Energy, Work, and Heat

- Consider energy and molecules.
  - Energy affects how molecules react. In particular the distribution of energy within a molecule influences how it behaves both chemically and physically.
- How do molecules have energy?
  - In chemical bonds. The more energy required to break a bond, the stronger the bond is.
  - In internal motions (such as vibration and rotation) and electronic excitations.
  - As kinetic energy of motion. Temperature is a way of measuring the average kinetic energy of a system of molecules at equilibrium.

Energy (from a Thermodynamic Perspective)

- Consider the exothermicity of a chemical reaction.
  - Food Calories
  - Fuel Combustion

  - Corrosion
  - Decomposition
- Energy is considered on a scale related to changes, not an absolute scale.
- In thermodyamics, two particular forms of energy are considered:
  - q heat
  - w work

What is energy?

- What are the properties of energy?
  - Cannot be created or destroyed
  - Can only change form such as be converted to heat, work, or internal energy.

First Law of Thermodynamics

- Energy is conserved.
- Energy is not created or destroyed.

What are “Laws of Thermodynamics”?

- The ”Laws of Thermodynamics” are a set of postulates from which theorems and other relationships may be derived.

The transfer of energy called work

- Work is only associated with the performance of a thermodynamic process.

- Some "types" of work:
    - mechanical
    - electrical
    - magnetic
    - gravitational
    - surface
- In this chapter, work will usually be in the form of mechanical work being done by or on a system.
- What is a system?

Systems

- Open - transfers mass and energy to and from the surroundings.
- Closed - does not transfer mass to or from the surroundings.
- Isolated - transfers neither mass or energy to or from the surroundings.

Surroundings

- Since we are dealing with equilibrium thermodynamics, the state variables describing the surroundings may be of interest.
    - For example, consider the temperature of a constant temperature bath. A process carried out at constant temperature is isothermal.

The variation of work with the path

- Work is a path function.
- How the work is done matters.

$$\text{work} = \int_{path} \mathbf{F}(\mathbf{r}) \cdot d\mathbf{r}$$

    - $\mathbf{F}(\mathbf{r})$ is the force vector which varies with $\mathbf{r}$
    - Both force and displacement have the same direction.
- Consider pressure volume work:
    - Ideal gas at P_i =1 atm confined in cylinder of volume V_i by a piston of area A.
    - This ideal piston at $x = x_0$ has no mass, no friction, and does not leak.
    - Surroundings include a constant temperature bath at temperature T_i.
    - Drop a brick on the piston, instantaneously increasing the pressure to P_f

How much work is done?

- Consider:
    - What is the force?
    - What is the displacement?

- The force is:

$$P_{ext} = \; P_i \; + \; \frac{Mg}{A}$$

  or

$$F(x) = P_i A + Mg$$

  - Note that $F(x)$ in this case is a constant independent of position.
  - Note that the direction of the force is downward, thus there is a negative sign since the x axis is positive upward.
- The displacement is the distance h, which the distance that the piston moved down when the brick was dropped on it.
  - The initial position of the piston is x_0.
  - The final position if $x_0 - h$.
- Therefore the work is:

$$\begin{aligned} w &= \int_{path} \mathbf{F}(\mathbf{r}) \cdot d\mathbf{r} = -\int_{path} F(x)dx \\ &= -\int_{x_0}^{x_0-h} (P_i A + Mg)\, dx \\ &= -(P_i A + Mg) \int_{x_0}^{x_0-h} dx \\ &= -(P_i A + Mg)(-h) \\ w &= (P_i A + Mg)\, h \end{aligned}$$

- The volume change during this process is:

$$\Delta V \; = \; V_f \; - \; V_i \; = \; A(x_0 \; - \; h) \; - \; Ax_0 \; = \; -Ah$$

- Therefore:

$$w = -\left(P_i + \frac{Mg}{A}\right) \Delta V = -P_{ext}\Delta V$$

Thermodynamic Sign Convention for Work

- Work is positive when work is done on the system.
- Work is negative when work is done by the system.
- The magnitude of work can be considered as the area in PV space under the curve representing the path.
  - This area will vary with the path, which is consistent with work being a path function.
- Consider now some different paths from (P_i, V_i) to (P_f, V_f). Recall that the process is isothermal since there is a constant temperature bath as surroundings.
  - Path 1: Break the brick in half and change the pressure in two steps.
  - Path 2: Crumble the brick to dust and change the pressure in very small increments by adding the dust one grain at a time.
- Which path gives the minimum amount of work to be done on the system?

Reversible Isothermal Work

- If the work is carried out in infinitesimal steps infinitely slowly, then the process is quasi-static.
- For such a process, deviations from equilibrium are infinitesimal.
- Therefore all points on the path may be described by the equation of state for the system.

- Consider an ideal gas undergoing reversible, isothermal expansion from (P_i, V_i) to (P_f, V_f). Therefore:

$$w = -\int_{V_i}^{V_f} P_{sys}(V)dV = -nRT\int_{V_i}^{V_f} \frac{dV}{V}$$

$$= -nRT\ln\left(\frac{V_f}{V_i}\right)$$

  - If the process is a compression (i.e. V_f smaller than V_i), work is positive and work is done on the system.
  - If the process is an expansion (i.e. V_f larger than V_i), work is negative and work is done by the system.
- Now consider a cyclic process.
  - First the gas is compressed isothermally at P_f from V_i to V_f.
  - Then the gas is expanded at P_i from V_f to V_i.
  - Therefore there is no overall change in state.
- What is the work done by or on the system over this path?
- What if the path were followed in the opposite direction?

The Transfer of Energy called Heat

- Consider the compression of a gas.
- What would happen if, instead of carrying out this process in a closed system in contact with a constant temperature bath, the process were carried out in an isolated system?
  - Would the temperature stay constant? Why or why not?
  - Compared to the isothermal reversible path, would more or less work be done on the system?

What is the Thermodynamic Definition of Temperature?

- Consider an ideal gas at reference temperature. his reference temperature has to be readily accessible experimentally. The triple point of water is convenient. By definition, the temperature is 273.16 K.

- Consider the PV product of any real gas at this temperature. Then the temperature can be defined as:

$$\frac{T}{273.16} = \lim_{P\to 0}\frac{(PV)_T}{(PV)_{273.16}}$$

- Consider the compression of an isolated system.
  - Will the (PV) product be higher or lower than that for a reversible isothermal compression starting at the same pressure and volume and going to the same final volume?
- When work is done by or on an isolated system, the process is called *adiabatic*.

  - In an adiabatic process no energy has been exchanged with the surroundings.
- Adiabatic work from a particular starting point to a particular final point is independent of the path.
  - Therefore adiabatic work must be a state function.

Internal Energy

- Internal energy is symbolized by U.
- Defined with respect to work done on an adiabatic path.

$$\Delta U = U_f - U_i = \int_{U_i}^{U_f} dU = \int_{\text{adiabatic path}} dw = w_{ad}$$

- Can we get to any state (P_f, V_f) on an adiabatic path?
  - Not all final states can be reached by an adiabatic path.
  - But if U is a state function, we need to be able to define ΔU for the change from any initial state to any final state. Therefore we must consider other types of processes, which can involve the transfer of heat.
- Heat is any form of energy transferred by a process other than work.
  - Recall that heat q is a path function.
- Consider heat along at path at constant volume.
  - Consider a gas cylinder with the piston fixed in position.

  - Apply a source of energy.
  - The temperature will rise.
  - This path does not involve work.
- For heat at constant volume, no work is done since $\Delta V = 0$.

$$\Delta U_V = U_f - U_i = \int_{U_i}^{U_f} dU$$

$$= \int_{\text{constant volume path}} dq = q_V$$

  - Therefore constant volume heat q_V is equivalent to the change in the state function internal energy (ΔU_V).

Thermodynamic sign convention for heat

- Heat is positive when energy is transferred to the system from the surroundings.
- Heat is negative when energy is transferred from the system to the surroundings.

- Internal energy of a system changes due to the additive effects of heat and work associated with a thermodynamic process:

$$dU = dq + dw$$

or in integrated form:

$$\Delta U = \int_{path} dq + \int_{path} dw$$

Cycles

- Associated with a cycle:
  - What would be ΔU?
  - What would be the work?
  - What would be the heat?

Simple Consequences of the First Law

- The transfer of heat alone often results in a change in temperature with the change in temperature being proportional to the heat transferred:

$$dq = CdT$$

- The proportionality factor, C is the heat capacity, which depends on the materials constituting the system and on the path of the process.
  - C_V is associated with a constant volume path.
  - C_P is associated with a constant pressure path.
- For an ideal gas statistical mechanics shows:

$$C_V = \frac{3}{2}nR \text{ or } \frac{\overline{C}_V}{R} = \frac{C_V}{nR} = \frac{3}{2}$$

$$C_P = \frac{5}{2}nR \text{ or } \frac{\overline{C}_P}{R} = \frac{C_P}{nR} = \frac{5}{2}$$

- Combined with our earlier expression for ΔU, we get:

$$\Delta U = \int_{path} dq + \int_{path} dw$$

$$= \int_{path} C_{path} dT - \int_{path} P_{ext} dV$$

- The expression for ΔU indicates that U varies with T and V, i.e. $U = U(T, V)$.

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Therefore:

$$dU = C_{path}\ dT - P_{ext}\ dV$$

  - If $\Delta V = 0$ then:

$$dU_V = \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dU_V = C_V dT$$

Therefore:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

- Suppose $dT = 0$. Then:

  $$dU = \left(\frac{\partial U}{\partial V}\right)_T dV$$

  but

  $$dU = C_{path}\ dT - P_{ext}\ dV$$

  retains both terms, since in order for $C_{path}\ dT$ to be zero, the path must be adiabatic and both T and V change on an adiabatic path.

The Joule Expansion

- What about $(\partial U/\partial V)_T$?
- Joule did some experiments to attempt to measure it. See Fig. 2.6.
  - Constant temperature maintained by a water bath.
  - Two chamber vessel
  - Volume of both chambers known
  - One chamber at high P
  - Other chamber at $P_{ext} \approx 0$
  - Chambers separated by stopcock
- Stopcock opened, gas expands against $P_{ext} \approx 0$
  - Therefore no work done
  - No temperature change observed.

- Problems with experimental design:
  - Temperature change may have been too small to observe.
  - Make the system bigger
  - Make the water bath smaller
- BUT conclusion is valid.
  - Rigorously for an ideal gas:

    $$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

  - In the low pressure limit for a real gas:

    $$\lim_{P\to 0}\left(\frac{\partial U}{\partial V}\right)_T = 0$$

General Adiabatic Processes

- Consider an adiabatic process.
  - Along the path of this process $dq = 0$.
  - Therefore $CdT = 0$, even though $dT \neq 0$.
  - Therefore $C_{ad} = 0$.

- For this path

$$dU_{ad} = -P_{ext}dV = dw_{ad}$$

- But for any path:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

  - We have already shown for an ideal gas that:

$$\left(\frac{\partial U}{\partial V}\right)_T \; = \; 0$$

  Therefore, for an ideal gas:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_v dT = \frac{3}{2}nRdT$$

- Thus:

$$\int dU_{ad} = \Delta U_{ad} = w_{ad} = \int C_v dT = \frac{3}{2}nR\Delta T$$

- Consider an adiabatic process with constant P_{ext}:

$$w_{ad} = -P_{ext}\Delta V$$

  - With the previous equation this gives:

$$\Delta T = -P_{ext}\frac{\Delta V}{C_v} = -\frac{2}{3}\frac{P_{ext}\Delta V}{nR}$$

- Consider adiabatic expansion against zero external pressure $P_{ext} = 0$:
  - Then $w_{ad} = 0$, $\Delta T = 0$ and this is the Joule experiment run adiabatically.
- Consider an adiabatic process with constant P_{ext}:

$$w_{ad} = -P_{ext}\Delta V$$

$$\Delta T = -P_{ext}\frac{\Delta V}{C_v} = -\frac{2}{3}\frac{P_{ext}\Delta V}{nR}$$

  - If ΔV is negative, a compression has occurred and w_{ad} and ΔT are positive.
  - If ΔV is positive, an expansion has occurred and w_{ad} and ΔT are negative.
- When w_{ad} is positive, energy has been put into the system.
  - Since the process is adiabatic, energy cannot escape as heat.
  - Therefore a temperature change occurs, the magnitude of which is controlled by the heat capacity.

Adiabatic Reversible Processes in an Ideal Gas

- Assume an ideal gas, therefore $PV = nRT$
- Reversible, therefore $P_{ext} = P_{sys} + dP$
- Adiabatic, therefore $dq = 0$.

- At all points of this path:

  $$dU = dw_{ad}$$

  $$C_V dT = -P_{sys} dV = \frac{-nRT}{V} dV$$

  Therefore:

  $$C_V \frac{dT}{T} = -nR\frac{dV}{V}$$

  Integration over the path yields:

  $$\int_{T_i}^{T_f} C_V \frac{dT}{T} = \int_{V_i}^{V_f} -nR\frac{dV}{V}$$

  $$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

  $$C_V \ln\left(\frac{T_f}{T_i}\right) = -nR\ln\left(\frac{V_f}{V_i}\right)$$

- Recall for an ideal gas that $C_V = 3nR/2$. Thus:

  $$\frac{3}{2}nR\ln\left(\frac{T_f}{T_i}\right) = -nR\ln\left(\frac{V_f}{V_i}\right)$$

  - Dividing through by nR and recognizing that $\ln(1/x) = -\ln x$ gives:

    $$\frac{3}{2}\ln\left(\frac{T_f}{T_i}\right) = -\ln\left(\frac{V_f}{V_i}\right) = \ln\left(\frac{V_i}{V_f}\right)$$

  - Dividing through by $3/2$ and recognizing that $a\ln x = \ln x^a$ gives:

    $$\ln\left(\frac{T_f}{T_i}\right) = \frac{2}{3}\ln\left(\frac{V_i}{V_f}\right) = \ln\left(\frac{V_i}{V_f}\right)^{2/3}$$

    or

    $$T_f = T_i\left(\frac{V_i}{V_f}\right)^{2/3}$$

- We now have an equation to describe our reversible adiabatic path for an ideal gas.

  $$T_i\ V_i^{2/3}\ =\ T_f\ V_f^{2/3}$$

- If T and V are known and since the equation of state holds along a reversible path, then P can be determined.

  - Substituting PV/nR for T gives:

    $$\left(\frac{P_i\ V_i}{nR}\right)\ V_i^{2/3}\ =\ \left(\frac{P_f\ V_f}{nR}\right)\ V_f^{2/3}$$

  - Factoring out nR on both sides gives:

    $$P_i\ V_i^{5/3}\ =\ P_f\ V_f^{5/3}$$

    or

    $$P\ V^{5/3}\ = \text{constant}$$

- The factor 5/3 is usually represented as γ can can be shown to originate from $(C_V + nR)/C_V$.
  - But $C_P = C_V + nR$, thus

    $$\gamma = \frac{C_P}{C_V}$$

    and

    $$PV^\gamma = \text{constant}$$
    $$TV^{\gamma-1} = \text{constant}$$

- Similarly, substituting nRT/P for V gives a relation between T and P:

$$T_i \left(\frac{nRT_i}{P_i}\right)^{\gamma-1} = T_f \left(\frac{nRT_f}{P_f}\right)^{\gamma-1}$$
$$\frac{T_i^\gamma}{P_i^{\gamma-1}} = \frac{T_f^\gamma}{P_f^{\gamma-1}}$$
$$\frac{T_i^{\gamma/(\gamma-1)}}{P_i} = \frac{T_f^{\gamma/(\gamma-1)}}{P_f}$$

Paths Equivalent to an Adiabatic Path

- Referring to Figure 2.7 on page 50 of Winn, consider the adiabatic reversible path I between an initial state (P_i, V_i) and final state (P_f, V_f) of an ideal gas.
  - We wish to determine ΔU_I associated with this change.
- Since U is a state function, we can construct any alternate path we deem convenient.
  - An especially convenient path consists of a path II from (P_i, V_i) to final V_f along an isotherm, followed by path III along an isochore (constant volume) to (P_f, V_f).
  - These path segments are especially convenient because it is very easy to determine ΔU_{II} and ΔU_{III}.
- For the any isothermal change in state of an ideal gas, there is no change in U. Therefore $\Delta U_{II} = 0$.
- For a constant volume change in an ideal gas, the change in U is determined by the constant volume heat capacity and the temperature change. Therefore:

  $$\Delta U_{III} = C_V(T_f - T_i)$$

  Thus:

  $$\Delta U_I = \Delta U_{II} + \Delta U_{III} = 0 + C_V (T_f - T_i)$$

Closer Look at the Meaning of Adiabaticity

- A real process approaches adiabaticity if it is carried out sufficiently quickly that the process is over before heat has had a chance to transfer to or from the surroundings.
- Examples:
- Expansion of compressed gas from a cylinder.
  - The valve can be observed to "ice" up.
- Air masses in meteorology.
  - As air rises, it cools adiabatically since air itself does not transfer heat readily.

  - If the air mass was not dry, this cooling can lead to precipitation.

A New State Function, Enthalpy

- Constant pressure conditions are encountered far more frequently than constant volume conditions.
  - We already have C_p which is the heat capacity along a path of constant pressure.
  - Recall $dq_p = C_p dT$.
  - Enthalpy is to constant pressure conditions what internal energy is to constant volume conditions.
- Consider $U + PV$. The corresponding total differential is:

$$d(U + PV) = dU + PdV + VdP$$

$$= dq - P_{ext}dV + PdV + VdP$$

- At constant pressure, $dP = 0$ and $P = P_{ext}$. Therefore:

$$d(U + PV) = dq - P_{ext}dV + P_{ext}dV + VdP$$

$$d(U + PV)_P = dq_P$$
$$H \equiv U + PV$$

  Consequently,

$$dH_P = dq_P = C_P dT$$

  and:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p$$

- If an ideal gas is under consideration, then

$$PV = nRT$$

  and

$$H(\text{ideal gas}) = U(\text{ideal gas}) + PV$$

  or

$$H = U + nRT.$$

- In differential form this becomes:

$$dH = dU + nRdT$$

  or:

$$C_P dT = C_V dT + nRdT$$

  Thus:

$$C_P - C_V = nR$$

  for an ideal gas.

- Although $H(P, T)$ has been defined with regard to constant pressure processes, it is a state function.
  - Therefore ΔH can be calculated for any change regardless of path followed by the process.

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

$$= C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

- Now consider $(\partial H/\partial T)_V$:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_P + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

  - What about $(\partial H/\partial T)_P$?
  - Recall the cyclic rule:

$$-1 = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial H}\right)_T$$

  - Thus:

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

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

  (A process during which dH = 0 is an isenthalp.)

- Therefore:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_P - C_P \left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial T}\right)_V$$

$$= C_P \left[1 - \left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial T}\right)_V\right]$$

- How is $(\partial T/\partial P)_H$ evaluated?

The Joule-Thomson Effect (Fig 2.8)

- Joule and Thomson devised an experiment that involved constant enthalpy.
  - Apparatus is insulated, therefore the process is adiabatic.
  - Two pistons and a porous wall.
  - Start with all the gas on left side of the wall at (P_i, V_i, T_i).
  - Push the gas through the porous wall with the left piston, while at the same time withdrawing the right piston, so as to maintain constant pressure.
  - Reach final state with the gas to the right side of the wall at (P_f, V_f, T_f).
  - Adiabatic, therefore $q = 0$. Thus:

$$\Delta U = w_{ad}$$

- The work must be considered in two parts.
  - The gas is compressed by the first piston to the barrier.
  - The work associated with this is $P_i V_i$, since the gas is compressed at constant P_i from V_i to zero.
  - The gas is expanded by the second piston at P_f from zero to V_f.
  - Therefore $-P_f V_f$ is the work associated with this.
  - Thus $w_{ad} = P_i V_i - P_f V_f = \Delta U$.
  - But $\Delta U = U_f - U_i$.

- Therefore:

$$U_i + P_i V_i = U_f + P_f V_f$$

$$H_i = H_f$$

- Since $\Delta H = 0$, the process is isenthalpic.

- Final temperature is measured at various final pressures for the same initial pressure and temperature.
  - The result is a temperature pressure isenthalp.
  - The slope of this $(\partial T/\partial P)_H$ is the Joule-Thompson coefficient:

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

  - $\mu_{JT}(T,P) = 0$ for an ideal gas.
  - The deviation of $\mu_{JT}(T,P)$ from zero contains information about the nonideal behaviour of the gas.
- In chapter 3, it will be shown that:

$$\mu_{JT}(T,P) = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

  - Recall the virial equation of state, through to the second virial coefficient:

$$\frac{P\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}}$$

  - This can be rearranged to:

$$\frac{RT}{P\overline{V}} = \frac{1}{1 + \frac{B(T)}{\overline{V}}}$$

  - If $\overline{V} >> B$, then this becomes:

$$\frac{RT}{P\overline{V}} = 1 - \frac{B(T)}{\overline{V}}$$

  - Multiplying through by $\overline{V}$ gives:

$$\frac{RT}{P} = \overline{V} - B(T)$$

  or

$$\overline{V} = \frac{RT}{P} + B(T)$$

  - Therefore:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \left(\frac{\partial B}{\partial T}\right)_P$$

  - Substituting this into the expression for μ_{JT} yields:

$$\mu_{JT}(T,P) = \frac{1}{C_P}\left[T\left(\frac{\partial B}{\partial T}\right)_P - B\right]$$

  - When $B = T\left(\partial B/\partial T\right)_P$, then $\mu_{JT} = 0$. The temperature at which that occurs is the Joule-Thomson inversion temperature, T_I.

- Recall that for the van der Waals virial expression,

$$B(T) = b - \frac{a}{RT}$$

  - Then at T_I,

$$b - \frac{a}{RT_I} = T_I\left(\frac{a}{RT_I^2}\right)$$

    and

$$T_I = 2\left(\frac{a}{Rb}\right) = 2T_B$$

- Below T_I gases cool when expanded.
- Above T_I gases warm up when expanded.
- Real gases exhibit a range of inversion temperatures that depend on initial pressure.
  - The van der Waals equation of state predicts:

$$\tilde{P} = \left[3\left(\frac{\tilde{T}}{2}\right)^{1/2} - 1\right]\left[1 - \left(\frac{\tilde{T}}{2}\right)^{1/2}\right]$$

- Recall

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

  Then

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_P\mu_{JT}$$

- Recall also:

$$\begin{aligned}\left(\frac{\partial H}{\partial T}\right)_V &= C_P - C_P\left(\frac{\partial T}{\partial P}\right)_H\left(\frac{\partial P}{\partial T}\right)_V \\ &= C_P\left[1 - \left(\frac{\partial T}{\partial P}\right)_H\left(\frac{\partial P}{\partial T}\right)_V\right]\end{aligned}$$

  This becomes:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_P\left[1 - \mu_{JT}\left(\frac{\partial P}{\partial T}\right)_V\right]$$

- The differential is:

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

  which becomes:

$$dH = C_P dT - C_P\mu_{JT} dP$$