

Chapter 11:

Thermodynamic Property Relations

A LITTLE MATH—PARTIAL DERIVATIVES AND ASSOCIATED RELATIONS

Many of the expressions developed in this chapter are based on the **state postulate**, which expresses that the state of a simple, compressible substance is completely specified by any two independent, intensive properties.

Mathematically speaking: $z = z(x, y)$

Most basic thermodynamic relations **involve differentials**.

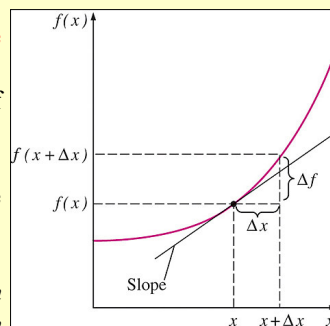
Therefore, we start by reviewing the derivatives of a function f that depends on a **single variable x** .

The **steepness** of the curve is a measure of the **degree of dependence** of f on x .

Therefore, *the derivative of a function $f(x)$ with respect to x represents the rate of change of f with*

x .

$$\frac{df}{dx} = \lim_{\Delta x \rightarrow 0} \frac{\Delta f}{\Delta x} = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}$$



Partial Differentials

Now consider a function that depends on two variables, such as $z=z(x, y)$.

It is sometimes desirable to examine the dependence of z on only one of the variables. This is called the **partial derivative** of z with respect to x , and it is expressed as:

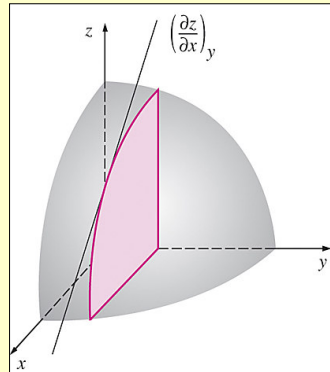
$$\left(\frac{\partial z}{\partial x}\right)_y = \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta z}{\Delta x}\right)_y = \lim_{\Delta x \rightarrow 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x}$$

The symbol d represents the **total** differential change of a function, whereas ∂ represents the **partial** differential change due to the variation of a single variable.

Note that the changes indicated by **both symbol** are identical for independent variables, but not for dependent variables.

For example,

$$(\partial x)_y = dx \quad \text{but} \quad (\partial z)_y \neq dz$$



Partial Differentials

To obtain a relation for the **total differential** change in $z(x, y)$ for simultaneous changes in x and y , consider a small portion of the surface $z(x, y)$ shown

$$\Delta z = z(x + \Delta x, y + \Delta y) - z(x, y)$$

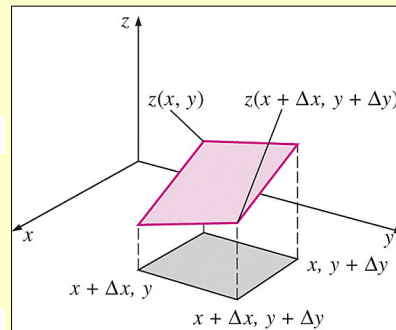
$$\Delta z = z(x + \Delta x, y + \Delta y) - z(x, y + \Delta y)$$

$$+ z(x, y + \Delta y) - z(x, y)$$

or

$$\Delta z = \frac{z(x + \Delta x, y + \Delta y) - z(x, y + \Delta y)}{\Delta x} \Delta x$$

$$+ \frac{z(x, y + \Delta y) - z(x, y)}{\Delta y} \Delta y$$



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

Example 11-2

Total Differential versus Partial Differential

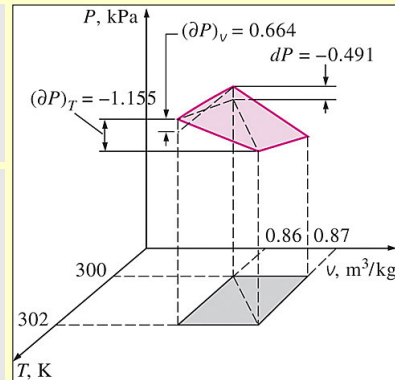
Consider air at 300 K and 0.86 m³/kg. The state of air changes to 302 K and 0.87 m³/kg as a result of some disturbance. Using Eq. 12-3, estimate the change in the pressure of air.

$$\begin{aligned} dP &= \left(\frac{\partial P}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial v}\right)_T dv = \frac{R dT}{v} - \frac{RT dv}{v^2} \\ &= (0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}) \left[\frac{2 \text{ K}}{0.865 \text{ m}^3/\text{kg}} - \frac{(301 \text{ K})(0.01 \text{ m}^3/\text{kg})}{(0.865 \text{ m}^3/\text{kg})^2} \right] \\ &= 0.664 \text{ kPa} - 1.155 \text{ kPa} \\ &= -0.491 \text{ kPa} \end{aligned}$$

$$\left(\frac{\partial P}{\partial T}\right)_v dT = (\partial P)_v = 0.664 \text{ kPa}$$

$$\left(\frac{\partial P}{\partial v}\right)_T dv = (\partial P)_T = -1.155 \text{ kPa}$$

$$dP = (\partial P)_v + (\partial P)_T = 0.664 - 1.155 = -0.491 \text{ kPa}$$



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Partial Differential Relations

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad \text{With Rewriting} \quad dz = M dx + N dy$$

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

Taking the partial derivative of M with respect to y and of N with respect to x yields

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \partial x}$$

Since properties are **continuous point functions** and have exact differentials, the following is true

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

This relation forms the basis for the development of the **Maxwell relations** discussed in the next section.

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Partial Differential Relations

Finally, we develop two important relations for partial derivatives:

the **reciprocity relation**.

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

the **cyclic relation**.

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

○

○

Function: $z + 2xy - 3y^2z = 0$

1) $z = \frac{2xy}{3y^2 - 1} \rightarrow \left(\frac{\partial z}{\partial x}\right)_y = \frac{2y}{3y^2 - 1}$

○

2) $x = \frac{3y^2z - z}{2y} \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = \frac{3y^2 - 1}{2y}$

Thus, $\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y}$

○

○

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Example 11-3

Verification of Cyclic and Reciprocity Relations

Using the ideal-gas equation of state, verify:

- (a) the cyclic relation and
- (b) the reciprocity relation at constant P .

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THE MAXWELL RELATIONS

The equations that **relate** the partial derivatives of properties P , v , T , and s of a simple compressible substance to each other are called the *Maxwell relations*.

They are obtained from *the four Gibbs equations*.
 The first two of the Gibbs equations are those resulting from the internal energy u and the enthalpy h .

$$du = T ds - P dv$$

$$dh = T ds + v dP$$

The second two Gibbs equations result from the definitions of the **Helmholtz** function a and the **Gibbs** function g defined as

$$a = u - Ts$$

$$g = h - Ts$$

$$da = du - T ds - s dT$$

$$dg = dh - T ds - s dT$$

$$da = -s dT - P dv$$

$$dg = -s dT + v dP$$

A **careful examination** of the four Gibbs relations reveals that they are of the form:

$$dz = M dx + N dy$$

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

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THE MAXWELL RELATIONS

The four Gibbs equations.

$$du = T ds - P dv$$

$$dh = T ds + v dP$$

$$dg = -s dT + v dP$$

$$da = -s dT - P dv$$

A **careful examination** of the four Gibbs relations reveals that they are of the form:

$$dz = M dx + N dy$$

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

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

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

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

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

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THE MAXWELL RELATIONS

Setting the **second mixed partial derivatives** equal for these four functions yields the *Maxwell relations*.

$$\begin{aligned} \left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial P}{\partial s}\right)_v \\ \left(\frac{\partial T}{\partial P}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_P \\ \left(\frac{\partial s}{\partial v}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_v \\ \left(\frac{\partial s}{\partial P}\right)_T &= -\left(\frac{\partial v}{\partial T}\right)_P \end{aligned}$$

They are **extremely valuable** in thermodynamics because they provide a means of determining the **change in entropy**, which **cannot be measured directly**, by **simply measuring** the changes in properties P , v , and T .

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Example 11-4

Verification of the Maxwell Relations

Verify the validity of the **last** Maxwell relation for steam at 250°C and 300 kPa.

$$\begin{aligned} \left(\frac{\partial s}{\partial P}\right)_T &\stackrel{?}{=} -\left(\frac{\partial v}{\partial T}\right)_P \\ \left(\frac{\Delta s}{\Delta P}\right)_{T=250^\circ\text{C}} &\stackrel{?}{=} -\left(\frac{\partial v}{\partial T}\right)_{P=300\text{ kPa}} \\ \left[\frac{s_{400\text{ kPa}} - s_{200\text{ kPa}}}{(400 - 200)\text{ kPa}}\right]_{T=250^\circ\text{C}} &\stackrel{?}{=} -\left[\frac{v_{300^\circ\text{C}} - v_{200^\circ\text{C}}}{(300 - 200)^\circ\text{C}}\right]_{P=300\text{ kPa}} \\ \frac{(7.3804 - 7.7100)\text{ kJ/kg} \cdot \text{K}}{(400 - 200)\text{ kPa}} &\stackrel{?}{=} -\frac{(0.87535 - 0.71643)\text{ m}^3/\text{kg}}{(300 - 200)^\circ\text{C}} \\ -0.00165\text{ m}^3/\text{kg} \cdot \text{K} &\cong -0.00159\text{ m}^3/\text{kg} \cdot \text{K} \end{aligned}$$

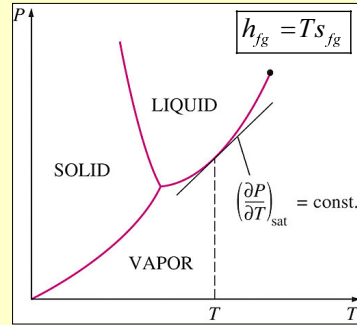
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THE CLAPEYRON EQUATION

The Clapeyron equation enables us to determine the enthalpy change associated with a phase change (such as the **enthalpy of vaporization** h_{fg}) from a knowledge of P , v , and T data alone.

$$\frac{s_{fg}}{v_{fg}} = \left(\frac{dP}{dT} \right)_{sat} \quad \frac{h_{fg}}{Tv_{fg}} = \left(\frac{dP}{dT} \right)_{sat}$$

It enables us to determine the enthalpy of vaporization h_{fg} at a given temperature by simply measuring the **slope of the saturation curve** on a P - T diagram and the specific volume of saturated liquid and saturated vapor at the given temperature.



The Clapeyron equation is applicable to **any phase-change process** that occurs at constant temperature and pressure. It can be expressed in a general form as

$$\frac{h_{12}}{Tv_{12}} = \left(\frac{dP}{dT} \right)_{sat}$$

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Example 11-5

Evaluating the h_{fg} of a Substance from the P - v - T Data

Using the Clapeyron equation, estimate the value of the enthalpy of vaporization of **refrigerant-134a at 20°C**, and compare it with the tabulated value.

$$v_{fg} = (v_g - v_f)_{@ 20^\circ\text{C}} = 0.035969 - 0.0008161 = 0.035153 \text{ m}^3/\text{kg}$$

$$\left(\frac{dP}{dT} \right)_{sat, 20^\circ\text{C}} \cong \left(\frac{\Delta P}{\Delta T} \right)_{sat, 20^\circ\text{C}} = \frac{P_{sat @ 24^\circ\text{C}} - P_{sat @ 16^\circ\text{C}}}{24^\circ\text{C} - 16^\circ\text{C}}$$

$$= \frac{646.18 - 504.58 \text{ kPa}}{8^\circ\text{C}} = 17.70 \text{ kPa/K}$$

since $\Delta T(^{\circ}\text{C}) \equiv \Delta T(\text{K})$. Substituting, we get

$$h_{fg} = (293.15 \text{ K})(0.035153 \text{ m}^3/\text{kg})(17.70 \text{ kPa/K}) \left(\frac{1 \text{ kJ}}{1 \text{ kPa} \cdot \text{m}^3} \right)$$

$$= \mathbf{182.40 \text{ kJ/kg}}$$

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THE CLAPEYRON EQUATION

Clapeyron-Clausius Equation

For liquid-vapor and solid-vapor phase-change processes **at low pressures**, an approximation to the Clapeyron equation can be obtained **by treating the vapor phase as an ideal gas** and neglecting the specific volume of the saturated liquid or solid phase compared to that of the vapor phase. At low pressures

$$\frac{h_{fg}}{Tv_{fg}} = \left(\frac{dP}{dT} \right)_{sat} \quad \begin{array}{l} v_g \gg v_f \\ v_{fg} \cong v_g \\ v_g = \frac{RT}{P} \end{array} \quad \frac{h_{fg}}{T} \frac{1}{P} = \left(\frac{dP}{dT} \right)_{sat}$$

For small temperature intervals, h_{fg} can be treated as a constant at some average value. Then **integrating** this equation between two saturation states yields:

$$\ln \left(\frac{P_2}{P_1} \right)_{sat} \cong \frac{h_{fg}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)_{sat}$$

This equation is called the **Clapeyron–Clausius equation**, and it can be used to determine the **variation of saturation pressure** with temperature. 15

Example 11-6

Extrapolating Tabular Data with the Clapeyron Equation

Estimate the saturation pressure of refrigerant-134a at **-50°F**, using the data available in the refrigerant tables.

$$\ln \left(\frac{P_2}{P_1} \right)_{sat} \cong \frac{h_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)_{sat}$$

In our case $T_1 = -40^\circ\text{F}$ and $T_2 = -50^\circ\text{F}$. For refrigerant-134a, $R = 0.01946$ Btu/lbm · R. Also from Table A-11E at -40°F , we read $h_{fg} = 97.100$ Btu/lbm and $P_1 = P_{sat @ -40^\circ\text{F}} = 7.432$ psia. Substituting these values into Eq. 12-24 gives

$$\ln \left(\frac{P_2}{7.432 \text{ psia}} \right) \cong \frac{97.100 \text{ Btu/lbm}}{0.01946 \text{ Btu/lbm} \cdot \text{R}} \left(\frac{1}{420 \text{ R}} - \frac{1}{410 \text{ R}} \right)$$

$$P_2 \cong \mathbf{5.56 \text{ psia}}$$

Extrapolation does not work !!!

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GENERAL RELATIONS FOR du , dh , ds , c_v , AND c_p

The calculation of the properties that **cannot be measured directly** (such as internal energy, enthalpy, and entropy) **from measurable ones** (such as pressure, temperature, and specific volume) depends on **the availability** of simple and accurate relations between the two groups.

In this section **we develop general relations** for changes in internal energy, enthalpy, and entropy in terms of pressure, specific volume, temperature, and specific heats alone.

We also develop some general relations **involving specific heats**.

We usually **start with** finding the total derivative of $z=z(x,y)$ where z is represented by one of the hard to measure properties (u , h , or s) and x , y are represented by any two of the measurable properties (T , v , or P).

Then, each partial differential term is replaced by other terms of the measurable properties with the help of **the four Gibbs equations** and **the four Maxwell relations**.

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Internal Energy Changes

$$u(T, v)$$

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

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

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

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

$$du = T ds - P dv \quad \text{1st Gibbs equations}$$

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

Maxwell relations.

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

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

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Internal Energy Changes

The change in internal energy of a simple compressible system associated with a change of state from (T_1, v_1) to (T_2, v_2) is determined by integration:

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

In reality, one needs only to determine either $u_2 - u_1$ or $h_2 - h_1$, depending on which is more suitable to the data at hand.

The other can easily be determined by using the definition of enthalpy $h = u + Pv$

Enthalpy Changes and Entropy Changes

We could also find the following relations for dh and ds where $h = h(T, P)$ and $s = s(T, v)$ or $s = s(T, P)$

$$dh = C_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

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

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

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Example 11-7

Internal Energy Change of a van der Waals Gas

Derive a relation for the internal energy change as a gas that obeys the **van der Waals** equation of state. Assume that in the range of interest c_v varies according to the relation $c_v = c_1 + c_2 T$, where c_1 and c_2 are constants.

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

The van der Waals equation of state is

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

Then

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

Thus,

$$T \left(\frac{\partial P}{\partial T} \right)_v - P = \frac{RT}{v - b} - \frac{RT}{v - b} + \frac{a}{v^2} = \frac{a}{v^2}$$

Substituting gives

$$u_2 - u_1 = \int_{T_1}^{T_2} (c_1 + c_2 T) dT + \int_{v_1}^{v_2} \frac{a}{v^2} dv$$

Integrating yields

$$u_2 - u_1 = c_1(T_2 - T_1) + \frac{c_2}{2}(T_2^2 - T_1^2) + a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$$

which is the desired relation.

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Specific Heats c_v and c_p

Recall that the specific heats of an **ideal gas** depend on **temperature only**.

For a general **pure substance**, however, the specific heats depend on specific volume or pressure as well as the temperature.

Below we **present** some general relations to relate the specific heats of a substance to pressure, specific volume, and temperature.

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

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

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

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

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

Let C_{p0} be the **ideal-gas**, zero-pressure, specific heat at constant pressure. The deviation of C_p from C_{p0} is determined **by integrating** from zero pressure to any pressure P along an isothermal path:

$$C_{p,T} - C_{p0,T} = -T \int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$$

Given the equation of state, we can evaluate the right-hand side and determine the actual specific heat as $C_p = C_p(T,P)$.

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Specific Heats c_v and c_p

Another desirable general relation involving specific heats is one that **relates the two** specific heats c_p and c_v .

The **advantage** of such a relation is **obvious**:

We will need to **determine only one** specific heat (usually c_p) and calculate the other one using that relation and the P - v - T data of the substance.

Here we present some general relations to relate these two specific heats to each other as:

$$C_p - C_v = T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v$$

An **alternative** form of this relation is obtained by using the cyclic relation:

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

$$C_p - C_v = \frac{vT\beta^2}{\alpha}$$

where β is the **volume expansivity** and α is the **isothermal compressibility**, defined as:

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P \quad \text{and} \quad \alpha = -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T$$

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Specific Heats c_v and c_p

It is called the **Mayer relation** in honor of the German physician and physicist J. R. Mayer (1814–1878).

$$C_p - C_v = \frac{\nu T \beta^2}{\alpha}$$

We can draw several conclusions from this equation:

1. The **isothermal compressibility** α is a **positive** quantity for all substances in all phases. The **volume expansivity** could be **negative** for some substances (such as liquid water below 4°C), but its square is always positive or zero. The temperature T in this relation is thermodynamic temperature, which is also positive. Therefore we conclude that *the constant-pressure specific heat is always greater than or equal to the constant-volume specific heat*:

$$C_p \geq C_v$$

2. The difference between c_p and c_v approaches zero as the **absolute temperature** approaches zero.

3. The two specific heats are identical for truly incompressible substances since $\nu = \text{constant}$. The difference between the two specific heats is very small and is usually disregarded for substances that are **nearly** ²³ **incompressible**, such as liquids and solids.

Example 11-9

The Specific Heat Difference of an Ideal Gas

Show that $C_p - C_v = R$ for an ideal gas.

$$c_p - c_v = -T \left(\frac{\partial \nu}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial \nu} \right)_T$$

$$P = \frac{RT}{\nu} \rightarrow \left(\frac{\partial P}{\partial \nu} \right)_T = -\frac{RT}{\nu^2} = -\frac{P}{\nu}$$

$$\nu = \frac{RT}{P} \rightarrow \left(\frac{\partial \nu}{\partial T} \right)_P = \left(\frac{R}{P} \right)$$

$$-T \left(\frac{\partial \nu}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial \nu} \right)_T = -T \left(\frac{R}{P} \right)^2 \left(-\frac{P}{\nu} \right) = R$$

$$c_p - c_v = R$$

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THE JOULE-THOMSON COEFFICIENT

When a fluid passes through a restriction such as a porous plug, a capillary tube, or an ordinary valve, its pressure decreases.

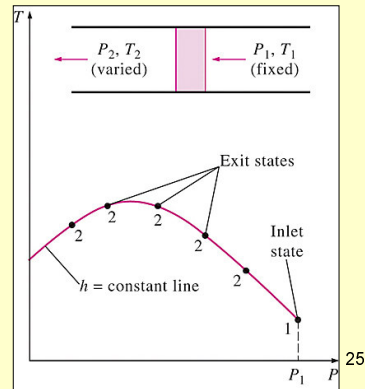
However, the enthalpy of the fluid remains approximately constant during such a throttling process.

You will remember that a fluid may experience a large drop in its temperature as a result of throttling, which forms the basis of operation for refrigerators and air conditioners.

This is not always the case, however. The temperature of the fluid may remain unchanged, or it may even increase during a throttling process.

The temperature behavior of a fluid during a throttling ($h = \text{constant}$) process is described by the **Joule-Thomson coefficient**, defined as:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$



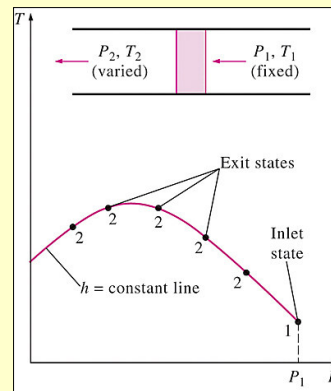
THE JOULE-THOMSON COEFFICIENT

Notice that during a throttling process

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$

$$\mu_{JT} \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

A careful look at its defining equation reveals that the Joule-Thomson coefficient represents the slope of $h = \text{constant}$ lines on a T - P diagram. Such diagrams can be easily constructed from temperature and pressure measurements alone during throttling processes. A fluid at a fixed temperature and pressure T_1 and P_1 (thus fixed enthalpy) is forced to flow through a porous plug, and its temperature and pressure downstream (T_2 and P_2) are measured. The experiment is repeated for different sizes of porous plugs, each giving a different set of T_2 and P_2 . Plotting the temperatures against the pressures gives us an $h = \text{constant}$ line on a T - P diagram, as shown.

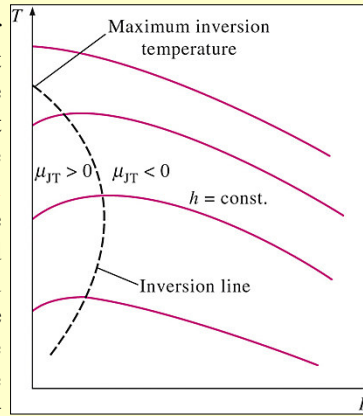


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THE JOULE-THOMSON COEFFICIENT

Repeating the experiment for **different sets of inlet** pressure and temperature and plotting the results, we can construct a T - P diagram for a substance with several $h = \text{constant}$ lines, as shown

Some constant-enthalpy lines on the T - P diagram pass through a point of **zero slope** or zero Joule-Thomson coefficient. The line that passes through these points is called the **inversion line**, and the temperature at a point where a constant-enthalpy line intersects the inversion line is called the **inversion temperature**. The temperature at the intersection of the $P = 0$ line (ordinate) and the upper part of the inversion line is called the **maximum inversion temperature**. Notice that the slopes of the $h = \text{constant}$ lines are negative ($\mu_{JT} < 0$) at states to the right of the inversion line and positive ($\mu_{JT} > 0$) to the left of the inversion line.



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THE JOULE-THOMSON COEFFICIENT

Next we would like to **develop a general relation** for the Joule-Thomson coefficient in terms of the specific heats, pressure, specific volume, and temperature.

This is easily **accomplished** by modifying the generalized relation for enthalpy change

$$dh = C_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

For an $h = \text{constant}$ process we have $dh = 0$.
Then this equation can be rearranged to give

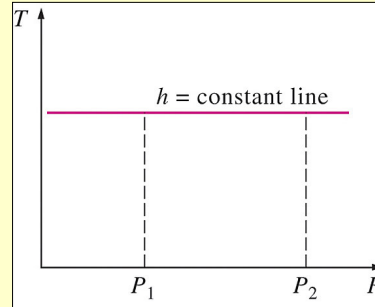
$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$

$$\mu_{JT} = -\frac{1}{C_p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]$$

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Example 11-10
Joule-Thomson Coefficient of an Ideal Gas

Show that the Joule-Thomson coefficient of an ideal gas is zero.



$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P}$$

Substituting this into Eq. 12-52 yields

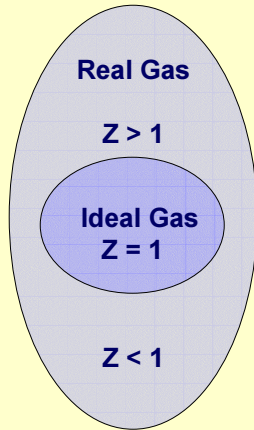
$$\mu_{JT} = \frac{-1}{c_p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] = \frac{-1}{c_p} \left[v - T \frac{R}{P} \right] = -\frac{1}{c_p} (v - v) = 0$$

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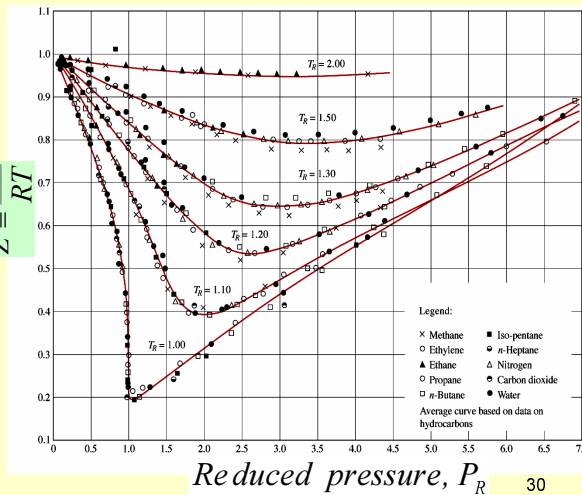
THE Δh , Δu , AND Δs OF REAL GASES

$$\frac{Pv}{RT} = 1 \quad \frac{Pv}{RT} = Z$$

Generalized Compressibility chart



$$Z \equiv \frac{Pv}{RT}$$



Reduced pressure, P_R 30

THE Δh , Δu , AND Δs OF REAL GASES

Enthalpy Changes of Real Gases

$$\bar{h}_2 - \bar{h}_1 = (\bar{h}_2 - \bar{h}_1)_{ideal} - R_u T_{cr} (Z_{h_2} - Z_{h_1})$$

$$h_2 - h_1 = (h_2 - h_1)_{ideal} - RT_{cr} (Z_{h_2} - Z_{h_1})$$

Z_h is the **enthalpy departure factor**.

Figure A-31

Internal Energy Changes of Real Gases

$$\bar{u}_2 - \bar{u}_1 = \bar{h}_2 - \bar{h}_1 - (P_2 \bar{v}_2 - P_1 \bar{v}_1)$$

$$= (\bar{h}_2 - \bar{h}_1) - R_u (Z_2 T_2 - Z_1 T_1)$$

$$u_2 - u_1 = (h_2 - h_1) - R (Z_2 T_2 - Z_1 T_1)$$

The internal energy change of a real gas is given as ($u = h - Pv$)

Entropy Changes of Real Gases

$$\bar{s}_2 - \bar{s}_1 = (\bar{s}_2 - \bar{s}_1)_{ideal} - R_u (Z_{s_2} - Z_{s_1})$$

$$s_2 - s_1 = (s_2 - s_1)_{ideal} - R (Z_{s_2} - Z_{s_1})$$

Z_s is the **entropy departure factor**.

Figure A-32

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Example 11-11

The Δh and Δs of Oxygen at High Pressures

Determine the enthalpy change and the entropy change of **oxygen per unit mole** as it undergoes a change of state from 220 K and 5 MPa to 300 K and 10 MPa

(a) by assuming ideal-gas behavior and

(b) by accounting for the deviation from ideal-gas behavior.

$$(a) \quad \begin{aligned} (\bar{h}_2 - \bar{h}_1)_{ideal} &= \bar{h}_{2,ideal} - \bar{h}_{1,ideal} \\ &= (8736 - 6404) \text{ kJ/kmol} \\ &= \mathbf{2332 \text{ kJ/kmol}} \end{aligned} \quad \begin{aligned} (\bar{s}_2 - \bar{s}_1)_{ideal} &= \bar{s}_2^\circ - \bar{s}_1^\circ - R_u \ln \frac{P_2}{P_1} \\ &= (205.213 - 196.171) \text{ kJ/kmol} \cdot \text{K} - (8.314 \text{ kJ/kmol} \cdot \text{K}) \ln \frac{10 \text{ MPa}}{5 \text{ MPa}} \end{aligned}$$

$$(b) \quad \left. \begin{aligned} T_{R_1} &= \frac{T_1}{T_{cr}} = \frac{220 \text{ K}}{154.8 \text{ K}} = 1.42 \\ P_{R_1} &= \frac{P_1}{P_{cr}} = \frac{5 \text{ MPa}}{5.08 \text{ MPa}} = 0.98 \end{aligned} \right\} Z_{h_1} = 0.53, Z_{s_1} = 0.25 \quad \left. \begin{aligned} T_{R_2} &= \frac{T_2}{T_{cr}} = \frac{300 \text{ K}}{154.8 \text{ K}} = 1.94 \\ P_{R_2} &= \frac{P_2}{P_{cr}} = \frac{10 \text{ MPa}}{5.08 \text{ MPa}} = 1.97 \end{aligned} \right\} Z_{h_2} = 0.48, Z_{s_2} = 0.20$$

$$\begin{aligned} \bar{h}_2 - \bar{h}_1 &= (\bar{h}_2 - \bar{h}_1)_{ideal} - R_u T_{cr} (Z_{h_2} - Z_{h_1}) \\ &= 2332 \text{ kJ/kmol} - (8.314 \text{ kJ/kmol} \cdot \text{K}) [154.8 \text{ K} (0.48 - 0.53)] \\ &= \mathbf{2396 \text{ kJ/kmol}} \end{aligned}$$

$$\begin{aligned} \bar{s}_2 - \bar{s}_1 &= (\bar{s}_2 - \bar{s}_1)_{ideal} - R_u (Z_{s_2} - Z_{s_1}) \\ &= 3.28 \text{ kJ/kmol} \cdot \text{K} - (8.314 \text{ kJ/kmol} \cdot \text{K}) (0.20 - 0.25) \\ &= \mathbf{3.70 \text{ kJ/kmol} \cdot \text{K}} \end{aligned}$$

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