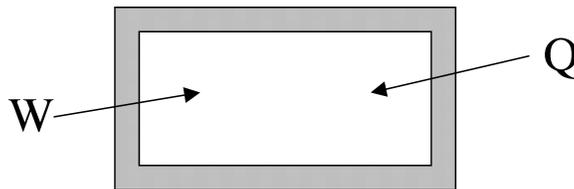


Problem Set 1
Solutions
3.20 MIT
Professor Gerbrand Ceder
Fall 2002

LEVEL 1 PROBLEMS

Problem 1.1

Gas is heating in a rigid container from $T_o = 40^\circ C$ to $T_1 = 315^\circ C$



$$\Delta U = U(T_1) - U(T_o) = W + Q \quad \text{(First Law)}$$

(a) $W = 0$ Since only PV work is possible & $\Delta V = 0$ since the container is rigid.

$$Q = \Delta U = (0.17T_1 + C) - (0.17T_o + C)$$

$$Q = \Delta U = -0.17(T_1 - T_o) = \boxed{46.75 \frac{kJ}{kg}}$$

(b) Entropy change:

$$dS = \frac{\delta Q}{T} \quad \text{(for reversible heating)}$$

since $\partial W = 0$

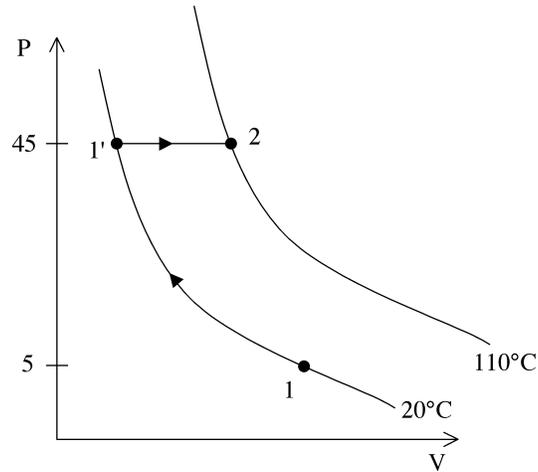
$$\boxed{\delta Q = dU} = 0.17dT$$

$$dS = \frac{0.17dT}{T}$$

or,

$$\Delta S = \int_{T_o}^{T_1} \frac{0.17dT}{T} = 0.17 \ln\left(\frac{T_1}{T_o}\right) = \boxed{0.107 \frac{kJ}{kgK}}$$

Problem 1.2



Calculate entropy change by going from 1 to 2 according to:

(1 → 1') A reversible isothermal compression

(1' → 2) Followed by an isobaric heating

Entropy change 1 → 1'

$$\Delta U = 0$$

$$(U = U(T))$$

$$Q = -W \text{ or } \delta Q = pdV = \frac{nRT}{V}dV$$

$$dS = \frac{\delta Q}{T} = \frac{nR}{V}dV$$

$$\Delta S^{1 \rightarrow 1'} = nR \ln \left(\frac{V_{1'}}{V_1} \right) = -nR \ln \left(\frac{P_{1'}}{P_1} \right) = -36.53 \frac{J}{\text{mole} \cdot K}$$

Entropy change 1' → 2

$$\delta Q = c_p dT$$

(isobaric heating)

$$C_p = n \frac{7}{2} R$$

$$dS = \frac{\delta Q}{T} = \frac{c_p dT}{T} = \frac{7}{2} nR \frac{dT}{T}$$

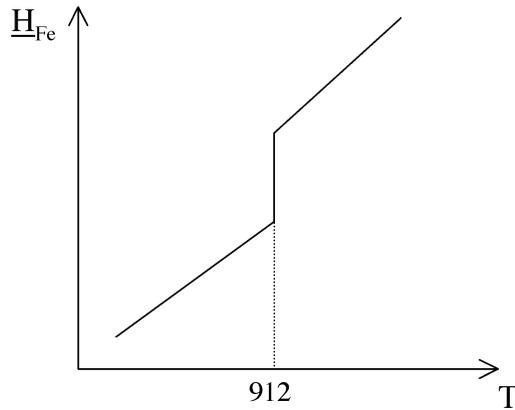
$$\Delta S^{1' \rightarrow 2} = \frac{7}{2} nR \ln \left(\frac{T_2}{T_{1'}} \right) = 15.59 \frac{J}{\text{mole} \cdot K}$$

Now for the total process

$$\Delta S^{tot} = \Delta S^{1 \rightarrow 1'} + \Delta S^{1' \rightarrow 2} = -20.94 \frac{J}{\text{mole} \cdot K}$$

Problem 1.3

(a)



$$\Delta \underline{H}_{Fe} = \int_{1100^{\circ}C}^{912^{\circ}C} c_{p,\gamma} dT + \Delta \underline{H}^{\gamma \rightarrow \alpha} + \int_{912^{\circ}C}^{0^{\circ}C} c_{p,\alpha} dT$$

$$\Delta \underline{H}_{Fe} = 34 \frac{J}{mole-K} (912^{\circ}C - 1100^{\circ}C) - 900 \frac{J}{mole} + 38 \frac{J}{mole-K} (0^{\circ}C - 912^{\circ}C)$$

$\Delta \underline{H}_{Fe} = -41.95 \text{ kJ}$

(b) System Fe+ice water is adiabatic $\rightarrow \Delta H = 0$

$$\Delta H_{Fe} = \Delta H_{icewater}$$

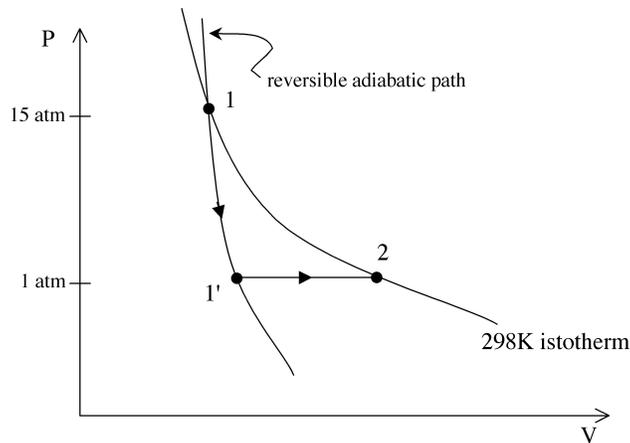
$$\Delta H_{Fe} = -(m_{ice} \Delta \underline{H}_{melting}), m_{ice} = \text{mass of ice transformed}$$

$$m_{ice} = -\frac{\Delta H_{Fe}}{\Delta \underline{H}_{melting}} = \frac{41950 \frac{J}{mole-K} * 100g * \frac{1mol}{56g}}{6048 \frac{J}{mole-K} * \frac{1mol}{18g}}$$

$m_{ice} = 223 \text{ g}$

Problem 1.4

Diatomic ideal gas $\Rightarrow c_p = \frac{7}{2}R$ and $c_v = \frac{5}{2}R$



Assume the process is reversible.

$1 \rightarrow 1'$

There are two methods one can use to find the work done along this path. For both approaches it will be useful to find p, V, T for the starting and ending points. We are given the starting pressure, volume and temperature and the final pressure. From this we can calculate the final volume and temperature.

$$p_1 V_1^\gamma = p_{1'} V_{1'}^\gamma \quad (\text{with } \gamma = \frac{c_p}{c_v} = \frac{7}{5})$$

$$V_{1'}^\gamma = \frac{p_1 V_1^\gamma}{p_{1'}}$$

$$V_{1'} = 6.919 \text{ m}^3$$

The final temperature can be found with a similar relation

$$V_1 T_1^c = V_{1'} T_{1'}^c \quad (\text{with } c = \frac{c_v}{R} = \frac{5}{2})$$

$$T_{1'}^c = \frac{V_1 T_1^c}{V_{1'}}$$

$$T_{1'} = 137 \text{ K}$$

It will also be useful to calculate the number of moles from $pV = nRT$ giving $n = 615 \text{ moles}$. In summary the conditions at each point are

	1	1'
$p \text{ (Pa)}$	101300	1519500
$V \text{ (m}^3\text{)}$	1	6.919
$T \text{ (K)}$	298	137

Method I

Start with

$$pV^\gamma = p_1 V_1^\gamma$$

with $\gamma = \frac{c_p}{c_v} = \frac{7}{5}$

$$p = \frac{p_1 V_1^\gamma}{V^\gamma}$$

So,

$$w = \int -pdV = -p_1 V_1^\gamma \int_1^{1'} \frac{dV}{V^\gamma}$$

$$w = \left[\frac{P_1 V_1^\gamma}{(\gamma - 1)} \left(\frac{1}{V^{(\gamma-1)}} \right) \right]_1^{1'} = \frac{P_1 V_1^\gamma}{(\gamma - 1)} \left(\frac{1}{V_{1'}^{(\gamma-1)}} - \frac{1}{V_1^{(\gamma-1)}} \right)$$

Inserting in the values for P, V, γ we get

$$w = -2.03 \text{ MJ}$$

Method II

Start with the known fact the the internal energy of an ideal gas is only a function of temperature.

$$\Delta U = Q + W = \int n c_v dT$$

However, since this is an adiabatic path, $Q = 0$ and the work done is simple $n c_v dT$

$$w = n c_v (T_{1'} - T_1)$$

$$w = -2.03 \text{ MJ}$$

$1' \rightarrow 2$

This process is at constant pressure, so the work is given by

$$w = - \int p dV = -p_2 \int_{1'}^2 dV$$
$$w = -p_2 (V_2 - V_{1'})$$

We just have to find V_2 . That can be done easily by using the equation of state of an ideal gas along an isotherm

$$P_2 V_2 = P_1 V_1$$
$$V_2 = 15 m^3$$

So,

$$w = -101300 \text{ Pa} \times (15 - 6.919 m^3)$$
$$\boxed{w = -819 kJ}$$

The total work done is then

$$w_{tot} = -2030 + -819 = \boxed{-2849 kJ}$$

Problem 1.5

Function 1: $df_1 = y(3x^2 + y^2)dx + x(x^2 + 2y^2)dy$

(1) Integrate along $y = x$ ($dy = dx$)

$$\int_0^1 x(3x^2 + x^2)dx + x(x^2 + 2x^2)dx$$
$$\int_0^1 (4x^3 + 3x^3)dx = \int_0^1 7x^3 dx = \left[\frac{7x^4}{4} \right]_0^1 = \boxed{\frac{7}{4}}$$

(2) Integrate along $y = x^2$ ($dy = 2x dx$)

$$\int_0^1 x^2(3x^2 + x^4)dx + x(x^2 + 2x^4)2x dx$$
$$\int_0^1 (5x^6 + 5x^4)dx = \left[x^5 + \frac{5x^5}{5} \right]_0^1 = \boxed{\frac{12}{5}}$$

Function 2: $df_2 = y(3x^2 + y)dx + x(x^2 + 2y)dy$

(1) Integrate along $y = x$ ($dy = dx$)

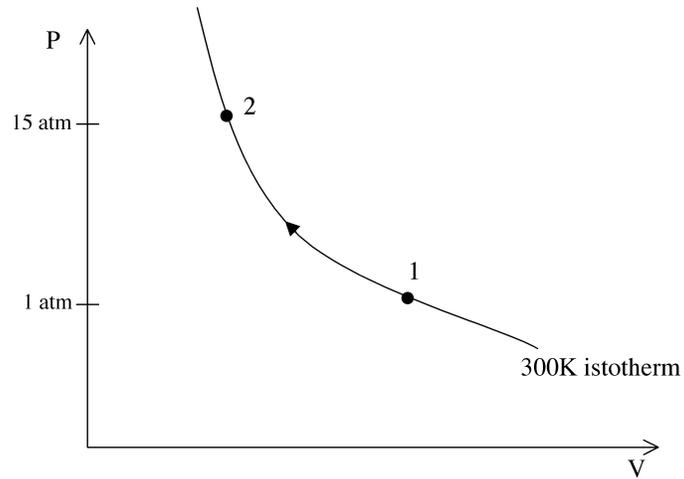
$$\int_0^1 x(3x^2 + x)dx + x(x^2 + 2x)dx$$
$$\int_0^1 (4x^3 + 3x^2)dx = \left[\frac{4x^4}{4} + \frac{3x^3}{3} \right]_0^1 = \boxed{2}$$

(2) Integrate along $y = x^2$ ($dy = 2x dx$)

$$\int_0^1 x^2(3x^2 + x^2)dx + x(x^2 + 2x^2)2x dx$$
$$\int_0^1 10x^4 dx = \left[\frac{10x^5}{5} \right]_0^1 = \boxed{2}$$

Since function 2 is path independent it is an exact differential.

Problem 1.6



$$dU = \delta w + \delta Q$$

This is an ideal gas so $dU = 0$ along an isothermal path.

(a)

$$\delta w = -pdV, p = \frac{RT}{V}$$

$$w = \int_2^1 -\frac{RT}{V} dV = -RT \ln\left(\frac{V_2}{V_1}\right) = RT \ln\left(\frac{p_2}{p_1}\right)$$

$$w = RT \ln(15) = \boxed{6754J}$$

(b)

$$dU = 0 \implies Q = -w$$

$$\boxed{Q = -6754J}$$

(c)

$$H_1 = U_1 + P_1V_1$$

$$H_2 = U_2 + P_2V_2$$

For an ideal gas at constant temperature ($T_1 = T_2$) $\implies U_1 = U_2$

Also, when $T_1 = T_2 \implies P_1V_1 = P_2V_2$

Therefore

$$\boxed{H_1 = H_2}$$

(d)

$$dS = \frac{\delta Q}{T} = \frac{pdV}{T} = \frac{nR}{V} dV$$

$$\Delta S = R \ln\left(\frac{V_2}{V_1}\right) = -R \ln\left(\frac{P_2}{P_1}\right)$$

$$\boxed{\Delta S = -22.5 \frac{J}{K}}$$

Problem 1.7

(a) Work done in the process is:

$$w = \int_{initial}^{final} -pdV$$

Define water as the system

Initial State = Liquid

Final State = Vapor

So we write

$$w = - \int_{V_{liq}}^{V_{vapor}} pdV$$

$$w = -p \int_{V_{liq}}^{V_{vapor}} dV$$

(Since p is constant)

$$w = -p(V_{vap} - V_{liq})$$

Since the specific volume of a vapor is much larger than for a liquid

$$w \approx -pV_{vap} = -\frac{p}{\rho_{vapor}} = \frac{10^5 Pa}{0.592 \frac{kg}{m^3}} = 167504 \frac{J}{kg} = \boxed{167 \frac{J}{g}}$$

This is about 7.5% of the heat of evaporation

(b)

$$H = U + pV$$

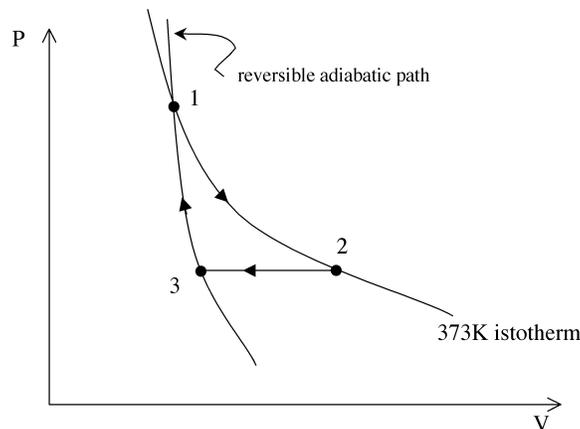
$$\Delta H = \Delta U + \Delta(pV) = \Delta U + p\Delta V$$

$$\Delta U = \Delta H - p\Delta V$$

$$\Delta U = 2261 \frac{J}{g} - 167 \frac{J}{g} = \boxed{2094 \frac{J}{g}}$$

Conclusion: The heat one has to transfer to water to evaporate it is partly used for increasing the internal energy of water ($2094 \frac{J}{g}$, breaking bonds) but also for the work required by the vapor expansion.

Problem 1.8



Given:

$$p_1 = 1 \text{ atm} = 101300 \frac{\text{N}}{\text{m}^2}$$

$$V_1 = 1 \text{ liter} = 0.001 \text{ m}^3$$

$$V_2 = 2 \text{ liters} = 0.002 \text{ m}^3$$

$$T_1 = T_2 = 373 \text{ K}$$

Need to know how many moles of gas:

$$n = \frac{p_1 V_1}{RT_1} = 0.033 \text{ moles}$$

1 → 2 (isothermal)

$$p_1 V_1 = p_2 V_2 \implies p_2 = \frac{1}{2} \text{ atm} = 50650 \frac{\text{N}}{\text{m}^2}$$

$$w^{1 \rightarrow 2} = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{-nRT}{V} dV = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$w^{1 \rightarrow 2} = -nRT \ln 2 = -70.9 \text{ J}$$

2 → 3 (isobaric)

$$p_3 = p_2$$

$$p_3 V_3^\gamma = p_1 V_1^\gamma$$

with $\gamma = \frac{c_p}{c_v} = \frac{5}{3}$ for monoatomic ideal gas

$$V_3 = \left(\frac{p_1 V_1^\gamma}{p_3} \right)^{\frac{1}{\gamma}} = 1.52 \text{ liters} = 0.00152 \text{ m}^3$$

$$w^{2 \rightarrow 3} = -p_2 \Delta V^{2 \rightarrow 3} = - \left(50650 \frac{\text{N}}{\text{m}^2} \right) (0.00152 - 0.002 \text{ m}^3)$$

$$w^{2 \rightarrow 3} = 24.3 \text{ J}$$

3 → 1 (reversible adiabatic)

$$w^{3 \rightarrow 1} = \int_{V_3}^{V_1} -p dV$$

$$pV^\gamma = p_1 V_1^\gamma \implies p = \frac{p_1 V_1^\gamma}{V^\gamma}$$

$$w^{3 \rightarrow 1} = \int_{V_3}^{V_1} - \frac{p_1 V_1^\gamma}{V^\gamma} dV = \frac{p_1 V_1^\gamma}{\gamma - 1} \left[\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_3^{\gamma-1}} \right]$$

$$w^{3 \rightarrow 1} = 37.1 \text{ J}$$

So the total work done is

$$w^{total} = w^{1 \rightarrow 2} + w^{2 \rightarrow 3} + w^{3 \rightarrow 1} = -70.9 + 24.3 + 37.1$$

$$\boxed{w^{total} = -9.5 \text{ J}}$$

Problem 1.9

(i) The amount of work done by the gas is zero, since the gas does no work on the surroundings outside of the chamber. The expression $w = \int -p dV$ cannot be applied since the process is not reversible.

(ii) The walls of the chamber are insulating, thus $Q = 0$ and from (i) $w = 0$. Thus $\Delta U = Q + W = 0$

(iii) For an ideal gas U is only a function of temperature. Since for a free expansion in an insulated chamber $\Delta U = 0 \implies T_{initial} = T_{final}$

(iv) For a non-ideal gas where $U = f(T, V)$, T will change after a free expansion in an insulated chamber since V changes and $\Delta U = U(T_{final}, V_{final}) - U(T_{initial}, V_{initial}) = 0$

(Most gasses at low pressures can be well approximated as being ideal gasses)

(v) If now the walls of the chambers conduct heat, for an ideal gas $U = U(T)$ is still true. The initial and final states are in equilibrium with the environment. Thus

$$T_{initial} = T_{final} = T_{environment}$$

(vi) For non-ideal gases $\Delta U \neq 0$ since $U = U(T, V)$ and V changes.

LEVEL 2 PROBLEMS

Problem 2.1

- (a) $\Delta S = 0$
- (b) $\Delta S > 0$
- (c) $\Delta S > 0$

Problem 2.2

Given information

$$\begin{array}{ll} V_i = 1m^3 & V_f = ? \\ P_i = 15 atm & P_f = 2 atm \\ T_i = 298K & T_f = 298K \end{array}$$

(a) Find the final volume after the expansion

$$\begin{aligned} P_i V_i &= P_f V_f \\ V_f &= \frac{P_i V_i}{P_f} = \frac{15 * 1}{2} \\ V_f &= 7.5m^3 \end{aligned}$$

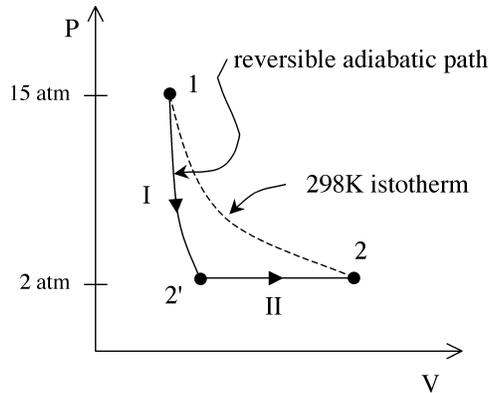
Finding the number of moles, n , will be useful for parts b & c

$$\begin{aligned} R &= 0.08205 \frac{L \cdot atm}{K \cdot mole}, 1m^3 = 1000L \\ \frac{PV}{RT} &= n = \frac{15 * 1000}{0.08205 * 298} \\ n &= 613.5 moles \end{aligned}$$

(b) Find the work done if the process is isothermal

$$\begin{aligned} w &= - \int p dV \\ w &= -nRT \ln \left(\frac{V_f}{V_i} \right) = -8.314 * 613.5 * 298 * \ln \left(\frac{7.5}{1} \right) \\ w &= -3006 kJ \end{aligned}$$

(c) Find the work in the multi-step process



Two parts:

- (I) Adiabatic expansion from 1 to 2'
- (II) Heating at constant P from 2' to 2

$$(w_I + w_{II}) + (Q_I + Q_{II}) = \Delta U_{sys}$$

Since state 1 and 2 are at the same temperature and U for an ideal gas is only a function of temperature, $\Delta U_{sys} = 0$ and

$$(w_I + w_{II}) = -(Q_I + Q_{II})$$

So we can calculate w 's or Q 's. Since $Q_I = 0$ (adiabatic process) let's calculate Q_{II}

$$Q_{II} = nc_p \Delta T = nc_p (T_2 - T_{2'})$$

$$n = 613.5 \text{ moles}, c_p = \frac{7}{2}R = 29 \frac{J}{\text{mole} \cdot K}$$

Need to find $T_{2'}$

$$T_{2'} = T_1 \left(\frac{P_{2'}}{P_1} \right)^{\frac{R}{c_p}}$$

$$T_{2'} = 298 \left(\frac{2}{15} \right)^{\frac{2}{7}} = 168K$$

Now for Q_{II}

$$Q_{II} = 613.3 \text{ moles} * 29 \frac{J}{\text{mole} \cdot K} * (298 - 168K)$$

$$\boxed{Q_{II} = 2313kJ}$$

So,

$$w_{total} = -(Q_I + Q_{II}) = -(0 + 2313kJ)$$

$$\boxed{w_{total} = -2313kJ}$$

Problem 2.3

$$U = Ap^2V$$

($A = \text{positive constant}$)

$$dU = \delta w + \delta Q$$

(First Law)

Along a reversible path, $\partial W = -pdV$ when only p-V work is possible.

Along a reversible adiabatic path, $\partial Q = 0$ and therefore

$$dU = \delta w$$

$$dU = \left(\frac{\partial U}{\partial p}\right)_V dp + \left(\frac{\partial U}{\partial V}\right)_p dV \quad (1)$$

$$\left(\frac{\partial U}{\partial p}\right)_V = 2ApV$$

$$\left(\frac{\partial U}{\partial V}\right)_p = Ap^2$$

Going back to equation 1

$$(2ApV)dp + (Ap^2)dV = -pdV$$

$$2AVdp = -(Ap + 1)dV$$

$$-\frac{dp}{(Ap + 1)} = \frac{dV}{2AV}$$

After intergration

$$\frac{\ln(Ap + 1)}{A} = -\frac{\ln V}{2A} + \text{constant}$$

$$\ln \left[(Ap + 1) V^{\frac{1}{2}} \right] = \text{new constant}$$

$$\boxed{(Ap + 1) V^{\frac{1}{2}} = \text{even newer constant}}$$

Problem 2.4

(a) Using the first law

$$\Delta U_{sys} = Q(500^\circ C) + Q(300^\circ C) + W + Q(25^\circ C) = 0$$

$$1.5MW + 0.5MW - 1MW + Q(25^\circ C) = 0$$

$$\boxed{Q(25^\circ C) = -1MW}$$

(b) Check to see if the second law is satisfied

$$dS_{machine} \geq \frac{\delta Q}{T}$$

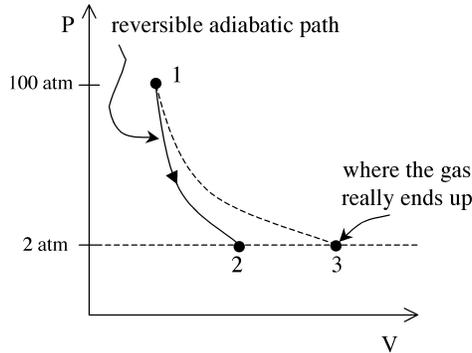
But $dS_{machine}$ has to be zero since we are operating at steady state

$$\frac{Q(500^\circ C)}{773} + \frac{Q(300^\circ C)}{573} + \frac{Q(25^\circ C)}{298} \leq 0$$

$$\frac{1.5MW}{773K} + \frac{0.5MW}{573K} - \frac{1MW}{298K} = -542.6 \frac{J}{K \cdot s}$$

$$\boxed{-542.6 \frac{J}{K \cdot s} \leq 0}$$

Problem 2.5



(a)

$$\Delta U = Q + w$$

Since the process is adiabatic, $Q = 0$

$$\Delta U = nc_v \Delta T = w$$

$$(10 \text{ moles}) \left(\frac{5}{2} \cdot 8.314 \frac{\text{J}}{\text{mole} \cdot \text{K}} \right) \Delta T = -80000 \text{ J}$$

$$\Delta T = -385 \text{ K}$$

$$\boxed{T_f = 388 \text{ K}}$$

(b)

$$\Delta S_{1 \rightarrow 3} = \Delta S_{1 \rightarrow 2} + \Delta S_{2 \rightarrow 3}$$

$\Delta S_{1 \rightarrow 2} = 0$ since this process is reversible and adiabatic

$\Delta S_{2 \rightarrow 3}$ is at constant pressure, temperature varies $\rightarrow \left(\frac{\partial S}{\partial T} \right)_p$

What is T_2 though? The temperature that would be reached if expansion was reversible.

$$T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{\frac{R}{c_p}} = 773 \left(\frac{2}{100} \right)^{\frac{2}{7}} = 253 \text{ K}$$

$$\Delta S_{2 \rightarrow 3} = \int_{253}^{388} c_p \frac{dT}{T} = \frac{7}{2} \cdot 8.314 \cdot \ln \left(\frac{388}{253} \right)$$

$$\Delta S_{2 \rightarrow 3} = 12.4 \frac{\text{J}}{\text{mole} \cdot \text{K}}$$

Problem 2.6

In case (b) extra work is done on the gas so that its internal energy will remain higher than in (a)

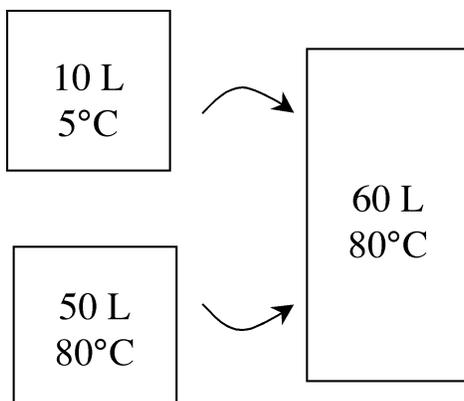
$$T_b > T_a$$

Problem 2.7

(a) Total amount of energy required

· Necessary heat input is the total enthalpy change of the material (since p is constant)

· Determined by the final and initial state



·Enthalpy change is only due to the 10 L (the 50 L remains in exactly the same state)

$$dH = nc_p dT$$

$$\Delta H = 10L * \frac{1000g}{L} * \frac{1 \text{ cal}}{g \cdot K} * 75K$$

$$\Delta H = 750 \text{ kcal} = 3140 \text{ kJ}$$

$$\boxed{\Delta H = 0.87 \text{ kWh}}$$

(b) Entropy change

·Again, entropy change is solely determined by the final and initial state

$$dS = nc_p \frac{dT}{T}$$

$$\Delta S = 10L * \frac{1000g}{L} * \frac{1 \text{ cal}}{g \cdot K} * \ln\left(\frac{353}{278}\right) = 2.38 \frac{\text{kcal}}{K}$$

$$\boxed{\Delta S = 9993 \frac{J}{\text{mol} \cdot K}}$$

Problem 2.8

$$w_1 = - \int p dV = -RT_1 \int \frac{dV}{V} = -RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$w_3 = -RT \ln\left(\frac{V_4}{V_3}\right)$$

The second step where $Q_2 = 0$ gives $dU = dw$

$$BdT = -pdV = -RT \frac{dV}{V}$$

$$B \ln\left(\frac{T_3}{T_1}\right) = -R \ln\left(\frac{V_3}{V_2}\right)$$

and the fourth step

$$B \ln\left(\frac{T_1}{T_3}\right) = -R \ln\left(\frac{V_1}{V_4}\right)$$

Thus

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \text{ or } \frac{V_1}{V_2} = \frac{V_4}{V_3}$$

and

$$\frac{w_1}{T_1} = R \ln \left(\frac{V_1}{V_2} \right) = R \ln \left(\frac{V_4}{V_3} \right) = \frac{-w_3}{T_3}$$

$$-w = -w_1 - w_3 = -w_1 + w_1 \left(\frac{T_3}{T_1} \right) = \frac{w_1 (T_3 - T_1)}{T_1} = -\frac{w_3 (T_3 - T_1)}{T_3} = -\frac{Q(T_3 - T_1)}{T_1} = \frac{Q_3(T_3 - T_1)}{T_3}$$

By drawing the heat Q_3 from a heat source at T_3 one may thus produce mechanical work in the amount of $\frac{Q_3(T_3 - T_1)}{T_3}$ if the rest of the energy, $\frac{Q_3 T_1}{T_3}$ can be disposed of as heat to a heat sink at T_1

Problem 2.9

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{environment}$$

There is no heat flow into the environment, so

$$\Delta S_{environment} = 0$$

But for the system (the gas) \rightarrow

·The gas goes from state 1 at P_i, V_i, T_i to a state 2 at $P_o, V_o, T_o (= T_i)$ with $P_o < P_i$

·To compute the ΔS_{gas} we need to know how the entropy changes with pressure (or volume) at constant T

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \text{(Maxwell Relation)}$$

and for an ideal gas

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

$$\Delta S_{gas} = -R \int_{P_i}^{P_o} \frac{1}{P} dP = -R \ln \left(\frac{P_o}{P_i} \right)$$

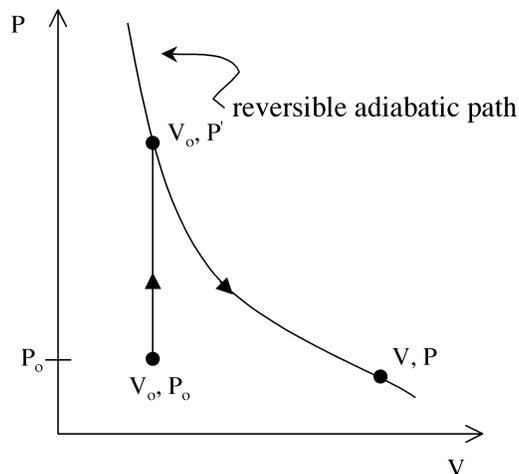
since $P_i > P_o$

$$R \ln \left(\frac{P_i}{P_o} \right) > 0$$

Since $\Delta S_{universe} > 0$ the process is irreversible

Problem 2.10

To calculate $U(P, V)$ for any (P, V) given a value $U(P_o, V_o)$ at some (P_o, V_o) it is suitable for this system to follow the path sketched below.



First go from $V_o, P_o \rightarrow V_o, P'$ (i.e. constant volume)

A constant volume, if only P-V work is possible

$$dU = \delta Q$$

$$\Delta U = U(P', V_o) - U(P_o, V_o) = Q = A(P' - P_o)$$

P' is unknown, but we do know because of the path we chose from $(V_o, P_o) \rightarrow (V, P)$ that (V_o, P') and (V, P) are connected by a reversible adiabat. Therefore,

$$P'V_o^\gamma = PV^\gamma \text{ or } P' = P \left(\frac{V}{V_o} \right)^\gamma$$

So,

$$\boxed{U(P', V_o) - U(P_o, V_o) = A(P'r^\gamma - P_o)} \quad (\text{with } r = \frac{V}{V_o})$$

Second go from $V_o, P' \rightarrow V, P$

Along the reversible adiabat $Q = 0$ and therefore

$$\Delta U = U(P, V) - U(P', V_o) = - \int_{V_o}^V P^* dV^*$$

with P^* and V^* representing values along the adiabat going through (V, P) . To calculate this integral use

$$P^*V^{*\gamma} = PV^\gamma$$

$$P^* = \frac{PV^\gamma}{V^{*\gamma}}$$

So,

$$\Delta U = - \int_{V_o}^V PV^\gamma \frac{dV^*}{V^{*\gamma}}$$

$$\Delta U = \left[\frac{PV^\gamma}{(\gamma-1)} \left(\frac{1}{V^{*(\gamma-1)}} \right) \right]_{V_o}^V = \frac{PV^\gamma}{(\gamma-1)} \left(\frac{1}{V^{(\gamma-1)}} - \frac{1}{V_o^{(\gamma-1)}} \right)$$

$$\boxed{\Delta U = U(P, V) - U(P', V_o) = \frac{PV^\gamma}{(\gamma-1)} (1 - r^{\gamma-1})} \quad (\text{with } r = \frac{V}{V_o})$$

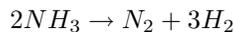
Combining the first and second step

$$\boxed{\Delta U_{tot} = U(P, V) - U(P_o, V_o) = A(P'r^\gamma - P_o) + \frac{PV^\gamma}{(\gamma-1)} (1 - r^{\gamma-1})} \quad (\text{with } r = \frac{V}{V_o})$$

LEVEL 3 PROBLEMS

Problem 3.1

The reaction at 1200K is



$P = \frac{nRT}{V}$, T and V are constant but n increases by a factor of 2 in the reaction. Therefore

$$P_f = 2P_i \rightarrow \boxed{P_f = 20atm}$$

(b) Heat flow

The system is under constant volume ($dV = 0$) so $W = 0$ and

$$\Delta U = Q$$

We can compute U from H because

$$U = H - PV$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - \Delta(nRT) = \Delta H - RT\Delta n$$

$$\Delta H = 87 \frac{\text{kJ}}{\text{mole}} \text{ and } \Delta n = 2 \text{ moles}$$

$$\Delta U = 87000 \frac{\text{J}}{\text{mole}} - (2) \left(8.314 \frac{\text{J}}{\text{mole} \cdot \text{K}} \right) (1200\text{K})$$

$$\Delta U = \boxed{Q = 67046 \frac{\text{J}}{\text{mole}}}$$

(c) System is adiabtic and under constant volume $\implies \Delta U = 0$

So,

$$\Delta U_{\text{reaction}} + \int_{1200}^{T_a} (c_{v,N_2} + 3c_{v,H_2}) dT = 0$$

$$T_a = 1200 - \frac{\Delta U_{\text{reaction}}}{c_{v,N_2} + 3c_{v,H_2}}$$

use $c_p - c_v = R$

$$T_a = 1200 - \frac{67046 \frac{\text{J}}{\text{mole}}}{4 * 24.686 \frac{\text{J}}{\text{mole} \cdot \text{K}}}$$

$$\boxed{T_a = 521\text{K}}$$

The system cools down which is expected given that the reaction is endothermic.

Problem 3.2

We can define the system as the gas in the tank (n_o moles) and the gas that will be squeezed into the tank (n_c moles). It will helpful to define some variables

- P_o = The initial pressure in the tank
- P_f = The external pressure pushing gas in
- T_o = The initial temperature of the gas
- T_f = The final temperature of the gas (what we want to solve for)
- V = The volume of the tank
- V_f = The volume of the gas pushed in

We can write the following relationships

$$n_o = \frac{P_o V}{RT_o}$$

$$n_o + n_c = \frac{P_f V}{RT_f}$$

$$V_c = \frac{n_c RT_o}{P_f}$$

Since this is an ideal gas we know that the internal energy change is only a function of temperature, given by

$$\Delta U = (n_o + n_c)c_v(T_f - T_o)$$

Givem that the process is adiabatic (isolated),

$$\Delta U = Q + W = W \quad (Q = 0)$$

But for this case we know that

$$W = P_f V_c = n_c RT_o$$

or the external pressure (which is constant) times the volume of gas pushed in. Now we can just work through eliminating variables to find the final temperature.

$$\begin{aligned}
 n_c RT_o &= (n_o + n_c) c_v (T_f - T_o) \\
 n_c RT_o &= \frac{P_f V}{RT_f} c_v (T_f - T_o) \\
 RT_o \left(\frac{P_f V}{RT_f} - \frac{P_o V}{RT_o} \right) &= \frac{P_f V}{RT_f} c_v (T_f - T_o) \\
 P_f RT_o - P_o RT_f &= P_f c_v (T_f - T_o) \\
 P_f T_o (R + c_v) &= T_f (P_o R + P_f c_v) \\
 T_f &= \frac{P_f T_o (R + c_v)}{P_o R + P_f c_v}
 \end{aligned}$$

Treating air as a diatomic ideal gas, we can use $c_v = \frac{5}{2} R$ and solve for T_f

$$T_f = \frac{298 \cdot 1 \cdot (R + \frac{7}{2} R)}{(0.5R + 1 \cdot c_v)} = \left(\frac{7}{6} \right) 298$$

$$\boxed{T_f = 347.6K}$$

Problem 3.3

Assume that the volume change resulting from the reaction $A + B \rightarrow AB$ is ΔV and the heat of reaction is Q . During the reaction, the system will perform work against the environment which has a constant pressure P_o . Since the pressure of the environment P_o is constant, the external work done by the system is

$$w = -P_o \Delta V$$

Using the first law

$$\Delta U = Q - P_o \Delta V$$

$$Q = \Delta U + P_o \Delta V$$

In the initial and final states of the reaction (both equilibrium states), the pressure of the gas has to equal P_o (otherwise they wouldn't be equilibrium states). Therefore if P is the pressure of the gas

$$P = P_o$$

or

$$Q = \Delta U + \Delta(PV)$$

$$\boxed{Q = \Delta H}$$

where ΔH is the difference of enthalpies in the initial and final states.

Problem 3.4

Closed system solution

System is gas flowing into the tank

$$U_2 - U_1 = Q + w = w \quad (Q = 0 \text{ (adiabatic)})$$

$$U_2 - U_1 = P_1 V_1$$

For an ideal gas,

$$U_2 - U_1 = n c_v (T_2 - T_1)$$

$$P_1 V_1 = n R T_1$$

So,

$$\begin{aligned}nc_v(T_2 - T_1) &= nRT_1 \\c_v T_2 &= (R + c_v)T_1 = c_p T_1 \\T_2 &= \frac{c_p}{c_v} T_1\end{aligned}$$

Open system solution

System is the tank

$$\begin{aligned}\underline{H}_i m_i &= U_f - U_i = \underline{U}_f m_f \\U_{initial} &= 0 \text{ because } m_{initial} = 0 \\m_{in} &= m_f \\\underline{H}_i &= \underline{U}_f = \underline{U}_{in} + P_{in} V_{in} \\\underline{U}_f - \underline{U}_i &= P_{in} V_{in} \\c_v(T_f - T_i) &= RT_i \\T_f &= \frac{c_p}{c_v} T_i\end{aligned}$$

Problem 3.5

(a) Gas in tank I is undergoing an adiabatic reversible expansion

$$\begin{aligned}\frac{T_2}{T_1} &= \left(\frac{P_2}{P_1}\right)^{\frac{R}{c_p}} \\T_2 &= 300 \left(\frac{5}{10}\right)^{\frac{R}{\frac{5}{2}R}} \\T_2 &= 246 K\end{aligned}$$

(b) Try to get T_{II} from the fact that

$$\Delta U_{tot} = \Delta U_I + \Delta U_{II} = 0$$

because the total system is isothermal. ΔU_I is the internal energy change of gas that remains in I and ΔU_{II} is the internal energy change of gas that ends up in tank II.

$$\begin{aligned}\Delta U_{II} &= n_{II} c_v (T_{II} - T_1) \\\Delta U_I &= n_I c_v (T_I - T_1)\end{aligned}$$

need to find n_I

$$\begin{aligned}n &= \frac{PV}{RT} \\\frac{n_I}{n_1} &= \frac{P_I T_1}{T_I P_1} = \frac{5 \text{ atm}}{10 \text{ atm}} \cdot \frac{300 K}{246 K} = 0.61 \\n_{II} &= 1 - n_I = n_1(1 - 0.61) = 0.39n_1\end{aligned}$$

now from $\Delta U_I + \Delta U_{II} = 0$

$$\begin{aligned}\Delta U_{II} &= -\Delta U_I \\0.39n_1 c_v (T_{II} - 300) &= -0.61n_1 c_v (246 - 300) \\T_{II} &= 384 K\end{aligned}$$

(c) Entropy change $\rightarrow S$ varies with T and P

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

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{c_p}{T} \text{ and } \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\frac{R}{P}$$

$$dS = \frac{c_p}{T} dT - \frac{R}{P} dP$$

For the gas remaining in tank I $dS_I = 0$ as it is undergoing an adiabatic reversible expansion.

For the gas ending up in tank II

$$\Delta S = n_{II} \left[c_p \ln \left(\frac{T_{II}}{T_o} \right) - R \ln \left(\frac{P_{II}}{P_o} \right) \right]$$

$$P_o = 10 \text{ atm}, T_o = 300K$$

$$n_{II} = 0.39 \text{ (per mole of gas initial in tank I)}$$

$$T_{II} = 384K$$

$$P_{II} = \frac{n_{II}RT_{II}}{V} = \frac{n_{II}}{n_1} \frac{T_{II}}{T_o} = 5 \text{ atm}$$

$$\Delta S = 0.39n_1 \left[\frac{7}{2} R \ln \left(\frac{384}{300} \right) - R \ln \left(\frac{5}{10} \right) \right]$$

$$\Delta S = 5.05n_1 \frac{J}{K \cdot mole}$$

LEVEL 4 PROBLEMS

Problem 4.1

This is a very tricky question which is why it is alone in Level 4.

First let's determine the equilibrium conditions. Assume that the system has somehow reached equilibrium with final values T_1^f, P_1^f, V_1^f for compartment 1 and T_2^f, P_2^f, V_2^f for compartment 2. We can ask what criteria must these variables satisfy for the system to be in equilibrium.

Well we know that for any reversible change around equilibrium

$$dU = dU_1 + dU_2 = 0$$

i.e. $U(V, S)$ must be minimal at equilibrium, and

$$dS = dS_1 + dS_2 = 0$$

i.e. $S(U, S)$ must be maximal at equilibrium.

Since there is no heat flow between compartments and between the chamber and the environment (since all walls are adiabatic)

$$dS_1 = 0$$

$$dS_2 = 0$$

So at equilibrium, the only reversible changes we can make are in the volume of the compartments, i.e.

$$dV_1 = -dV_2$$

Then we can write (for a reversible change)

$$dU_1 = -P_1^f dV_1 = +P_1^f dV_2$$

$$dU_2 = -P_2^f dV_2$$

$$dU = dU_1 + dU_2 = (P_1^f - P_2^f)dV_2 = 0$$

since this should hold for arbitrary dV_2 ,

$$P_1^f = P_2^f$$

i.e. equilibrium is characterized by mechanical equilibrium.

NOTE: Since $dS_1 = 0$ and $dS_2 = 0$, the equilibrium condition that $dU = 0$ does not yield any information about the final temperatures T_1^f and T_2^f . This means that the final temperatures of this system depend on the path followed by the system to attain equilibrium.

The question remains: can we obtain equilibrium from the initial state $T_1 = T_o, T_2 = T_o, P_1 \neq P_2$, and $n_1 \neq n_2$ by following a reversible path?

The answer is: probably not.

One candidate reversible path is to allow the piston to very slow move until the equilibrium pressures are attained (i.e. $P_1^f = P_2^f$). This path, however, cannot proceed reversible for the following reason:

Assume that it can proceed reversibly. Then an infinitesimal change in the volume of compartment 1 by dV_1 will result in an increase of the internal energy of compartment one by

$$dU_1 = -P_1 dV_1$$

The change in internal energy of compartment 2 is

$$dU_2 = -P_2 dV_2 = P_2 dV_1$$

But since both compartments are adiabatically sealed from the environment,

$$dU = 0 \implies dU_1 = -dU_2$$

or

$$-P_1 dV_1 = -P_2 dV_1$$

or

$$P_1 = P_2$$

But this is not true except in the final equilibrium state. In the initial state $P_1 \neq P_2$ by assumption.

\implies Therefore the suggested path cannot proceed reversibly. The suggested path must be accompanied by dissipation (through friction between the piston and the walls for example). This dissipation will be accompanied by a production of heat. We cannot predict a-priori how much of that heat evolves to compartment 1 or compartment 2 though.