

February 6, 2014

Example 1: Given Argonum (*Ar*) at $P_1 = 140 \text{ kPa}$, $T_1 = 10^\circ\text{C}$, $V_1 = 200 \text{ liters}$ which undergoes a polytropic compression to $P_2 = 700 \text{ kPa}$, $T_2 = 180^\circ\text{C}$, find Q_1^2 .

In order to calculate Q_1^2 , we will need to invoke the first law,

$$U_2 - U_1 = Q_1^2 - W_1^2$$

For ideal gases, we need to calculate ΔU (based on ΔT) and we can easily compute W_1^2 from its definition as $\int_1^2 P dV$. Using the following data for noble gas *Ar*:

$$MW^1 = 39.948 \text{ kg. (kmole)}^{-1} \quad R = 0.2081 \text{ kJ. (kg.K)}^{-1} \quad C_v = 0.312 \text{ kJ. (kg.K)}^{-1}$$

The mass of *Ar* can be calculated from state 1:

$$m = \frac{P_1 V_1}{R T_1} = \frac{(140 \text{ kPa})(0.2 \text{ m}^3)}{\left(0.2081 \frac{\text{kJ}}{\text{kg.K}}\right)(283.15 \text{ K})} = 4.75192 \times 10^{-1} \text{ kg}$$

The volume at state 2 can be easily calculated as,

$$P_2 V_2 = m R T_2 \\ V_2 = \frac{(4.75192 \times 10^{-1} \text{ kg}) \left(0.2081 \frac{\text{kJ}}{\text{kg.K}}\right) (453.15 \text{ K})}{700 \text{ kPa}} = 6.40155 \times 10^{-2} \text{ m}^{-3}$$

For polytropic processes,

$$P_i V_i^n = \text{constant} = C \\ \frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^n \\ \ln\left(\frac{P_1}{P_2}\right) = \ln\left(\frac{V_2}{V_1}\right)^n \\ n = \frac{\ln\left(\frac{P_1}{P_2}\right)}{\ln\left(\frac{V_2}{V_1}\right)} = 1.41279$$

So the work in polyprotic processes can be defined as,

$$W_1^2 = \int_1^2 \frac{C}{V^n} dV = C \int \frac{dV}{V^n} \\ \frac{C}{1-n} V^{(1-n)} \Big|_1^2 = \frac{C}{1-n} \left(V_2^{(1-n)} - V_1^{(1-n)}\right)$$

¹MW: Molecular weight; R: Universal gas constant; C_v : Heat capacity at constant volume.

As $C = P_1V_1 = P_2V_2$,

$$W_1^2 = \frac{P_2V_2 - P_1V_1}{1-n} = -40.7251\text{kJ}$$

The work is negative \Rightarrow Ar was worked upon in compression. From the first law,

$$\begin{aligned} U_2 - U_1 &= Q_1^2 - W_1^2 \\ Q_1^2 &= U_2 - U_1 + W_1^2 \end{aligned}$$

Assuming that Ar behaves like an ideal gas, i.e., $u = u(T)$ (with $u = \frac{U}{m}$),

$$\frac{du}{dT} = C_v$$

and hence,

$$\begin{aligned} Q_1^2 &= mC_v(T_2 - T_1) + W_1^2 \\ &= (4.75192 \times 10^{-1}\text{kg}) (0.312\text{kJ.(kg.K)}^{-1}) (453.15\text{K} - 283.15\text{K}) + (-40.7251\text{kJ}) \\ &= \color{red}{-15.5209\text{kJ}} \end{aligned}$$

The variation of heat (or heat transfer) is negative \Rightarrow heat was lost from the system although temperature increased. This is because the raise in internal energy was mainly due to work than by the heat exchanged.

Example 2: Given air (assuming ideal gas behaviour) expanding reversibly and adiabatically from $T_1 = 450\text{K}$ and $V_1 = 3.0 \times 10^{-3}\text{m}^3$ to the final volume, $V_2 = 5.0 \times 10^{-3}\text{m}^3$. T and V relationship for constant heat capacities is represented by

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

(a) Derive a relationship between T and P ; Assuming that $C_p = 5.0\text{cal.(mol.K)}^{-1}$ and $C_v = 3.0\text{cal.(mol.K)}^{-1}$, calculate (b) T_2 , (c) the work done during the process and the (d) enthalpy change.

The total energy change, ΔE can be split into

$$\Delta E = \Delta E_K + \Delta E_P + \Delta U = Q - W$$

where ΔE_K , ΔE_P and ΔU represent the change in kinetic, potential and internal energy, respectively. Assuming that the expansion process, the sum of the kinetic and potential energies of the system does not change,

$$\Delta E = \Delta U = Q - W$$

or in differential form

$$dU = \delta Q - \delta W$$

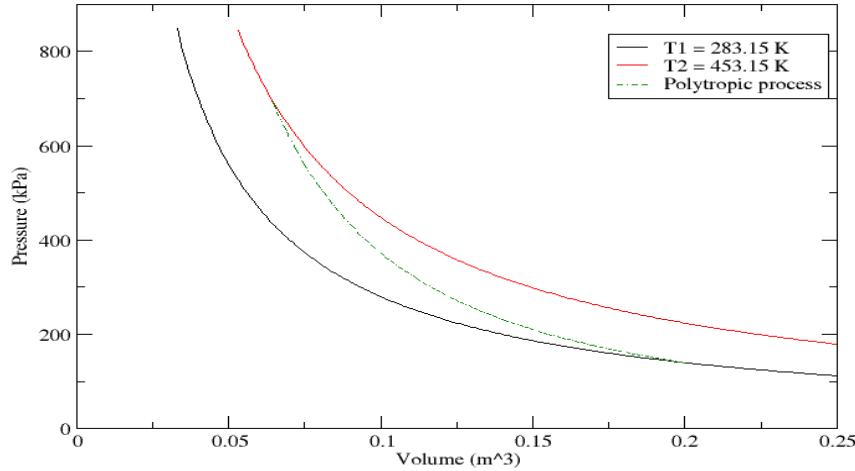


Figure 1: Polytropic compression of argonium (green) from state 1 ($V_1 = 0.2m^3$) to 2 ($V_2 = 6.40 \times 10^{-2}m^3$). Ideal processes with isothermal temperature $T_1 = 10^\circ\text{C}$ (black) and $T_2 = 180^\circ\text{C}$ (red).

and all energy exchange with the surroundings are used to only change the internal energy. As the process is adiabatic ($Q = 0$),

$$dU = -\delta W = -PdV$$

Since the gas is ideal, $dU = C_v dT = -PdV$ and,

$$V = \frac{RT}{P}$$

and applying the chain rule to $V = V(T, P)$

$$dV = \frac{\partial V}{\partial T}dT + \frac{\partial V}{\partial P}dP = -\frac{RT}{P^2}dT + \frac{R}{P}dP$$

thus replacing dV ,

$$C_v dT = -PdV = -P \left[-\frac{RT}{P^2}dT + \frac{R}{P}dP \right] = RT \frac{dP}{P} - RdT$$

Since $C_p - C_v = R$ and replacing C_v in the equation above,

$$C_p dT = RT \frac{dP}{P} \Rightarrow \frac{dT}{T} = \frac{R}{C_p} \frac{dP}{P} \Rightarrow \frac{dT}{T} = \frac{C_p - C_v}{C_p} \frac{dP}{P} = \left(\frac{\gamma - 1}{\gamma} \right) \frac{dP}{P}$$

where $\gamma = C_p/C_v$. Integrating from state 2 to 1:

$$\ln \frac{T_2}{T_1} = \left(\frac{\gamma - 1}{\gamma} \right) \ln \frac{P_2}{P_1} \quad \text{or}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}}$$

Temperature, T_2 is obtained from

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = (450 \text{ K}) \left[\frac{3.0 \times 10^{-3} \text{ m}^3}{5.0 \times 10^{-3} \text{ m}^3} \right] \left(\frac{5.0 \text{ cal. (mol.K)}^{-1}}{3.0 \text{ cal. (mol.K)}^{-1}} - 1 \right)$$

$$\color{red} T_2 = 320.12 \text{ K}$$

The work done during the process is,

$$W = -\Delta U = -C_v \Delta T = \left[-3.0 \text{ cal. (mol.K)}^{-1} \right] (320 - 450 \text{ K})$$

$$\color{red} W = 390 \frac{\text{cal}}{\text{mol}} = 1632.85 \frac{\text{J}}{\text{mol}}$$

$W > 0$ indicates that in the expansion process, work is done by the system. The enthalpy change of the gas can be calculated as,

$$\Delta H = C_p \Delta T = \left[5.0 \text{ cal. (mol.K)}^{-1} \right] (320 - 450 \text{ K})$$

$$\color{red} \Delta H = -650 \frac{\text{cal}}{\text{mol}} = -2721.42 \frac{\text{J}}{\text{mol}}$$

Problem 1: Gaseous CO₂ ($m_{CO_2} = 4g$) is contained in a vertical piston-cylinder assembly by a piston of mass 50 kg and having a face area of $1.0 \times 10^{-2} m^2$. The CO₂ initially occupies a volume of $5 \times 10^{-3} m^3$ and has a specific internal energy of 657 kJ.kg^{-1} . The atmosphere exerts a pressure of 100 kPa on the top of the piston. Heat transfer in the amount of 1.95 kJ occurs slowly from the CO₂ to the surroundings, and the volume of the CO₂ decreases to $2.5 \times 10^{-3} m^3$. Friction between the piston and the cylinder wall can be neglected. The local acceleration of gravity is 9.81 m.s^{-2} . For the CO₂, determine (a) the pressure in kPa and (b) the final specific internal energy in kJ.kg^{-1} .

Problem 2: CO gas contained within a piston-cylinder assembly undergoes three processes in series:

Process 1-2: expansion from $p_1 = 5 \text{ bar}$, $V_1 = 0.2 \text{ m}^3$ to $V_2 = 1.0 \text{ m}^3$, during which the pressure-volume relationship is $pV = \text{constant}$.

Process 2-3: constant volume heating from state 2 to state 3, where $p_3 = 5 \text{ bar}$.

Process 3-1: constant pressure compression to the initial state.

Sketch the processes in series on p-V coordinates and evaluate the work for each process, in kJ.

Problem 3: A reversible power cycle receives 100 kJ by heat transfer from a hot reservoir at 327°C and rejects 40 kJ by heat transfer to a cold reservoir at T_{cold} . Determine:

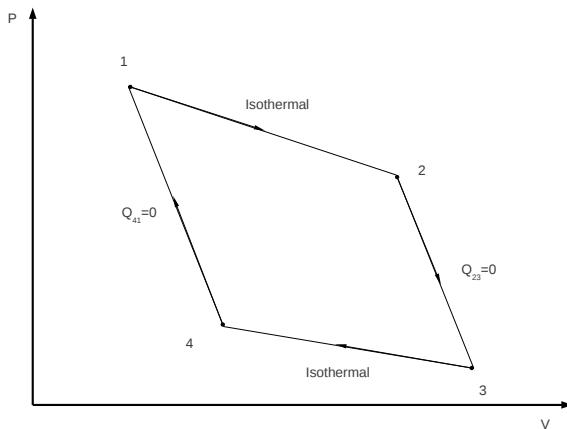
- (a) The thermal efficiency;
- (b) The temperature T_{cold} ;
- (c) Maximum theoretical thermal efficiency for any power cycle operating between hot and cold reservoirs at 602°C and 112°C , respectively;
- (d) Assuming that two power cycles – PC_A and PC_B, operate at the same thermal efficiency. PC_A with hot and cold reservoir temperatures of 2000 K and 1000 K, respectively, and PC_B with T_{cold} an 500 K. Calculate T_{hot} .

Problem 4: The pressure-volume diagram of a Carnot power cycle executed by an ideal gas with constant specific heat ratio κ is shown in Fig. 2. Demonstrate that: (a) $V_4V_2 = V_1V_3$, (b) $\frac{T_2}{T_3} = \left(\frac{P_2}{P_3}\right)^{\frac{\kappa-1}{\kappa}}$ and (c) $\frac{T_2}{T_3} = \left(\frac{V_3}{V_2}\right)^{\kappa-1}$.

Problem 5: A reversible refrigeration cycle A and an irreversible refrigeration cycle B operate between the same two reservoirs and each removes Q_c from the cold reservoir. The net work input required by A is W_A , while the net work input for B is W_B . The reversible cycle discharges Q_H to the hot reservoir, while the irreversible cycle discharges Q'_H . Using the Clausius inequality,,

$$\oint \left(\frac{\delta Q}{T} \right) = -\sigma_{cycle} \quad (1)$$

show that $W_B > W_A$ and $Q'_H > Q_H$. Using Eqn. 1, complete the following involving reversible and irreversible cycles:

Figure 2: **Problem 4:**

- (a) Reversible and irreversible power cycles each discharge energy Q_C to cold reservoir at temperature T_C and receive energy Q_H from hot reservoirs at temperatures T_H and T'_H , respectively. There are no other heat transfers in the system. Show that $T'_H > T_H$.
- (b) Reversible and irreversible refrigeration cycles each discharge energy Q_H to a hot reservoir at temperature T_H and receive Q_C from cold reservoirs at temperatures T_C and T'_C , respectively. There are no other heat transfer. Show that $T'_C > T_C$.
- (c) Reversible and irreversible heat pump cycles each receive energy Q_C from a cold reservoir at temperature T_C and discharge energy Q_H to hot reservoirs at temperatures T_H and T'_H , respectively. There are no other heat transfers. Show that $T'_H < T_H$.

Problem 6: Large quantities of liquefied natural gas (LNG) are shipped by ocean tanker. At the unloading port provision is made for vaporisation of the LNG so that it may be delivered to pipelines as gas. The LNG arrives in the tanker at atmospheric pressure and 113.7 K, and represents a possible heat sink for use as the cold reservoir of a heat engine. For unloading of LNG as a vapour at the rate of $9000 \text{ m}^3 \cdot \text{s}^{-1}$, as measured at 298.15 K and 1.0133 bar, and assuming the availability of an adequate heat source at 303.15 K, what is the maximum possible power obtainable and what is the rate of heat transfer from the heat source? Assume that LNG at 298.15 K and 1.0133 bar is an ideal gas with the molar mass of 17. Also assume that the LNG vaporises only, absorbing only its latent heat of 512 kJ/kg at 113.7 K.

Problem 7: Given saturated ammonia vapour at $P_1 = 200 \text{ kPa}$ compressed by a piston to $P_2 = 1.6 \text{ MPa}$ in a reversible adiabatic process, (a) find the work done per unit mass; (b) sketch the T-s and P-v diagrams. Given:

T	P_{sat}	v_f	v_g	u_f	u_g	h_f	h_g	s_f	s_g
-20	190.2	1.504×10^{-3}	0.62334	88.76	1299.5	89.05	1418.0	0.3657	5.6155
-15	236.3	1.519×10^{-3}	0.50838	111.3	1304.5	111.66	1424.6	0.4538	5.5397

with $[T] = {}^\circ\text{C}$; $[P] = \text{kPa}$; $[v] = \frac{\text{m}^3}{\text{kg}}$; $[u] = [h] = \frac{\text{kJ}}{\text{kg}}$, $[s] = \frac{\text{kJ}}{\text{kg.K}}$

Problem 8: Derive the Maxwell relations below,

$$\left(\frac{\partial T}{\partial V}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_V \quad \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial s}\right)_P \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial s}{\partial V}\right)_T \quad \left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial s}{\partial P}\right)_T$$

from the fundamental thermodynamic equations,

$$du = -PdV + Tds$$

$$dh = Tds + VdP$$

$$df = -PdV - sdT$$

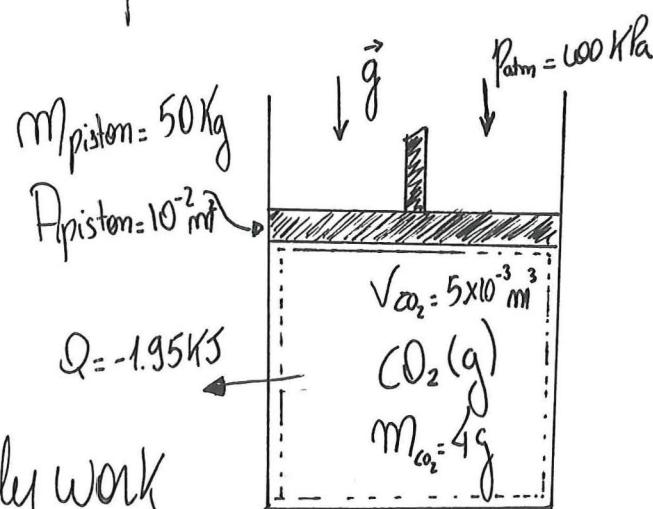
$$dg = -VdP - sdT$$

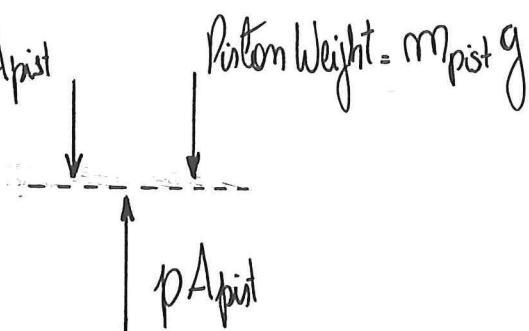
Module 01 : Review of Thermodynamics

~~(3)~~ Problem ~~X~~: 1

Assuming :

- (a) CO_2 is a closed system;
 - (b) the moving boundary is the only work mode;
 - (c) as cooling occurs slowly, there is no acceleration of the piston. Gravity force remains constant;
 - (d) Friction between the piston and cylinder can be ignored;
 - (e) For the CO_2 , Kinetic and potential energy can be ignored;
- (3. a) Since there is no friction and the piston is not accelerated, the force exerted by the CO_2 in the cylinder on the bottom of the piston is equal to the weight of the piston \oplus the force exerted by the atmosphere on the top of the piston:





Thus, the force balance is

$$pApist = PatmApist + m_{pist}g \quad (\div Apist)$$

$$p = Patm + \frac{m_{pist}}{Apist} g$$

$$p = 100 \text{ kPa} + \frac{50 \text{ kg}}{0.01 \text{ m}^2} \times \frac{9.81 \text{ m}}{\text{s}^2} \times \frac{\text{Pa}}{\text{kg m}^{-2}}$$

$$p = 149.05 \text{ kPa} \times \frac{10^{-5} \text{ bar}}{1 \text{ Pa}}$$

$$p = 1.491 \text{ bar} = 149.05 \text{ kPa}$$

$$(3.b) V_1 = 5 \times 10^{-3} \text{ m}^3 \quad V_2 = 2.5 \times 10^{-3} \text{ m}^3$$

$$\mu_1 = 657 \text{ kJ/kg} \quad \mu_2 = ?$$

The work can be calculated through (assuming constant pressure):

$$W_i = \int_1^2 p dV = p(V_2 - V_1) = 1.491 \text{ bar} (-5 \times 10^{-3} + 2.5 \times 10^{-3}) \text{ m}^3 \\ = -372.75 \text{ J}$$

The energy balance for CO_2 ,

$$\Delta U + \cancel{\Delta E_k^{\rightarrow 0}} + \cancel{\Delta E_p^{\rightarrow 0}} = Q - W$$

$$\Delta U = Q - W = -1.95 \times 10^3 \text{ J} - (-372.75 \text{ J})$$

$$\Delta U = -1577.25 \text{ J}$$

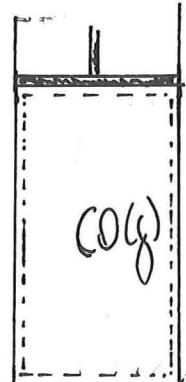
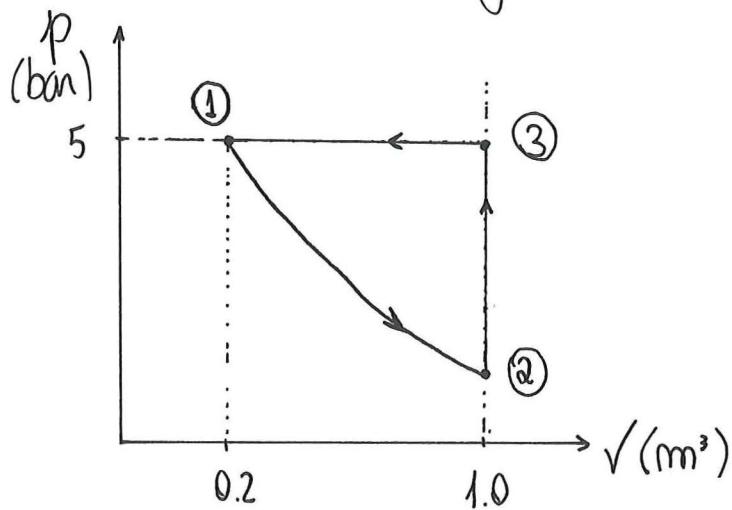
Then with $\Delta U = m (\mu_2 - \mu_1)$

$$\frac{\Delta U}{m} + \mu_1 = \mu_2$$

$$\mu_2 = \frac{-1577.25 \text{ J}}{4.0 \times 10^{-3} \text{ kg}} + 657 \times 10^3 \frac{\text{J}}{\text{kg}}$$

$$\boxed{\mu_2 = 262.69 \frac{\text{KJ}}{\text{kg}}}$$

Problem 2: CO gas



Assuming:

- (i) Gas is a closed system;
- (ii) Volume change is the only work mode;

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(a) Process 1-2: $pV = \text{constant} = K$ $\therefore p = K/V$

$$\begin{aligned} W_{12} &= \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{K}{V} dV = \int_{V_1}^{V_2} K \ln \frac{V_2}{V_1} = p_1 V_1 \ln \frac{V_2}{V_1} \\ &= 5 \text{ bar} \times 0.2 \text{ m}^3 \times \ln \left(\frac{1.0}{0.2} \right) \end{aligned}$$

$$W_{12} = 1.61 \times 10^5 \text{ J}$$

(b) Process 2-3: the piston does not move ($V = \text{constant}$)

Therefore $W_{23} = 0$

(c) Process 3-1:

$$W_{31} = \int_{V_3}^{V_1} pdV$$

As p is constant between states ③ and ①,

$$W_{31} = p_3 (V_3 - V_1) = 5 \text{ bar} (0.2 - 1) \text{ m}^3$$

$$W_{31} = -4 \times 10^5 \text{ J} = -400 \text{ kJ}$$

Problem 10: 3 Reversible power cycle

Given: $Q_H = 100 \text{ KJ}$ $Q_C = 40 \text{ KJ}$
 $T_H = 327^\circ\text{C} = 600.15 \text{ K}$

(a) Thermal efficiency is given

$$\eta = \frac{W_{cycle}}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{40 \text{ KJ}}{100 \text{ KJ}}$$

$\eta = 0.6 \therefore 60\%$

(b) As the cycle operates reversibly :

$$\eta = \eta_{Max} = 1 - \frac{T_C}{T_H}$$

$$0.6 = 1 - \frac{T_C}{600.15} \quad \therefore \boxed{T_C = 240.06 \text{ K} (-33.1^\circ\text{C})}$$

(c) The max. theoretical efficiency for $T_H = 602^\circ\text{C}$ and
 $T_C = 112^\circ\text{C}$

$$\eta_{Max} = 1 - \frac{T_C}{T_H} = 1 - \frac{112 + 273.15}{602 + 273.15}$$

$\eta_{Max} = 0.56 \quad (56\%)$

(d) $T_H^{(a)} = 2000K$ $T_E^{(b)} = 500K$
 $T_C^{(a)} = 1000K$ $T_B^{(b)} = ?$

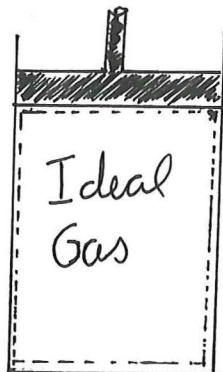
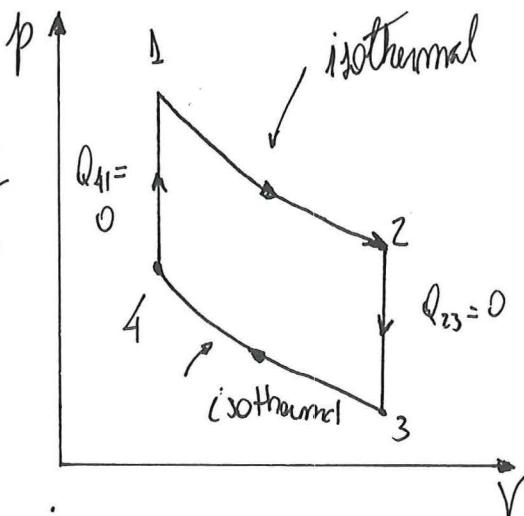
$$\gamma^{(a)} = \gamma^{(b)}$$

$$\gamma^{(a)} = 1 - \frac{T_C^{(a)}}{T_H^{(a)}} = 1 - \frac{1000}{2000} = \gamma^{(b)} = 1 - \frac{T_C^{(b)}}{T_H^{(b)}}$$

$$1 - \frac{1}{2} = 1 - \frac{500}{T_H^{(b)}} \quad \therefore \boxed{T_H^{(b)} = 1000K}$$

Problem 4:

A Carnot cycle is executed by an ideal gas with constant specific heat ratio γ .



(a) The thermal efficiency is

$$\eta = \frac{W_{\text{cycle}}}{Q_{\text{in}}} = \frac{W_{12} + W_{23}}{Q_{\text{in}}}$$

As $U = U(T)$, the energy balance for process 1-2 reduces to

$$U_2 - U_1 = Q_{12} - W_{12}$$

where $U_2 = U_1$, and ~~therefore~~ therefore

$$Q_{12} = W_{12}$$

Then

$$W_{12} = \int_1^2 pdV = \int_1^2 \frac{m RT_H}{V} dV = m RT_H \ln \frac{V_2}{V_1}$$

For 2-3:

$$W_{23} = m RT_C \ln \frac{V_4}{V_3}$$

Replacing ω_{12} and ω_{23} in the thermal efficiency expression

$$\eta = \frac{W_{\text{cycle}}}{Q_{\text{in}}} = \frac{\omega_{12} + \omega_{23}}{Q_{\text{in}}} = \frac{\omega_{12} + \omega_{23}}{\omega_{12}} = 1 + \frac{\omega_{23}}{\omega_{12}}$$

$$\eta = 1 + \frac{mRT_c \ln(\sqrt{V_4}/\sqrt{V_3})}{mRT_u \ln(\sqrt{V_2}/\sqrt{V_1})} = 1 + \frac{T_c}{T_u} \frac{\ln(\sqrt{V_4}/\sqrt{V_3})}{\ln(\sqrt{V_2}/\sqrt{V_1})}$$

$$\eta = 1 + \left(-\frac{T_c}{T_u} \frac{\ln(\sqrt{V_3}/\sqrt{V_4})}{\ln(\sqrt{V_2}/\sqrt{V_1})} \right)$$

However, for the Carnot cycle $\eta_{\text{Carnot}} = 1 - \frac{T_c}{T_u}$, thus

$$\frac{\ln(\sqrt{V_3}/\sqrt{V_4})}{\ln(\sqrt{V_2}/\sqrt{V_1})} = 1 \quad \therefore \quad \ln(\sqrt{V_3}/\sqrt{V_4}) = \ln(\sqrt{V_2}/\sqrt{V_1})$$

$$\frac{\sqrt{V_3}/\sqrt{V_4}}{\sqrt{V_2}/\sqrt{V_1}} = \frac{\sqrt{V_2}/\sqrt{V_1}}{\sqrt{V_4}/\sqrt{V_2}} \quad \boxed{\text{(a)}}$$

(b) As process 2-3 is adiabatic, the energy balance in differential form ~~is~~

$$dU = \delta Q - \delta W$$

with $\delta W = p dV$ and assuming $dU = mC_v dT$. Also assuming ideal gas

$$PV = mRT \quad \text{and}$$

and for ideal gas

$$\kappa = \frac{C_p(T)}{C_v(T)} \quad \left\{ \text{specific heat ratio} \right.$$

and

$$C_p(T) + C_v(T) = R$$

$$\kappa C_v + C_v = R$$

$$C_v(T) = \frac{R}{\kappa - 1}$$

Then

$$dU = -\delta W$$

$$m C_v dT = -pdV$$

$$\cancel{m} \frac{R}{\kappa-1} dT = - \frac{\cancel{m} RT}{V} dV$$

$$\frac{1}{T(\kappa-1)} dT = - \frac{1}{V} dV \quad \cdot(S)$$

constant $\rightarrow \frac{1}{\kappa-1} \ln T \Big|_a^b = - \ln V \Big|_a^b$

$$\ln \left(\frac{T_3}{T_2} \right) = - \ln \left(\frac{V_2}{V_3} \right)^{\kappa-1}$$

$$\boxed{\frac{T_3}{T_2} = \left(\frac{V_2}{V_3} \right)^{\kappa-1}} \quad (c)$$

and using $V = mRT/P$

$$\frac{T_3}{T_2} = \left[\frac{mRT_2}{P_2} \cdot \frac{P_3}{mRT_3} \right]^{1/K-1}$$

$$\frac{T_3}{T_2} = \left[\frac{T_2}{T_3} \cdot \frac{P_3}{P_2} \right]^{1/K-1} = \left(\frac{T_2}{T_3} \right)^{1/K-1} \left(\frac{P_3}{P_2} \right)^{1/K-1}$$

$$\left(\frac{T_2}{T_3} \right)^{-(1/K-1)} \left(\frac{T_2}{T_3} \right)^{-1} = \left(\frac{P_2}{P_3} \right)^{-1/K+1}$$

$$\left(\frac{T_2}{T_3} \right)^{-1/K} = \left(\frac{P_2}{P_3} \right)^{-1/K+1} \quad \leftarrow \text{Applying ln to both sides}$$

$$-1/K \ln \left(T_2 / T_3 \right) = (-1/K+1) \ln \left(P_2 / P_3 \right)$$

$$\ln \left(T_2 / T_3 \right) = \frac{1/K-1}{1/K} \ln \left(P_2 / P_3 \right)$$

$$\boxed{\left(\frac{T_2}{T_3} \right) = \left(\frac{P_2}{P_3} \right)^{\frac{1/K-1}{1/K}}} \quad (b)$$

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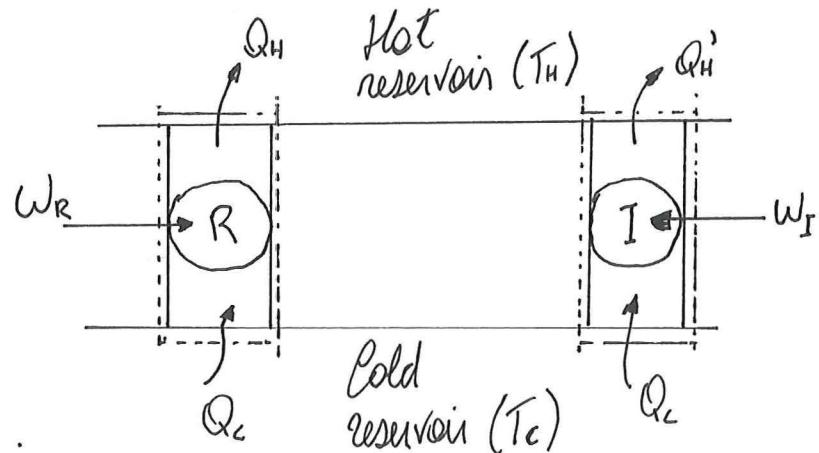
Problem 12: 5

A reversible refrigeration cycle

R and an irreversible

refrigeration cycle I operate

between the same two reservoirs.



The systems shown in the figure above refer to

refrigeration cycles with $\begin{cases} R: \text{reversible} \\ I: \text{irreversible} \end{cases}$ Each system receives Q_c at T_c from the cold reservoir and discharges energy at T_H to the ~~hot~~ hot reservoir.

For cycle I, the second law takes the form

$$\Omega_{\text{cycle}} = - \oint \left(\frac{\partial Q}{T} \right)_b \quad (\text{Clausius inequality})$$

$$\Omega_{\text{cycle}} = - \oint \left(\frac{\partial Q}{T} \right)_b = - \left[\frac{Q_c}{T_c} - \frac{Q'_H}{T_H} \right] \quad (1)$$

Energy balance for cycles R and I (see Fig.)

$$\begin{cases} Q_H = W_R + Q_c \\ Q'_H = W_I + Q_c \end{cases} \Rightarrow Q'_H = Q_H + W_I - W_R \quad (2)$$

Inserting ~~(2)~~ (2) into (1)

$$\begin{aligned}\sigma_{\text{cycle}} &= - \left[\frac{Q_c}{T_c} - \frac{Q_H + W_I - W_R}{T_H} \right] \\ &= - \left[\left(\frac{Q_c}{T_c} - \frac{Q_H}{T_H} \right) - \left(\frac{W_I - W_R}{T_H} \right) \right]\end{aligned}\quad (3)$$

Since R is reversible,

$$\left(\frac{Q_c}{Q_H} \right)_{\substack{\text{rev.} \\ \text{cycle}}} = \frac{T_c}{T_H}$$

then first term (in brackets) in the rhs of (3) vanishes,

$$\sigma_{\text{cycle}} = \frac{W_I - W_R}{T_H}$$

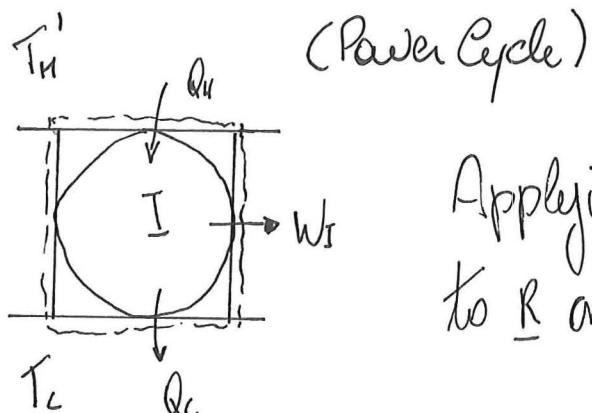
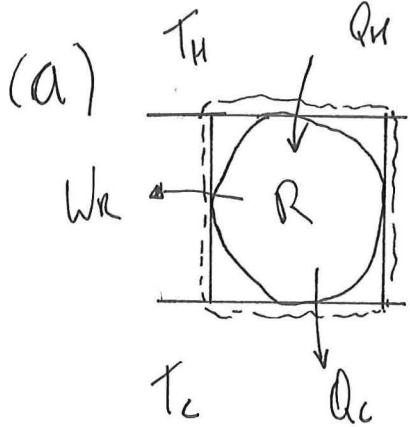
Since cycle I is irreversible, $\sigma_{\text{cycle}} > 0$. Thus

$$W_I - W_R > 0$$

$$\boxed{W_I > W_R}$$

Eqn. (2) then gives

$$\boxed{Q'_H > Q_H}$$



Applying the Clausius inequality (1) to R and I

$$R : \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = -\sigma_{cycle} \quad \therefore \quad Q_C = \frac{T_C}{T_H} Q_H \quad (a.1)$$

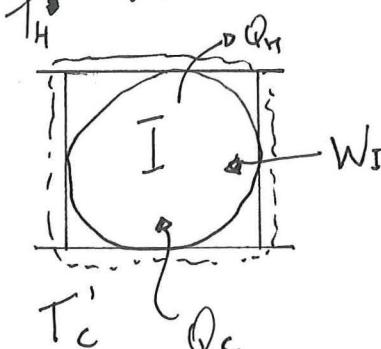
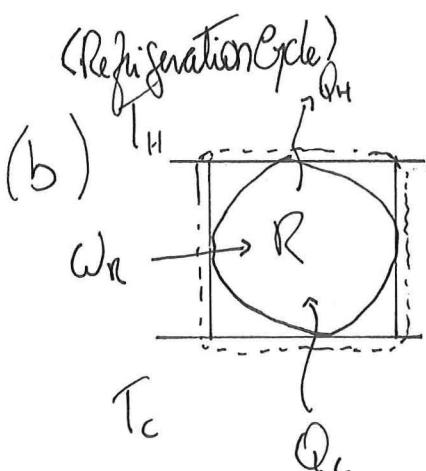
$$I : \frac{Q_H}{T_H'} - \frac{Q_C}{T_C} = -\sigma_{cycle} \quad \therefore \quad (a.2)$$

Combining (a.1) and (a.2) :

$$\frac{Q_H}{T_H'} - \frac{T_C}{T_H} \frac{Q_H}{T_C} = -\sigma_{cycle} \quad \therefore \quad Q_H \left[\frac{1}{T_H'} - \frac{1}{T_H} \right] = -\sigma_{cycle} \quad (a.3)$$

As the lhs of (a.3) is < 0 and $Q_H > 0$,

$$\frac{1}{T_H'} - \frac{1}{T_H} < 0 \quad \therefore \quad \boxed{T_H' > T_H} \quad (a)$$



Similarly to (a) :

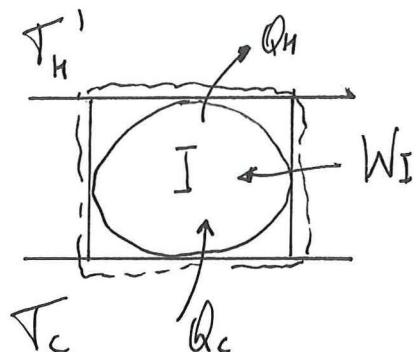
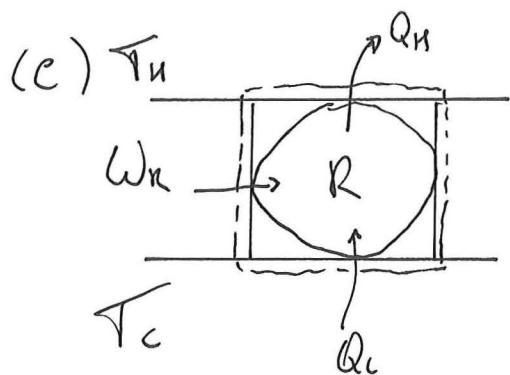
$$R : \frac{Q_C}{T_C} - \frac{Q_H}{T_H} = 0 \quad \therefore \quad Q_H = T_H \frac{Q_C}{T_C} \quad (b.1)$$

$$I : \frac{Q_C}{T_C'} = \frac{Q_H}{T_H} = -\sigma_{cycle} \quad (b.2)$$

Replacing (b.1) in (b.2) :

$$\frac{Q_C}{T_C'} - \frac{T_H Q_C}{T_H T_C} = -\sigma_{cycle} \quad \therefore \quad Q_C \left[\frac{1}{T_C'} - \frac{1}{T_C} \right] = -\sigma_{cycle}$$

$$\boxed{T_C' > T_C} \quad (b)$$



(Pump Cycle) $\frac{\partial S/\partial S}{\partial S}$

Similar to (a) or (b):

$$R: \frac{Q_C}{T_C} - \frac{Q_H}{T_H} = 0 \therefore Q_C = \frac{Q_H T_C}{T_H} \quad (c.1)$$

$$I: \frac{Q_C}{T_C} - \frac{Q_H}{T_H'} = -\text{Cycle} \quad (c.2)$$

Replacing (c.1) in (c.2):

$$\frac{Q_H T_C}{T_H} \frac{1}{T_C} - \frac{Q_H}{T_H'} = -\text{Cycle} \therefore Q_H \left[\frac{1}{T_H} - \frac{1}{T_H'} \right] = -\text{Cycle}$$

$$\boxed{T_H' < T_H} \quad (c)$$

Problem 6: LNG ($MW = 57 \text{ g/mol}$)

$$V = 9000 \text{ m}^3/\text{s} \quad P = 1.0133 \text{ bar} \\ T = 298.15 \text{ K}$$

Calculating the mass of LNG (assuming ideal gas behaviour),

$$m_{\text{LNG}} = \frac{PV}{RT} \quad MW = \frac{(1.0133 \text{ bar})(9000 \text{ m}^3/\text{s})}{(8.314 \times 10^{-3} \frac{\text{bar} \cdot \text{m}^3}{\text{K} \cdot \text{mol}})(298.15 \text{ K})} \times \frac{57 \text{ g}}{\text{mol}}$$

$$\boxed{m_{LNG} = 6254.39 \frac{kg}{s}}$$

$$\hookrightarrow T_H = 303.15 K \quad T_C = 113.7 K$$

$$Q_C = 512 \frac{KJ}{kg} \times m_{LNG} = 3.20 \times 10^9 W$$

Maximum power is introduced by a Carnot engine,

$$\frac{\omega}{Q_C} = \frac{Q_H - Q_C}{Q_C} = \frac{Q_H}{Q_C} - 1 = \frac{T_H}{T_C} - 1$$

Thus, the work can be computed as

$$\omega = Q_C \left[\frac{T_H}{T_C} - 1 \right] = (3.20 \times 10^9 W) \left[\frac{303.15}{113.7} - 1 \right]$$

$$\boxed{\omega = 5.34 \times 10^6 KW} \quad \hookrightarrow \text{max power (a)}$$

And the heat,

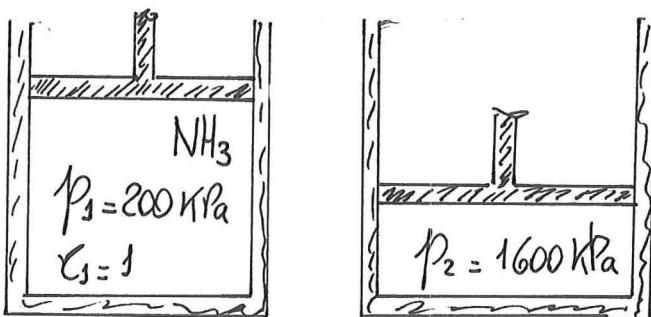
$$Q_H = Q_C + \omega$$

$$Q_H = 3.20 \times 10^9 KW + 5.34 \times 10^6 KW$$

$$\boxed{Q_H = 8.54 \times 10^9 KW} \quad (b)$$

Problem 17: 7

The reversible and adiabatic compression implies an isentropic process.



The thermodynamic table of NH_3 can be read as (*)

$T(^{\circ}\text{C})$	$P_{\text{sat}}(\text{kPa})$	specif. volume v_g (m^3/kg)	int. energy u_f (kJ/kg)	enthalpy h_f (kJ/kg)	entropy s_f (kJ/(kg K))
-20	190.2	1.504×10^{-3} 0.62334	88.76 / 1299.5	89.05 / 1418.0	0.3657 / 5.6155
-15	236.3	1.519×10^{-3} 0.50838	113. / 1304.5	111.66 / 1424.6	0.4538 / 5.5397

By interpolating the table above for $p_1 = 200 \text{ kPa}$

$$T_1 = -18.94^{\circ}\text{C}$$

$$v_1 = v_g = 0.5989 \text{ m}^3/\text{kg}$$

$$s_1 = s_g = 5.5994 \text{ kJ/(kg.K)}$$

$$u_1 = 1300.56 = u_g$$

$$\begin{aligned} (236.3 - 190.2) \text{ kPa} &= (0.50838 - 0.62334) \text{ m}^3/\text{kg} \\ (200 - 190.2) \text{ kPa} &= X \\ X &= -0.024438 \\ v_g(P_1) &= 0.62334 + X \\ v_g(P_1) &= 0.5989 \text{ m}^3/\text{kg} \end{aligned}$$

As the process is isentropic

$$s_2 = s_1 = 5.5994 \text{ kJ/(kg.K)}$$

At $p_2 = 1600 \text{ kPa}$, the saturation tables indicates that

$$s_g \sim 4.8 \text{ kJ/(kg.K)} < s_2$$

This means that the ammonia is superheated at this state. Knowing P_2 and s_2 , we can check the superheated ammonia table and by interpolation,

$$T_2 = 134.9^\circ\text{C}$$

$$v_2 = 0.18337 \text{ m}^3/\text{kg}$$

$$u_2 = 1548.4 \text{ kJ/kg}$$

$T_2 > (T_c^{(NH_3)} = 132.3^\circ\text{C})$ but P_2 is well below the critical pressure ($P_c = 11333.2 \text{ kPa}$). Also $u_2 < u_s$. From the First Law,

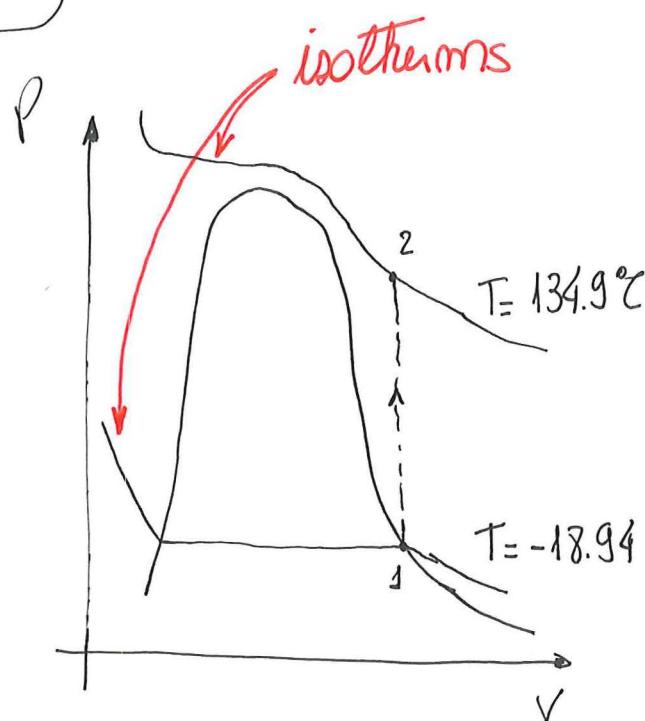
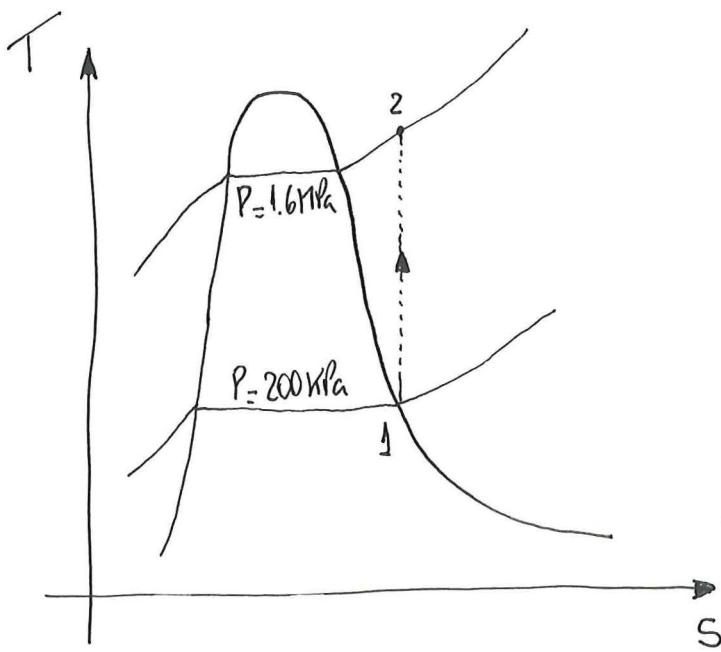
0 (proc. is isentropic)

$$u_2 - u_3 = q_1' - w_1'^2$$

$$w_1'^2 = -1548.4 + 1300.56$$

$$\boxed{w_1'^2 = -247.84 \text{ kJ/kg}}$$

(a)



General Solution for Problem 8

A Introduction to Partial Differentiation

Eight properties of a system – pressure (P), volume (V), temperature (T), internal energy (u), enthalpy (h), entropy (s), Helmholtz free energy (f) and Gibbs free energy (g) have been introduced in EG2004 (Fluid Mechanics and Thermodynamics) and EG3020 (Process Thermodynamics). h, f and g are sometimes referred to as thermodynamic potentials. Both f and g are extremely important when considering chemical reactions (e.g., combustion) and processes involving phase change (e.g., water/steam industrial systems, atmospheric and crystallisation processes etc).

From the aforementioned (eight) properties, only pressure, temperature and volume can be directly measurable. Therefore it is convenient to introduce other combination of properties which are relatively easily measurable and which, along with P , T and V , enable the values of the remaining properties to be determined. These combinations of properties are commonly referred as *thermodynamic gradients* – i.e., they are defined as the rate of change of one property with another while a third is kept constant.

Let's consider three variables x, y and z , and their functional relationship, $f(x, y, z) = 0$ with $x = x(y, z)$, $y = y(x, z)$ and $z = z(x, y)$. The intrinsic relationship of the differential dependent variable $x = x(y, z)$ in relation to the independent variables y and z can be represented as

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz \quad (6)$$

in which dx is the exact differential. Renaming $M = \left(\frac{\partial x}{\partial y} \right)_z$ and $N = \left(\frac{\partial x}{\partial z} \right)_y$, and Eqn. 6 can be rewritten as,

$$dx = M dy + N dz \quad (7)$$

The partial differentiation of M and N with respect to z and y , respectively, leads to,

$$\frac{\partial M}{\partial z} = \frac{\partial^2 x}{\partial y \partial z} \quad \text{and} \quad \frac{\partial N}{\partial y} = \frac{\partial^2 x}{\partial z \partial y} \iff \frac{\partial M}{\partial z} = \frac{\partial N}{\partial y} \quad (8)$$

Similarly for $y = y(x, z)$ and $z = z(x, y)$,

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

Replacing dz in dy above,

$$\begin{aligned} dy &= \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x \left[\left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \right] \\ &= \left[\left(\frac{\partial y}{\partial x} \right)_z + \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y \right] dx + dy \end{aligned}$$

Clearly, the term in the square-brackets vanishes,

$$\begin{aligned} \left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= 0 \\ \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= - \left(\frac{\partial y}{\partial x}\right)_z \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x &= -1 \end{aligned} \quad (9)$$

Replacing x, y and z by P, V and T ,

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial T}{\partial P}\right)_V = \left(\frac{\partial V}{\partial T}\right)_P = -1 \quad (10)$$

B Thermodynamic Relations

From the Course Notes we saw that the First Law applied to a closed system in a reversible process states that,

$$dQ = du + PdV, \quad (11)$$

and the Second Law,

$$ds = \left(\frac{dQ}{T}\right)_{\text{rev}} \quad (12)$$

we can combine these equations to obtain

$$du = -PdV + Tds \quad (13)$$

We can similarly derive the equations for enthalpy, free Gibbs and free Helmholtz energy equations as

$$dh = Tds + VdP \quad (14)$$

$$df = -PdV - sdT \quad (15)$$

$$dg = -VdP - sdT \quad (16)$$

As du, dh, df and dg are exact differentials, we can express them as the following set of chain rule -based differentials,

$$\begin{aligned} du &= \left(\frac{\partial u}{\partial s}\right)_V ds + \left(\frac{\partial u}{\partial V}\right)_s dV \\ dh &= \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP \\ df &= \left(\frac{\partial f}{\partial V}\right)_T dV + \left(\frac{\partial f}{\partial T}\right)_V dT \\ dg &= \left(\frac{\partial g}{\partial P}\right)_T dP + \left(\frac{\partial g}{\partial T}\right)_P dT \end{aligned} \quad (17)$$

C Maxwell Relations

Comparing the Gibbs equation (13) with Eqn. 7 for dx ,

$$du = -PdV + Tds \quad \text{and} \quad dx = Mdy + Ndz$$

We can easily notice the mathematical equivalences,

$$x \Rightarrow u, \quad y \Rightarrow V, \quad z \Rightarrow s, \quad M \Rightarrow -P, \quad N \Rightarrow T$$

With the analogy of $x = x(y, z)$ and $u = u(V, s)$, Eqn. 8 leads to,

$$-\left(\frac{\partial P}{\partial s}\right)_V = \left(\frac{\partial T}{\partial V}\right)_s, \quad (18)$$

$\left(\frac{\partial u}{\partial V}\right)_s = -P$ and $\left(\frac{\partial u}{\partial s}\right)_V = T$. Eqn. 18 is known as a *Maxwell relation*. Similar relations can be obtained from the remaining fundamental thermodynamics equations – Eqns. 14-16 leading to the whole set of *Maxwell relations*:

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_s &= -\left(\frac{\partial P}{\partial s}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_s &= \left(\frac{\partial V}{\partial s}\right)_P \end{aligned} \quad (19)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial s}{\partial V}\right)_T \quad (20)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \quad (21)$$

with,

$$\left(\frac{\partial u}{\partial s}\right)_V = T = \left(\frac{\partial h}{\partial s}\right)_P \quad (22)$$

$$\left(\frac{\partial u}{\partial V}\right)_s = -P = \left(\frac{\partial f}{\partial V}\right)_T \quad (23)$$

$$\left(\frac{\partial h}{\partial P}\right)_s = V = \left(\frac{\partial g}{\partial P}\right)_T \quad (24)$$

$$\left(\frac{\partial f}{\partial T}\right)_V = -s = \left(\frac{\partial g}{\partial T}\right)_P \quad (25)$$

Equations 18-25 do not refer to a process, but do express relations between properties which must be satisfied when any system is in a state of equilibrium.