- The force of all molecules is

$$F_x = \sum \frac{mV_x^2}{L}$$

or, since m and L are constant,

$$F_x = \frac{m}{L} \sum V_x^2$$

- Define the average V^2 of n molecules as

$$\overline{V_x^2} \equiv \frac{\sum_{i=1}^n V_x^2}{n} \quad (\text{a})$$

then

$$F_x = \frac{mn\overline{V_x^2}}{L}$$

- The pressure is thus

$$P_x = \frac{F_x}{\text{area}} = \frac{mn\overline{V_x^2}}{L(\text{area})} = \frac{mn\overline{V_x^2}}{(\text{volume})} \quad (\text{b})$$

- If it is assumed that the pressure is the same in all directions, and that all directions of velocity are equally probable,

$$P = \frac{mn\overline{V_x^2}}{(\text{volume})} = \frac{mn\overline{V_y^2}}{(\text{volume})} = \frac{mn\overline{V_z^2}}{(\text{volume})} \quad (\text{c})$$

$$\overline{V_x^2} = \overline{V_y^2} = \overline{V_z^2} \quad (\text{d})$$

- Also, since V_x , V_y , and V_z are components of V ,

$$V^2 = V_x^2 + V_y^2 + V_z^2$$

and it can be shown that

$$\overline{V^2} = \overline{V_x^2} + \overline{V_y^2} + \overline{V_z^2} \quad (\text{e})$$

where $\overline{V^2}$ is the average of the squared velocity magnitudes for all molecules.

- Combining (d) and (e),

$$\overline{V^2} = 3\overline{V_x^2} = 3\overline{V_y^2} = 3\overline{V_z^2}$$


and (c) becomes

$$P = \frac{mn\overline{V^2}}{3(\text{vol})}$$

$$P(\text{vol}) = \frac{1}{3} nm\overline{V^2} \quad (\text{f})$$

- If we assume the temperature of an ideal gas is proportional to the kinetic energy of the molecules,

$$T = D \frac{m\overline{V^2}}{2} \quad (g)$$


 Proportionality constant

- Combining (f) and (g) gives

$$P(vol) = \frac{2}{3D} nT = \left(\frac{2n}{3DN} \right) NT \quad (h)$$

where n/N is Avogadro's number (#molecules/mole).

- The term $(2n/3DN)$ is a constant, call it \bar{R} , the universal gas constant.

→ $P(vol) = \bar{R}T$ "ideal gas"

- Following (f), we assumed that T was proportional to kinetic energy of molecules.
- Conversely, we could have just compared (f) with the experimentally derived ideal gas law....

$$P(vol) = \frac{1}{3} nm\overline{V^2} \quad \dots \text{equation (f)}$$

$$P(vol) = \bar{R}T \quad \dots \text{from experiment}$$

or, equating RHS,

$$T = \frac{1}{3} \frac{n}{\bar{R}} m\overline{V^2} = \frac{2}{3} \frac{n}{\bar{R}} m \frac{\overline{V^2}}{2} = \text{constant} \frac{m\overline{V^2}}{2}$$

- Using the physical constant $k \equiv \frac{\bar{R}}{n}$ (Boltzmann's constant), we could write

$$\frac{3}{2} kT = \frac{m\overline{V^2}}{2} \quad (i)$$

Keypoint: Equation (i)

- Average kinetic energy at a given T is the same for any gas.
- Thus, heavier gas molecules have lower mean speeds than lighter molecules at the same T .

- Now let's look at C_p and C_v under the kinetic theory.

- Internal energy of an ideal gas is sum of molecular kinetic and potential energies
- Since ideal gas is very dilute, molecules are far apart, and gravitational forces between them are small.
- If we change the volume (i.e. density), the distance between the molecules changes, and the potential energy changes. However, since this change is extremely small for an ideal gas, this change does not have an effect on internal energy.
- Thus, for ideal gas, internal energy is only dependent on kinetic energy of molecules.

→
$$U = NMu = \frac{nm\overline{V^2}}{2}$$

where	u = specific internal energy	(J/kg)
	M = molar mass	(kg/kmol)
	N = # moles	(kmol)
	U = internal energy	(J)

- The molar internal energy $\bar{u} = Mu$

$$\bar{u} = Mu = \frac{n}{N} \frac{3}{2} kT = \frac{3}{2} \bar{R} T$$

where we have used (g) from above, and finally,

$$\boxed{C_v = \left. \frac{\partial \bar{u}}{\partial T} \right|_v = \left(\frac{\partial Mu}{\partial T} \right)_v = \frac{3}{2} \bar{R}}$$

- Now, what about a *diatomic* gas?
- Monatomic gas has 3 degrees of freedom (i.e. one must specify 3 independent quantities to determine the energy, in this case V_x , V_y , and V_z)
- Equipartition of Energy Principle:

“Total energy of molecules is divided equally among all degrees of freedom.”

- Thus, monatomic gas has 3 degrees of freedom, each with $\frac{1}{2}\bar{R}T$ of energy, for a total energy of

$$\frac{3}{2}\bar{R}T$$

- Each additional degree of freedom must contribute $\frac{1}{2}\bar{R}T$ to total energy. Thus, the molar internal energy is

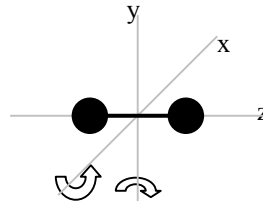
$$\bar{u} = Mu = \frac{f}{2}\bar{R}T$$

for f degrees of freedom.

- Also,

$$\left. \begin{aligned} \bar{C}_v &= \left(\frac{\partial(Mu)}{\partial T} \right)_v = \frac{f}{2}\bar{R} \\ \bar{C}_p &= \bar{C}_v + \bar{R} = \left(\frac{f+2}{2} \right)\bar{R} \end{aligned} \right\} k = \frac{C_p}{C_v} = \frac{f+2}{f}$$

- Diatomic gases have



3 degrees of freedom in translation (rotation about z is not a degree of freedom)

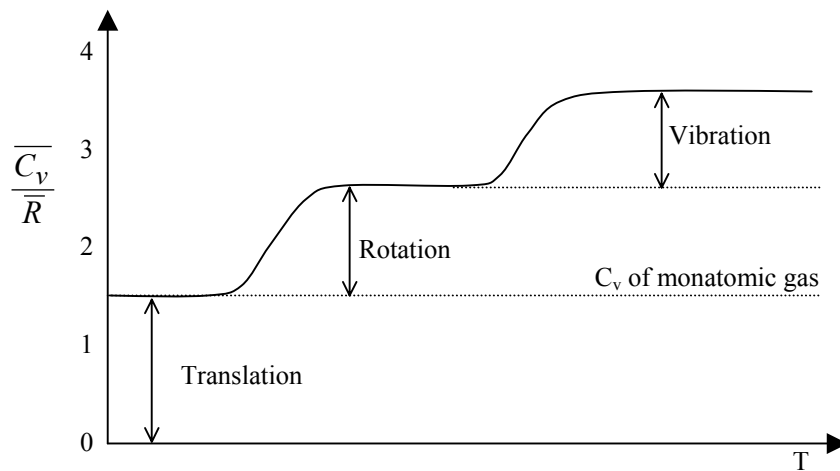
2 degrees of freedom in rotation

2 degrees of freedom in vibration along axis connecting them (z axis)

Note: vibration usually only occurs at high T

7 total (at high T)
5 total (at intermediate T)
3 total (at low T)

→ At low temperatures:	$\bar{C}_v = \frac{3}{2}\bar{R}$	$\bar{C}_p = \frac{5}{2}\bar{R}$	$k = \frac{5}{3}$
At intermediate temperatures:	$\bar{C}_v = \frac{5}{2}\bar{R}$	$\bar{C}_p = \frac{7}{2}\bar{R}$	$k = \frac{7}{5}$
At high temperatures:	$\bar{C}_v = \frac{7}{2}\bar{R}$	$\bar{C}_p = \frac{9}{2}\bar{R}$	$k = \frac{9}{7}$



Gas	Experimental Values at 1atm, 0° C		From Kinetic Theory (no vibration)	
	\bar{C}_v	\bar{C}_p	\bar{C}_v	\bar{C}_p
Ar	12.5	20.8	12.5	20.8
He	12.7	21.0	12.5	20.8
Air	20.8	29.1	20.8	29.1
CO	20.8	29.1	20.8	29.1
N ₂	20.8	29.1	20.8	29.1
O ₂	21.0	29.3	20.8	29.1

Specific Heat Relations

- Let's look more closely at specific heats, considering first some mathematical relations, and also some data for specific substances.
- Although for an ideal gas specific heats are a function only of temperature, in general $C_p = C_p(T, P)$, and $C_v = C_v(T, P)$. Let's consider three important concepts:
 - Variation of C_p with P at constant T
 - Variation of C_v with v at constant T
 - Relation between C_p and C_v .

Variation of C_p with P at constant T

- Look at the differential form of the entropy equation from before.

$$ds = \frac{C_P}{T} dT - \left(\frac{\partial v}{\partial T} \right)_P dP$$

Compare to

$$dz = M dx + N dy$$

Using $\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$, we have

$$\left(\frac{\partial}{\partial P} \right)_T \frac{C_P}{T} = - \left(\frac{\partial}{\partial T} \right)_P \left(\frac{\partial v}{\partial T} \right)_P$$

or

$$\boxed{\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 v}{\partial T^2} \right)_P}$$

Variation of C_V with v at constant T

- Another form of the entropy equation is

$$ds = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dv$$

Following the previous approach yields

$$\boxed{\left(\frac{\partial C_V}{\partial v} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_v}$$

Keypoints:

- Both variations can be calculated given the PvT surface.
- Both = 0 for an ideal gas ($Pv=RT$).

Relation between C_P and C_V

- We have used two forms for the ds equation, one involving C_P and the other C_V . Let's equate them:

$$ds = \frac{C_P}{T} dT + \left(\frac{\partial v}{\partial T} \right)_P dP = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dv$$

or

$$dT = \frac{T \left(\frac{\partial P}{\partial T} \right)_v}{C_P - C_V} dv + \frac{T \left(\frac{\partial v}{\partial T} \right)_P}{C_P - C_V} dP$$

Compare this to the differential we obtain from writing $T=T(v,P)$ directly,

$$dT = \left(\frac{\partial T}{\partial v} \right)_P dv + \left(\frac{\partial T}{\partial P} \right)_v dP$$

Equating either of the pairs of coefficients yields

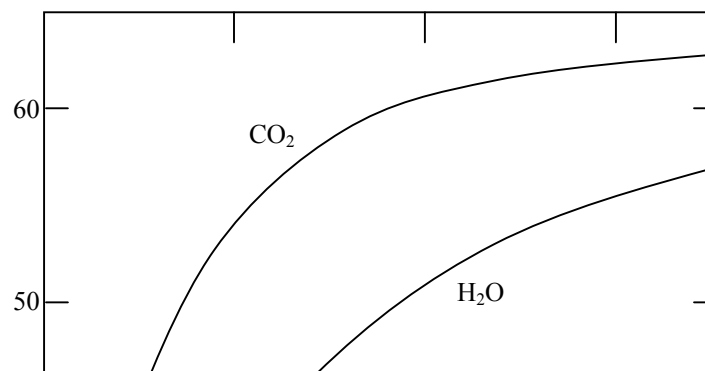
$$C_P - C_V = -T \left(\frac{\partial v}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial v} \right)_T = \frac{T \beta^2 v}{\kappa}$$

Keypoints:

1. $C_P \geq C_V$ since $\left(\frac{\partial v}{\partial T} \right)_P^2 \geq 0$ and $\left(\frac{\partial P}{\partial v} \right)_T < 0$ for all known substances.
2. In the ideal gas limit, $C_P - C_V = R$
3. For solids and liquids, $\left(\frac{\partial v}{\partial T} \right)_P \approx 0 \Rightarrow C_P \approx C_V$
4. In the incompressible limit, $\left(\frac{\partial v}{\partial T} \right)_P = 0$ and $C_P = C_V$ exactly. This is true for water at 4°C, where the density is maximum.

Cp Data for Ideal Gases

- Data for some common ideal gases at low pressures (e.g. atmospheric) are shown in the sketch below:

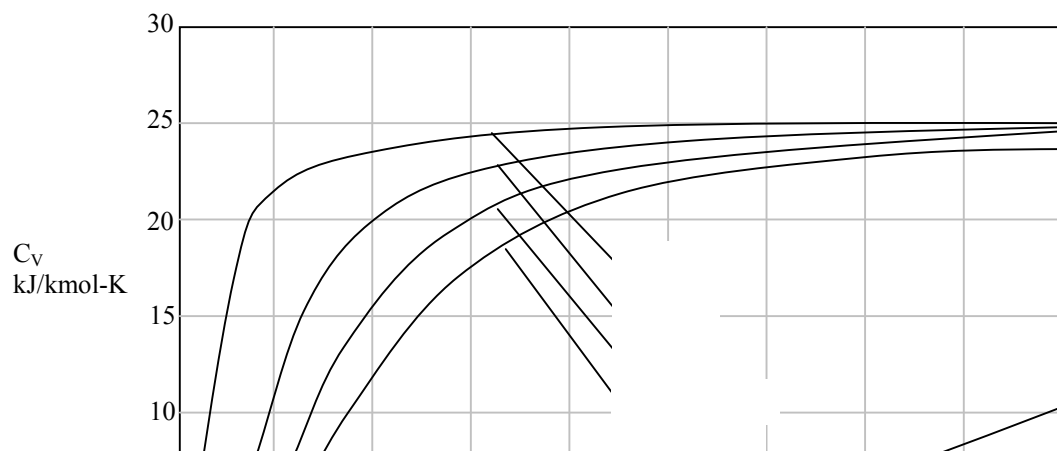


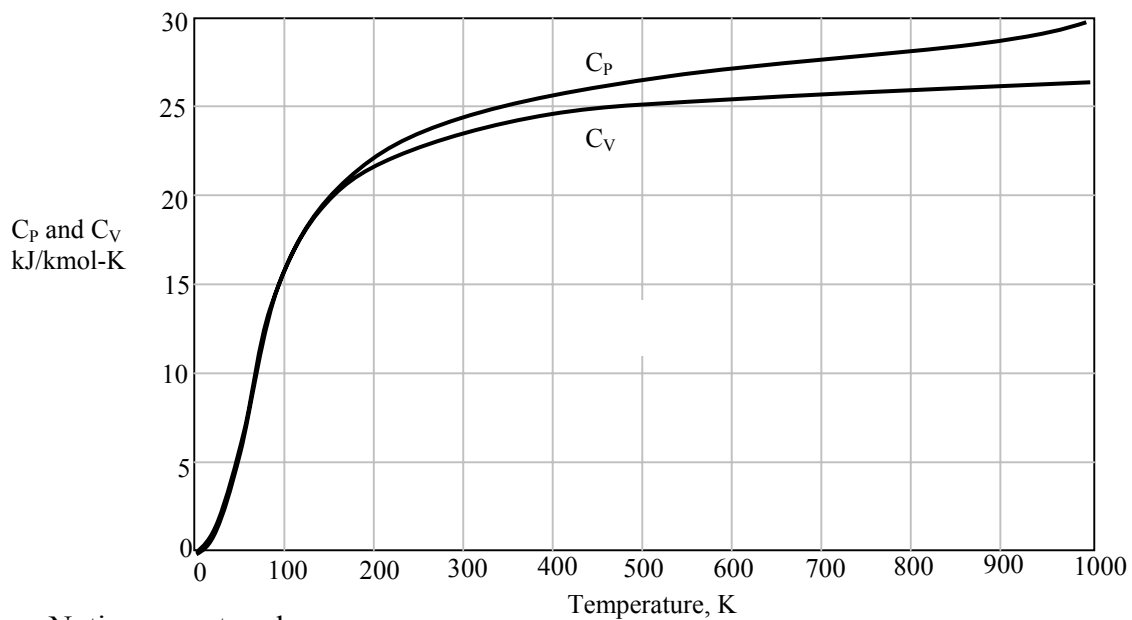
Recall, kinetic theory gives

	C_p	C_v
monatomic	$\frac{5}{2} \bar{R} = 20.8 \frac{J}{mol \cdot K}$	$\frac{3}{2} \bar{R} = 12.5 \frac{J}{mol \cdot K}$
diatomic	$\frac{7}{2} \bar{R} = 29.1 \frac{J}{mol \cdot K}$	$\frac{5}{2} \bar{R} = 20.8 \frac{J}{mol \cdot K}$

Specific Heat Data for Solids

- Specific heat data for some common solids are sketched below:





- Notice some trends:
 - * At low temperatures, Cp and Cv are nearly identical.
 - * At high temperatures, Cp and Cv diverge, with Cv approaching a nearly constant value of

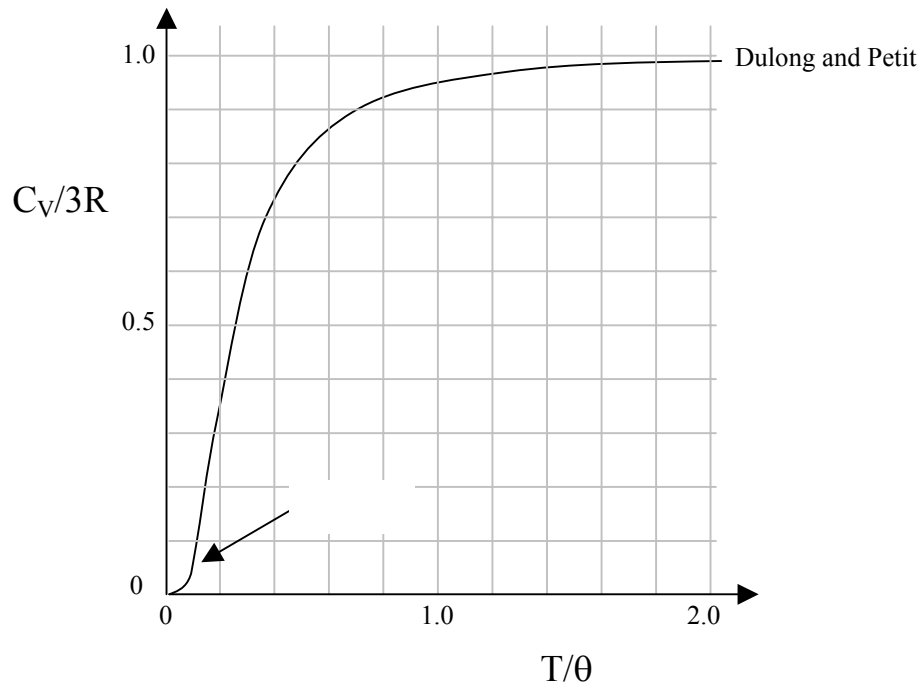
$$\bar{C}_V \cong 3\bar{R} \cong 25 \text{ kJ/kmol} \cdot \text{K}$$

This is known as the Dulong and Petit value, after the scientists who first noticed this trend.

- * Curves for different materials show a similar shape, suggesting that all curves might be made to fit the same functional form (the law of corresponding states).
- Peter Debye, using quantum statistical mechanics, developed the formula

$$\bar{C}_V = 3\bar{R}f\left(\frac{T}{\Theta_D}\right)$$

where Θ_D is a characteristic temperature of the substance in question, known as the “Debye Temperature”, and f is a universal function of the dimensionless temperature ratio T/Θ_D .



- Debye temperatures for some common substances are:

Substance	$\Theta_D(\text{K})$	$\Theta_D(^{\circ}\text{R})$
Aluminum	428	770
Cadmium	209	376
Calcium	230	414
Copper	343	617
Diamond	2230	4014
Graphite	420	756
Iron	467	841
Lead	105	189
Mercury	72	130
Silver	225	405
Sodium	158	284
Zinc	327	589

- The complete expression for the Debye formula is:

$$\bar{C}_V(T) = 3\bar{R} \left[12 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^3}{e^x - 1} dx - \frac{3\Theta_D/T}{e^{\Theta_D/T} - 1} \right]$$

For high temperatures ($T/\Theta_D \gg 1$), this is approximated by

$$\bar{C}_V \approx 3\bar{R} \left[1 - \frac{1}{20} \left(\frac{\Theta_D}{T} \right)^2 \right]$$

For low temperatures ($T/\Theta_D \ll 1$), this is approximated by

$$\bar{C}_V \approx 3\bar{R} \frac{4\pi^4}{5} \left(\frac{T}{\Theta_D} \right)^3$$

This is known as the “Debye T^3 Law” and is accurate to <1% for $(T/\Theta_D) < 0.1$ for isotropic nonmetals.

Keypoints: Debye formula

- Θ_D is the “Debye temperature”.
- $f(T/\Theta_D)$ is the same function for all substances.
- At high temperatures, $f \rightarrow 1$, and $\bar{C}_V \cong 3\bar{R} \cong 25 \text{ kJ} / \text{kmol} \cdot \text{K}$
- At low temperatures, $C_V \propto T^3$
- The Debye formula is a good approximation, but is not always correct. For example:

$$\text{H}_2\text{O}: \quad \bar{C}_V = 4.5\bar{R}$$

$$\text{Barium}: \quad \bar{C}_V = 4.7\bar{R}$$

- Regarding the divergence of C_P and C_V , recall that the difference can be calculated as

$$C_P - C_V = \frac{T\beta^2 v}{K}$$

Calculated Property Relations

- Now that we have developed some mathematical tools and defined some measurable properties, let's go about calculating some non-measurable properties (u , h , and s).

Enthalpy Relations

- Start by writing differential form of $h=h(T,P)$.

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP$$

By definition, the first derivative is C_p . Use the Bridgman table to express the second:

$$\left(\frac{\partial h}{\partial P} \right)_T = \frac{(\partial h)_T}{(\partial P)_T} = \frac{-v + \beta T v}{-1}$$

Thus

$$dh = C_p dT + [v - \beta T v] dP$$

or

$$h_2 - h_1 = \int_{T_1}^{T_2} C_p dT + \int_{P_1}^{P_2} [v - \beta T v] dP$$

Special cases:

Ideal Gas: $v - \beta T v = 0$, $C_p = C_p(T)$

$$h_2 - h_1 = \int_{T_1}^{T_2} C_p dT$$

Incompressible Substance: $v = \text{constant}$, $\beta = 0$, $C_p = C(T)$

$$h_2 - h_1 = \int_{T_1}^{T_2} C_p dT + v(P_2 - P_1)$$

- Now let's examine $h_2 - h_1$ in more detail.

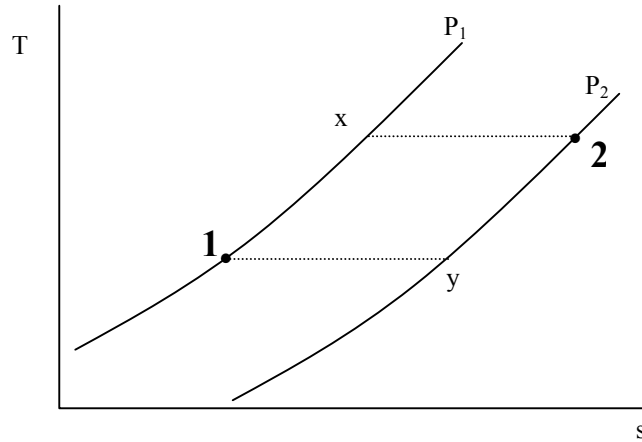
Along an isobar, $P = \text{constant}$, $dP = 0$, and

$$h_2 - h_1 = \int_{T_1}^{T_2} C_p dT$$

Along an isotherm, $T=\text{constant}$, $dT=0$, and

$$h_2 - h_1 = \int_{P_1}^{P_2} [v - \beta T v] dP$$

Since h is a point function (path independent), the integral $(h_2 - h_1)$ can be evaluated along any convenient path. For example, consider T-s space:



The quantity $(h_2 - h_1)$ can be evaluated along either $1 \rightarrow x \rightarrow 2$, or $1 \rightarrow y \rightarrow 2$. Along the former path, we have

$$h_2 - h_1 = \int_{T_1}^{T_2} C_P(P_1, T) dT + \int_{P_1}^{P_2} (v - \beta T v) dP$$

Keypoints:

- Enthalpy can be evaluated at any state given $C_p(T)$ data at any reasonable reference pressure, and an equation of state.
- Many numerical codes and standard handbooks give $C_p(T)$ as a polynomial fit at a reference pressure of 1 atm.

$$C_P^\circ(T) = \sum_{n=1}^N R(a_n T^{n-1})$$

- Since C_P represents a partial derivative of two properties $\left. \frac{\partial h}{\partial T} \right|_P$, it alone is sufficient to completely define other properties.

Energy Relations

- We can use the same procedure as for enthalpy to express internal energy in terms of measurable properties.

$$u = u(T, v)$$

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

The first derivative is C_V by definition, the second can be transformed by the Bridgman Table,

$$\left(\frac{\partial u}{\partial v} \right)_T = \frac{(\partial u)_T}{(\partial v)_T} = \frac{\beta}{\kappa} T - P = T \left(\frac{\partial P}{\partial T} \right)_v - P$$

Thus

$$u_2 - u_1 = \int_{T_1}^{T_2} C_V dT + \int_{v_1}^{v_2} \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

Special cases:

Ideal Gas: $T \left(\frac{\partial P}{\partial T} \right)_v = P$, $C_V = C_V(T)$

$$u_2 - u_1 = \int_{T_1}^{T_2} C_V dT$$

Incompressible Substance: $v = \text{constant}$, $dv = 0$, $C_V = C(T)$

$$u_2 - u_1 = \int_{T_1}^{T_2} C dT$$

Entropy Relations

- Following previous derivations for Δh and Δu , write

$$Tds = dh - vdP$$

This yields

$$s_2 - s_1 = \int_{T_1}^{T_2} C_P \frac{dT}{T} - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T} \right)_P dP$$

- For some equations of state, $\left(\frac{\partial v}{\partial T} \right)_P$ is often difficult to evaluate. In these cases, it may be easier to express $s=s(T,v)$, i.e.

$$s = s(T, v)$$

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv$$

$$ds = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dv$$

or

$$s_2 - s_1 = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T} \right)_v dv$$

EXAMPLE: Energy, Enthalpy, and Entropy for the Van der Waals Equation of State

The $P=P(v,T)$ equation of state for a van der Waals gas is

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

in which R , a , and b are constants.

- (a) Prove that if C_v is also constant, the “caloric” equation of state $u = u(T,v)$ of the same gas is

$$u = u_o + C_V (T - T_o) + a \left(\frac{1}{v_o} - \frac{1}{v} \right)$$

where $u_o = u(T_o, v_o)$

(b) Derive the expression for the entropy function

$s = s(T, v)$, which is valid under the same conditions.

(c) Combining this last result with $dh = Tds + vdP$, derive the corresponding expression for enthalpy, $h = h(T, v)$.

Solution:

(a) Energy

Writing the differential of $u = u(T, v)$, we have

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

$$du = C_v dT + \left[T \left(\frac{\partial s}{\partial v} \right)_T - P \right] dv$$

$$du = C_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

For the $P(v, T)$ equation of state given above,

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{v-b}$$

and

$$\begin{aligned} T \left(\frac{\partial P}{\partial T} \right)_v - P &= \cancel{\frac{RT}{v-b}} - \left(\cancel{\frac{RT}{v-b}} - \frac{a}{v^2} \right) \\ &= \frac{a}{v^2} \end{aligned}$$

Thus

$$du = C_v dT + \frac{a}{v^2} dv$$

Since $u - u_o$ is independent of path, we can choose any convenient path to integrate from (T_o, v_o) to (T, v) .

If we choose two segments, one along an isochor from (T_o, v_o) to (T, v_o) , and one along an isotherm from (T, v_o) to (T, v) , we obtain

$$u - u_o = \int_{T_o}^T C_v dT + \int_{v_o}^v \frac{a}{v^2} dv$$

$$u - u_o = C_V(T - T_o) + a\left(\frac{1}{v_o} - \frac{1}{v}\right)$$

(b) Entropy

The same procedure can be used for deriving the function

$s(T, v)$:

$$\begin{aligned} ds &= \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \\ &= \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv \\ &= \frac{C_v}{T} dT + \frac{R}{v-b} dv \end{aligned}$$

Integrating as before from (T_o, v_o) to (T, v) we obtain

$$s - s_o = C_V \ln\left(\frac{T}{T_o}\right) + R \ln\left(\frac{v-b}{v_o-b}\right)$$

(c) Enthalpy

Starting from $dh = Tds + vdP$ and substituting ds from above and dP from the equation of state, we have:

$$\begin{aligned} dh &= Tds + vdP \\ &= T\left[\frac{C_V}{T} dT + \frac{R}{v-b} dv\right] + v\left[\frac{R}{v-b} dT - \frac{RT}{(v-b)^2} dv + \frac{2a}{v^3} dv\right] \\ &= \left(C_V + R\frac{v}{v-b}\right)dT + \left(\frac{-RTb}{(v-b)^2} + \frac{2a}{v^2}\right)dv \end{aligned}$$

Integrating as before from (T_o, v_o) to (T, v) we obtain

$$\begin{aligned} h - h_o &= RT_o \frac{b(v_o - v)}{(v-b)(v_o-b)} - 2a\left(\frac{1}{v} - \frac{1}{v_o}\right) \\ &\quad + \left(C_V + R\frac{v}{v-b}\right)(T - T_o) \end{aligned}$$

Summary of Energy, Enthalpy, and Entropy Calculations

Closed Symple System	Ideal Gas Limit	Incompressible Limit
$du = c_v dT + \left(\frac{\beta}{K} T - P \right) dv$	$du = c_v dT$	$du = cdT$
$dh = c_p dT + (1 - \beta T) v dP$	$dh = c_p dT$	$dh = cdT + v dP$
$ds = \frac{c_p}{T} dT - \beta v dP$ $ds = \frac{c_v}{T} dT + \frac{\beta}{K} dv$ $ds = \frac{c_p}{v \beta T} dv + \frac{K c_v}{\beta T} dP$	$ds = \frac{c_p}{T} dT - \frac{R}{P} dP$ $ds = \frac{c_v}{T} dT + \frac{R}{v} dv$ $ds = \frac{c_p}{v} dv + \frac{c_v}{P} dP$	$ds = \frac{c}{T} dT$

Generating Thermodynamic Data Tables

- Let's assume the following data are known for a pure substance.

- #1) Vapor-Pressure data (i.e. P_{sat} over a wide range of T_{sat}).
- #2) PvT data in the vapor region (e.g. from measurements of P and T in a closed fixed vessel).
- #3) Density of saturated liquid ($v_f(T_{\text{sat}})$).
- #4) Critical pressure and temperature. (P_c, T_c).
- #5) $C_p^\circ(T)$ at low pressure (1 bar or less).

- From these data, a complete set of thermodynamic tables for saturated liquid, saturated vapor, and superheated vapor can be generated.

Step 1:

- Determine $P=P(v,T)$ equation of state for vapor region from #2. (Can piece together several equations of state if needed.)

Step 2:

- Fit saturation data to $P_{\text{sat}}=P_{\text{sat}}(T_{\text{sat}})$. One common fit is

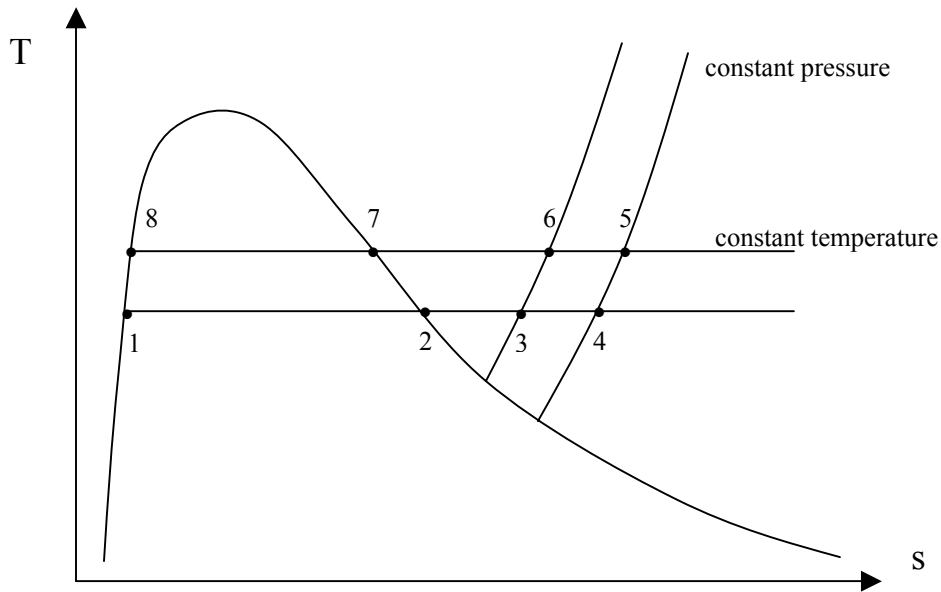
$$\ln(P_{\text{sat}}) = A + \frac{B}{T_{\text{sat}}} + C \ln(T_{\text{sat}}) + D T_{\text{sat}}$$

Step 3:

- Complete P_{sat} using above equation (i.e. fill in between data points).

Step 4:

- Use step 1 to fill in between PTv data points in the vapor region.
- Use steps 1 and 2 to find v_{sat} along vapor side of vapor dome.



Step 5:

- Pick a reference state (“1” in the figure above) and define $h_f=0$, $s_f=0$ at that state. Calculate h_{fg} from the Clapeyron equation:

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{h_{fg}}{T(v_g - v_f)}$$

- $\left(\frac{\partial P}{\partial T}\right)_{sat}$ comes from differentiating the equation from step 2.
- v_g comes from step 4
- v_f is known (#3)
- T is independent

- Thus h_2 can be calculated:

$$h_2 = h_1 + h_{fg} = h_{fg}$$

Step 6:

- Calculate s_2 as follows:
- Since $s_{fg} = h_{fg}/T$,

$$s_2 = s_1 + s_{fg} = h_{fg}/T$$

Step 7:

- Proceed along isotherm to $P=P_3$ (superheated vapor)
- v_3 is known from E.O.S.
- Calculate h_3 and s_3 :

$$h_3 - h_2 = \int_{P_2}^{P_3} [v - \beta T v] dP \quad (\text{along isotherm})$$

$$s_3 - s_2 = - \int_{P_2}^{P_3} \left(\frac{\partial v}{\partial T} \right)_P dP \quad (\text{along isotherm})$$

- Repeat for state 4, where P_4 is low enough to assume ideal gas.

Step 8:

- Proceed up $P=P_4$ (ideal gas) to elevated temperature T_5 .
- Calculate h_5 and s_5 :

$$h_5 - h_4 = \int_{T_4}^{T_5} C_P^\circ dT$$

$$s_5 - s_4 = \int_{T_4}^{T_5} \frac{C_P^\circ}{T} dT$$

Step 9:

- Etc.