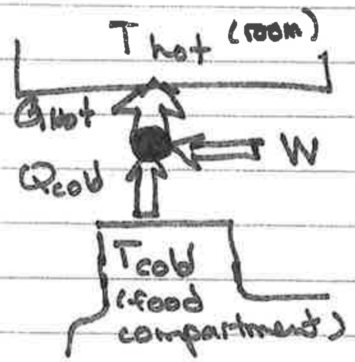
Phys 114
Seminar 2
Problem Solutions

1: Ideal fridge
G & T Problem 2.19

A fridge (see picture ...
The symbol ● is our engine)



$$COP = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{cold}}{W}$$

TS: Maximum (for reversible fridge)

is $COP = \dfrac{T_{cold}}{T_{hot} - T_{cold}}$ ⓪

Solution: $\left\{ \begin{array}{l} \text{1st Law} \\ \text{Conservin of energy ... no} \end{array} \right.$
frictional losses ... means $Q_{cold} + W = Q_{hot}$ ①

And $$\Delta S = \underbrace{-\frac{Q_{cold}}{T_{cold}}}_{S_{fridge}} + \underbrace{\frac{Q_{hot}}{T_{hot}}}_{S_{room}}$$ Entropy additivity ②

assuming, again, engine is $\left\{ \begin{array}{l} \text{ideal} \\ \underline{\text{not}}\text{ ideal} \end{array} \right.$. $\Delta S \left\{ \begin{array}{l} = 0 \\ > 0 \end{array} \right.$ ③

Combining ② & ③ → $$\frac{Q_{hot}}{Q_{cold}} \underset{\text{if not ideal}}{\overset{\text{if ideal}}{\geq}} \frac{T_{hot}}{T_{cold}}$$ ④

So $$COP = \frac{Q_{cold}}{Q_{hot} - Q_{cold}} \underset{\text{if not ideal}}{\overset{\text{if ideal}}{\leq}} \underline{\underline{\frac{T_{cold}}{T_{hot} - T_{cold}}}}$$

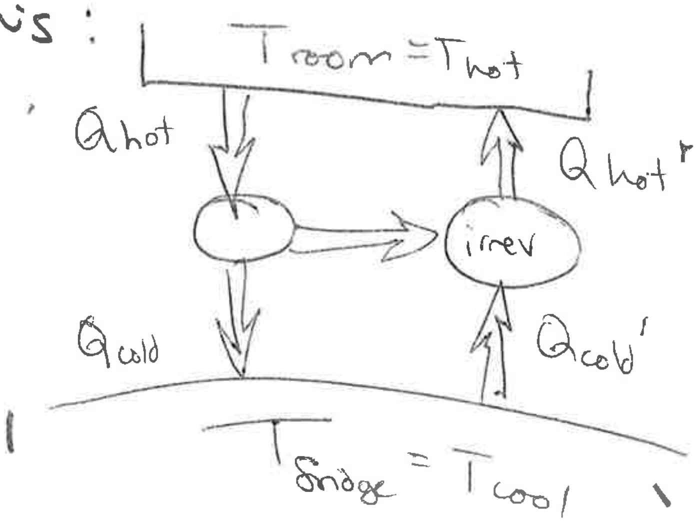
From ⓪ and ①

from ④

QED

1: continued

Q/ Why not an irreversible fridge ... can't it have a higher η? A/ No, this was taken care of by sign at bottom of previous page. But here is yet another way: Let's suppose we had a better fridge with $\eta_{irr} > \eta$ between same two baths. We could do this:



Since original fridge is reversible, work it in reverse as an engine

$$W = Q_{hot} - Q_{cold} = Q_{hot}' - Q_{cold}'$$

If we want

$$\begin{array}{c} \eta' > \eta \\ \shortparallel \\ \dfrac{Q_{cold}'}{W} \end{array}$$

We must have $Q_{cold}' > Q_{cold}$. And to keep W same, must thus have

(since $W = Q_{hot}' - Q_{cold}'$) $Q_{hot}' > Q_{hot}$

But the result is that $Q_{hot}' - Q_{hot} > 0$ is heat given to hot place, and $Q_{cold}' - Q_{cold} > 0$ is heat taken from cold place. Work is internal ... none from outside. This device violates Clausius statement of 2nd Law.

2: Partial derivatives

a) G + T Prob 2.3

$$z(x,y) = x^2y + 2x^4y^6$$

Find partials wrt x & y ... includind second mixed partials, which should be equal.

other Notn

Soln

$$\left.\frac{\partial z}{\partial x}\right|_y = 2xy + 8x^3y^6 \equiv \left(\frac{\partial z}{\partial x}\right)_y$$

$$\left.\frac{\partial z}{\partial y}\right|_x = x^2 + 12x^4y^5 \equiv \left(\frac{\partial z}{\partial y}\right)_x$$

$$\frac{\partial^2 z}{\partial x \partial y} = 2x + 48x^3y^5 = \frac{\partial^2 z}{\partial y \partial x}$$ ✓

do me first I guess ...

b) Spose $u(x,y) = xy$

What is $\left(\frac{\partial z}{\partial x}\right)_u$?

Answer

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

so

$$\left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y \underbrace{\left(\frac{\partial x}{\partial x}\right)_u}_{1} + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_u \leftarrow \left(\frac{\partial y}{\partial x}\right)_u = \frac{-u}{x^2} = \frac{-xy}{x^2} = -y/x$$

since $u = xy$
$y = u/x$

$$= 2xy + 8x^3y^6 + (x^2 + 12x^4y^5)\left(\frac{-y}{x}\right)$$

$$= 2xy + 8x^3y^6 - xy - 12x^3y^6$$

$$\therefore \left(\frac{\partial z}{\partial x}\right)_u = xy - 4x^3y^6$$

3: Establishing Equilibrium

a. From Callen

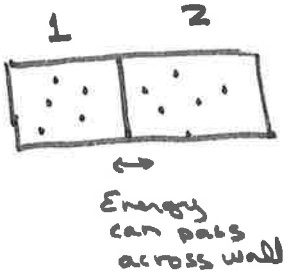
2.6-3. Two particular systems have the following equations of state:

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}}$$

and

$$\frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}}$$

where R is the gas constant (Problem 2.6-2). The mole number of the first system is $N^{(1)} = 2$ and that of the second is $N^{(2)} = 3$. The two systems are separated by a diathermal wall, and the total energy in the composite system is 2.5×10^3 J. What is the internal energy of each system in equilibrium?



$U_1 + U_2 = 2.5 \times 10^3$ J

What is $U_1 + U_2$?

Idea: $S_1 + S_2 = S$ is maximized ...

This will occur when (see Equ's 2.48 - 2.53 of Callen) $\frac{1}{T_1} = \frac{1}{T_2}$ (or $T_1 = T_2$)

and Thus, $\frac{3}{2} R \frac{N_1}{U_1} = \frac{5}{2} R \frac{N_2}{U_2}$

divide by R's & sub in N's

$\Rightarrow \frac{3}{2} \cdot 2 \cdot \frac{1}{U_1} = \frac{5}{2} \cdot 3 \cdot \frac{1}{U_2}$

$\Rightarrow \frac{U_1}{3} = \frac{2U_2}{15}$; $U_1 = \frac{6U_2}{15} = \frac{2}{5}U_2$

Now using $U_1 + U_2 = 2.5 \times 10^3 J = \frac{7}{5} U_2$

$\Rightarrow U_2 = 1.79 \times 10^3 J$

$U_1 = .71 \times 10^3 J$

(Prob 5 (cont))

b) From Callen

2.7-2. Two particular systems have the following equations of state:

$$\frac{1}{T^{(1)}} = \frac{3}{2}R\frac{N^{(1)}}{U^{(1)}}, \qquad \frac{P^{(1)}}{T^{(1)}} = R\frac{N^{(1)}}{V^{(1)}}$$

and

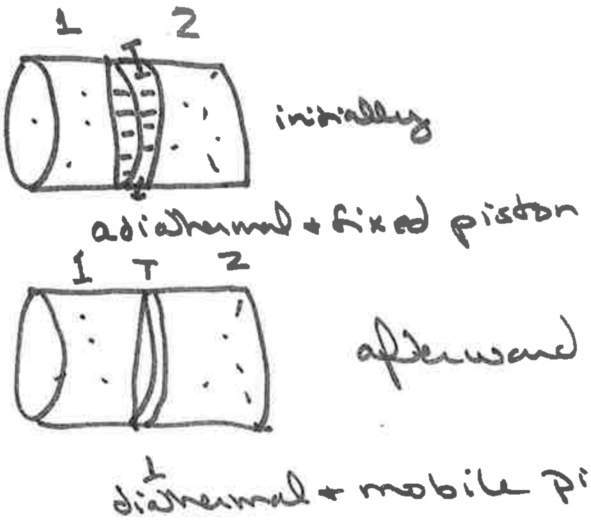
$$\frac{1}{T^{(2)}} = \frac{5}{2}R\frac{N^{(2)}}{U^{(2)}}, \qquad \frac{P^{(2)}}{T^{(2)}} = R\frac{N^{(2)}}{V^{(2)}}$$

The mole number of the first system is $N^{(1)} = 0.5$ and that of the second is $N^{(2)} = 0.75$. The two systems are contained in a closed cylinder, separated by a fixed, adiabatic, and impermeable piston. The initial temperatures are $T^{(1)} = 200$ K and $T^{(2)} = 300$ K, and the total volume is 20 liters. The "setscrew" which prevents the motion of the piston is then removed, and simultaneously the adiabatic insulation of the piston is stripped off, so that the piston becomes moveable, diathermal, and impermeable. What is the energy, volume, pressure, and temperature of each subsystem when equilibrium is established?

It is sufficient to take $R \simeq 8.3$ J/mole K and to assume the external pressure to be zero.

Answer:
$U^{(1)} = 1700$ J

$N_1 = 0.5$
$N_2 = 0.75$
$T_1 = 200K$
$T_2 = 300K$
$V_1 + V_2 = 20\,l$



Solve : Afterward $\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{2}R\frac{N_1}{U_1} = \frac{5}{2}R\frac{N_2}{U_2}$

Need total energy.
Find from initial conditions: initial $\frac{1}{T_i} = f_i R \frac{N_i}{U_i}$ $f_i = \begin{cases} 3/2 & i=1 \\ 5/2 & i=2 \end{cases}$; $U_2 = 4674.38J$
$U_1 = 1246.5J$

$\Rightarrow U_{TOTAL} = 5920.88$

Thence, equating $\frac{1}{T_1}$ & $\frac{1}{T_2}$ $\Rightarrow$ $U_1 = 1691.68 \approx \underline{1700\,J}$
$U_2 = 4229.2 \approx \underline{4200\,J}$

Now have some simultaneous equs to solve:

First confirm that $\frac{1}{T} = f_i R \frac{N_i}{U_i}$ gives $T = 271.416$ K
$\underline{T \approx 271K}$

Now need to solve some simultaneous equ's

(Prob 3b) (cont)

$$\frac{P_1}{T} = \frac{P_2}{T} \; ; \; P_1 = \frac{R N_1 T}{V_1} \; ; \; P_2 = \frac{R N_2 T}{V_2} \; ;$$

$$V_1 + V_2 = 20 \; \ell \; = 20 \times 10^{-3} \; m^3 .$$

Use Mathematica

```
= Solve[{P1 / T == P2 / T, P1 == R * N1 * T / V1, P2 == R * N2 * T / V2, V1 + V2 == 20 * 10^-3},
   {P1, P2, V1, V2}]

  Solve::ratnz : Solve was unable to solve the system with inexact coefficients.
        The answer was obtained by solving a corresponding exact system and numericizing the result. >>

= {{P1 → 140 967., P2 → 140 967., V1 → 0.008, V2 → 0.012}}
```

↖ N/m^2 or Pa ↖ m^3 ...

so $V_1 = 8 \; \ell$, $V_2 = 12 \; \ell$

4: Write vdW equ of state in form $P = f(T,\rho)$. Here goes ...

$$\left[P + a\left(\frac{n}{V}\right)^2\right]\left[\frac{V}{n} - b\right] = RT$$

$$\therefore \quad P = \frac{RT}{\frac{V}{n} - b} - a\left(\frac{n}{V}\right)^2$$

now, $\rho = \frac{N}{V} = \frac{nN_A}{V} \quad \therefore \quad \frac{n}{V} = \frac{\rho}{N_A} \quad ; \quad \frac{V}{n} = \frac{N_A}{\rho}$

↗ Number density... physicists like it ☺

$$\therefore \quad P = \frac{RT}{\frac{N_A}{\rho} - b} - \frac{a}{N_A^2}\rho^2$$

$$P = \frac{RT\rho}{N_A - b\rho} - \frac{a}{N_A^2}\rho^2 = f(T,\rho) \quad ✓$$

Thus, homog + zero order in extensive variables. If increase as in

$$U, V, N \rightarrow \lambda U, \lambda V, \lambda N \quad \text{then}$$

$$P \rightarrow P \equiv \lambda^0 P \quad ☺$$

homog. + of order 0

5. Free expansion of a non-ideal Gas

To find: $\left(\frac{\partial T}{\partial V}\right)_E$ for vdW energy equ of state

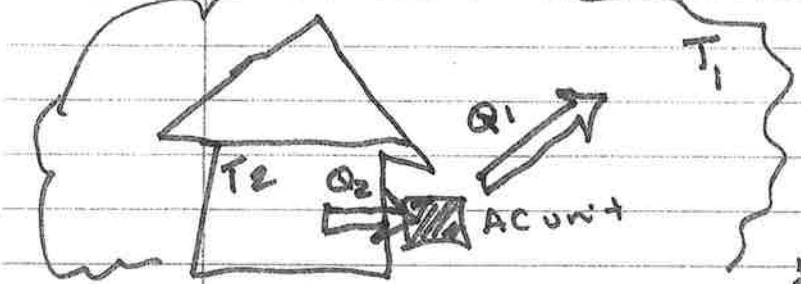
Sol'n: This is $E = \frac{3}{2}NkT - \frac{N^2}{V}a$

Thus since $dE = 0$, $0 = \frac{3}{2}Nk\left(\frac{\partial T}{\partial V}\right)_E + \frac{N^2}{V^2}a$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_E = -\frac{2}{3}\frac{N}{k}\frac{a}{V^2}$$

Since this quantity is less than zero, $V \uparrow \Rightarrow T \downarrow$ ... hence cooling when E is constant. This is, for example, during a free expansion.

6: Realistic fridge B+B 13.6



Electrical energy E is consumed. But heat leaks back into house according to "Newton's Law of heating/cooling"

Note E is W, really the electrical work done by AC unit

$$Q = A\left[T_1 - T_2\right] \quad ⓪$$

To find: $T_2(T_1, E, A)$ for operation of this AC unit.

Answer: In steady state, will have $Q_2 = Q$ ①

Also, cons of energy (1st law) means $Q_2 + E = Q_1$ ②

Reversible, Carnot means $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ ③

Thus use ③ in ② $\Rightarrow$ $Q_2 + E = Q_2 \frac{T_1}{T_2}$

Now use ① $\Rightarrow$ $E = Q\left(\frac{T_1}{T_2} - 1\right)$

Now use ⓪ $E = A(T_1 - T_2)\left(\frac{T_1}{T_2} - 1\right) = \frac{A}{T_2}(T_1 - T_2)^2$

algebra $\Longrightarrow$ $T_2^2 - \left(2T_1 + \frac{E}{A}\right)T_2 + T_1^2 = 0$

$$\frac{0.3E_{max}}{A} = \frac{10^2}{293}$$

$\Rightarrow E_{max} = 1.14A$

6: (continued)

$T_2 < T_1$ so want − root

Solving:

$$T_2 = T_1 + \frac{E}{2A} \pm \sqrt{\left(\frac{E}{2A}\right)^2 + \frac{ET_1}{A}}$$

System is designed so that, though it can produce E_{max} of work, 30% E_{max} will keep inside at 20°C when outside is at 30°C.

Note: 20°C = 293 K = T_2
30°C = 303 K = T_1

Let $\frac{E}{A} = E$ Let $\frac{E_{max}}{A} = r$

6: (cont)

$$T_2 - T_1 = \frac{.3}{2}x - \sqrt{\left(\frac{.3}{2}x\right)^2 + .3x(303)}$$

///

10 here, for $E = 0.3\,E_{max}$

Thus, $10 - 0.15x = \sqrt{(.15x)^2 + .3x(303)}$

square both sides

$$100 - 3.0x + \cancel{(.15x)^2} = \cancel{(.15x)^2} + .3x(303$$

$$100 = 93.9\,x$$

$$\Rightarrow \quad x = 1.14 = \frac{E_{max}}{A}$$

☺ as on p. 2

Now go back.... same $T_2 = 20°C = 293\,K$

what is T_1?

Or, let $T_1 = T_2 + \Delta T$ & find ΔT:

$$\Delta T = \frac{x}{2} - \sqrt{\left(\frac{x}{2}\right)^2 + x(293 + \Delta T)}$$

$$\Delta T - \frac{x}{2} = \sqrt{\left(\frac{x}{2}\right)^2 + x(293 + \Delta T)}$$

$$\Delta T^2 - x + \cancel{\left(\frac{x}{2}\right)^2} = \cancel{\left(\frac{x}{2}\right)^2} + x(293 + \Delta T)$$

$x = 1.064$:

$$\Delta T^2 - 1.14\,\Delta T - 294(1.14) = 0 \Rightarrow \underline{\underline{\Delta T = 18.3^{\circ}}}$$

☺

7: a) Solid copper cooled from $42^\circ C$ to $20^\circ C$.

First of all, how much copper. Eh, say 1kg. Then since $C = 0.385 \frac{J}{g\,^\circ C}$

$$Q = mc\Delta T = 10^3 \frac{g}{kg}\, 0.385 \frac{J}{g\,^\circ C} (-22^\circ C)$$

$$= -8470 \text{ J}$$

But not quite what we want now: need it later

Rather,

$$\Delta S_{system} = \int_{T_1}^{T_2} \frac{C\,dT}{T}$$

$$= 385 \frac{J}{K} \ln \frac{T_2}{T_1}$$

$$= 385 \frac{J}{K} \ln \frac{293}{315}$$

$$\Delta S_{system} = -27.87 \text{ J/K}$$

or e.u. for entropy units

NB for any other mass of Cu, m just multiply this by ratio of $\frac{m\text{ kg}}{1\text{ kg}}$,

How about $\Delta S_{system} + \Delta S_{universe}$?

What was process? Make one up... huuuuge heat bath at $20^\circ C$. Then in limit it is huge with enormouse C_{bath}, $\frac{\Delta Q_{bath}}{T} = \Delta S_{bath}$ where $T = 20^\circ C = 293 K$

! this is $-Q_{system} \equiv Q_{bath}$

$$\therefore \Delta S_{bath} = +\frac{8470 \text{ J}}{293 \text{ K}} = +28.91 \frac{J}{K}$$

Vau! I didn't break thermodynamics! $\Delta S_{bath} + \Delta S_{system} = +1.04$ e.u.

7: (cont)

b) Now 100g of ice melts at 0°C.

ΔQ is latent heat of melting ...

$$\Delta Q = 334\frac{J}{g} \times 100g = {}^{+}33{,}400\,J$$

So $\Delta S_{system} = \frac{\Delta Q}{T} = \frac{33{,}400\,J}{273.15K} = {}^{+}122\frac{J}{K}$ (or e.u)

Oddly, spose we do this with bath (huuuge!) at temperature only slightly above 0°C ... say $(273.15+\epsilon)K$

Then $\Delta S_{bath} = \frac{-33{,}400J}{(273.15+\epsilon)K}$

$= -122\,J/K + \epsilon\, 33{,}400\,J$

So $\Delta S_{system} + \Delta S_{bath} = \epsilon\,(33{,}400)\,J/K$

Virtually zero....

c) Look at data in back of Schroeder

$\Delta S_{system + surroundings} = S_{andalusite} - S_{kyanite}$

$= (93.22 - 83.81)\,J/K$

$= \underline{+\,9.41\,J/K}$

for one mole

(Magicians can violate thermo, but this one doesn't need too ☺)

d) one mole, isothermal quasistatic $\Delta S_{gas} = R\ln\frac{V_2}{V_1} = R\ln 2$

$\Delta S_{surroundings} = -R\ln 2$ b/c

$\Delta S_{gas + surroundings} = 0$ b/c reversible ☺

Schroeder good reference for these ↓ see section 14.4

7 (cont)

e) adiabatic expansion ... $\Delta S_{gas} = \frac{3}{2} Nk \ln \frac{T_2}{T_1} + Nk \ln \frac{V_2}{V_1}$

one mole

assume monatomic

$$= \frac{3}{2} R \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

Since $TV^{\gamma - 1} = \text{const} = TV^{2/3}$

monatomic

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{2/3} \Rightarrow R \ln \frac{V_1}{V_2} + R \ln \frac{V_2}{V_1} = 0$$

$\Delta S_{gas} = 0$ ... but we knew that!

For universe? If quasistatic + <u>ideal</u>

(no friction) $\Delta S_{surroundings} = 0$

$\therefore$ $\Delta S_{system + surroundings} = 0$

reversible ☺

f) Joule / Free expansion?

1 mole $\Delta S_{gas} = + R \ln 2$

$\Delta S_{surroundings} = 0$

$\therefore$ $\Delta S_{system + surroundings} = R \ln 2 > 0$

irreversible

8: Exact differentials

a) $df = \underbrace{F(P,V)}_{\equiv PV}\, \partial P + \underbrace{G(P,V)}_{\equiv P^2}\, \partial V$

Is df exact?

Nope. if we thought it was,

F would be $\left.\frac{\partial f}{\partial P}\right|_V$

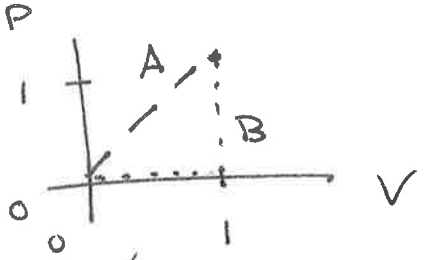
G " $\left.\frac{\partial f}{\partial V}\right|_P$

so mixed partials would be

$$\left.\frac{\partial F}{\partial V}\right|_P \overset{?}{=} \left.\frac{\partial G}{\partial P}\right|_V$$

$$P \overset{?}{=} 2P$$ No!

b) $\int_{00}^{11} df$ on



On B this is $\int_{V=0}^{V=1,\,P=0} (P\cancelto{0}{V}\, dP + \cancelto{0}{P^2}\, dV)$

on A, $P = V \equiv q$

$\int_{00}^{11} df = \int_0^1 (q^2 dq + q^2 dq)^{V=0,\,P=0} + \int_{V=1,\,P=0}^{V=1,\,P=1} (PV\, dP + P^2 \cancelto{0}{dV})$

$= 2\cdot\frac{1}{3} q^3\Big|_0^1 = \underline{2/3}$ $\qquad = 1\cdot\int_0^1 P\, dP = \frac{P^2}{2}\Big|_0^1 = \underline{\underline{1/2}}$

9: I broke thermodynamics ...

What is wrong with this expression which a scientist has found:

$$S = NR \ln\left(c\frac{UV}{N^2}\right) \quad c \text{ const. } ?$$

Why does it violate the 3rd Law?

B/c $$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

$$= \frac{\partial}{\partial U}\left(NR\ln U + NR\ln c\frac{V}{N^2}\right)_{V,N}$$

so $\frac{1}{T} = \frac{NR}{U}$, so $T = \frac{U}{NR}$

Thus as $T \to 0$, $U \to 0$. But if this is the case, then

$$\lim_{T\to 0} S = \lim_{U \to 0} NR\ln\left(\frac{cV}{N^2}U\right)$$

$$= -\infty$$

This is bad. Want, rather

$$\lim_{T\to 0} S = 0 \quad \ldots$$

or at least a unique constant like $\ln \Omega_0$

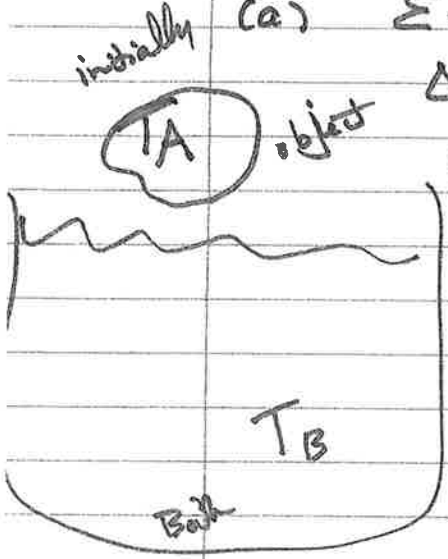
10: Positive Change of Entropy:

G&T 2.61

(a) Example 2.16 told us for thermal contact transfer with bath at temperature T_B

$\Delta S_{\text{total}} = C_A f\left(\frac{T_B}{T_A}\right)$

(Bath + object)



and $f(x) = \ln x + \frac{1}{x} - 1$

TS / To find: $f(x=1)$, $\frac{df}{dx}$

and that total entropy increases when $x > 1$ (so $T_B > T_A$)

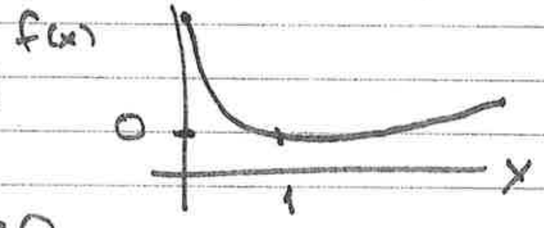
Answer

$f(x=1) = \ln 1 + \frac{1}{1} - 1 = \underline{0}$

also (c) $\frac{df}{dx} = \frac{1}{x} - \frac{1}{x^2} = \frac{1}{x}\left(1 - \frac{1}{x}\right)$

$= y(1-y)$, where $y = \frac{1}{x}$

This has change in slope at $y = 1$, hence $x = 1$



$\frac{df}{dx} < 0$ if $x < 1$

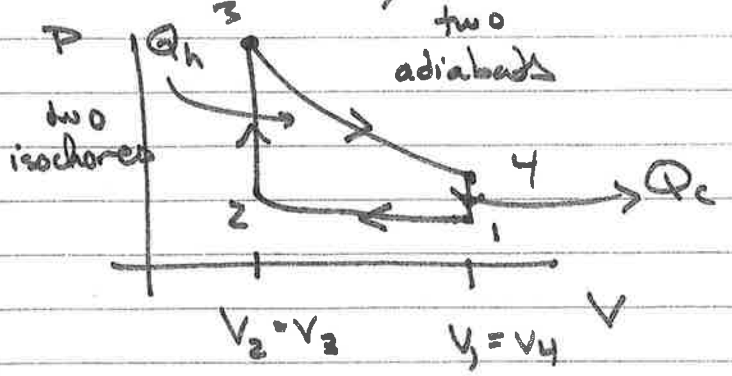
$\frac{df}{dx} > 0$ if $x > 0$

$\frac{df}{dx} = 0$ at $x = 0$ (minimum of entropy change ... where $\Delta S = 0$)

(b) Hmmm, what about cooling process?

We just have to look at function ... which is well-illustrated in plot above. Cooling is $x = T_B/T_A < 0$. It is still the case that $f\left(\frac{T_B}{T_A}\right) > 0$ .... so heat or cool, the entropy of the universe increases, except when $T_B = T_A$ in which case it stays the same.

Otto cycle   B+B 13.5



TS $\eta = 1 - r^{1-\gamma}$

$r = \frac{V_1}{V_2}$ compression ratio

Now $\eta = \frac{W}{Q_h}$ and $W = Q_h - Q_c$

Since have isochores for steps where Q enters/leaves

$$Q_h = C_v (T_3 - T_2)$$
$$Q_c = C_v (T_4 - T_1)$$

$$\Rightarrow \eta = \frac{T_3 - T_2 - T_4 + T_1}{T_3 - T_2}$$

$$\eta = 1 - \frac{(T_4 - T_1)}{T_3 - T_2}$$

Also recall $TV^{\gamma-1}$ = const. on adiabat

So $T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1}$ on top adiabat

But isochore...
$V_3 = V_2$
$V_4 = V_1$
$\Rightarrow T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$ ①

And $T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$ on bot adiabat ②

Subtracting ② from ① ...

$$(T_3 - T_2) V_2^{\gamma-1} = (T_4 - T_1) V_1^{\gamma-1}$$

$$\therefore \frac{(T_4 - T_1)}{(T_3 - T_2)} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

problem 11: (cont)

Hence

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

$$= 1 - \left(\frac{V_1}{V_2}\right)^{1-\gamma} = 1 - r^{1-\gamma} \quad \text{QED}$$

As for efficiency...

Carnot works between two temps, not four!

We could try to ascertain highest + lowest temperatures here...

Well, $T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

Dividing these row $\Rightarrow \frac{T_2}{T_3} = \frac{T_1}{T_4}, \quad \frac{T_3}{T_2} = \frac{T_4}{T_1}$

$$\text{so } \eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{(T_4/T_1 - 1)\, T_1}{\underbrace{(T_3/T_2 - 1)}\, T_2}$$

$$= 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3} \quad 1$$

which looks like Carnot efficiency between two temps, T_1 + T_2

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

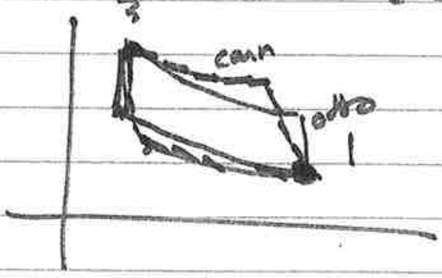
problem 11 (cont)

The only question is, which is highest temp + which lowest....

$T_1 < T_2$ and clearly $T_2 < T_3$

$T_4 < T_3$

So lowest temp is T_1 and highest is T_3. If Carnot operated btwn T_3 (hi) + T_1 (low) would have $\eta_{carnot} = 1 - \frac{T_1}{T_3} > \eta_{otto}$.



but that would be different cycle

Problem 12 - 13h

A problem to help us understand what it means for entropy to be maximal ...

This is a mockup of Callen problem 1.10-3. It is here to help us understand the somewhat mysterious statement that (Callen's Postulate II on p. 27) "the values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states."

For this example, I have chosen to look at a system with $\mathbf{S = (NVU)^{1/3}}$

The "constrained equilibrium state" could be a box divided in two by a wall that prevents anything being exchanged between the two sides. The "manifold of constrained equilibrium states" are equilibrium states with such walls in place. The "absence of the external constraint" could be taking away the wall. We could also look at just a partial absence of the constraint - a wall that can move so volume is exchanged, but still keep particles and energy separate, or can let particles through or energy through or .... If all three quantities can pass through the wall, the wall is absent and the constraint is truly gone.

Let us assume N = 50, V = 13 and U = 80 for our unconstrained system. We will play with constraining it ... dropping a wall that lets energy pass through (a "diathermal" or "conductive" wall.)

In terms of *Mathematica* functions, I will just write $S_{\text{uncostained}}$ as a function of U, and let N and V be fixed parameters. (We can always play with them later.)

```
Sunconstrained[U_] := (NN * V * U) ^ (1 / 3)
NN = 50; V = 13;
N[Sunconstrained[80]]

37.3251
```

This value, 37.3251 is the **entropy of the unconstrained system.**

OK, now we will constrain. Divide the box into A and B sides so particles and "volume" cannot cross the wall. Let S[U_A] be the entropy that results from having energy U_A on the A side and U - U_A on the B side. Total energy is U = 80. I will make, just on a whim, the choices of V_A , V_B , N_A and N_B that you see below ... being careful to be sure volumes sum to 13 and particle numbers to 50, as before!

```
NA = 30; NB = 20; VA = 9; VB = 4; U = 80;
```

The entropy is the sum of S_A and S_B ...

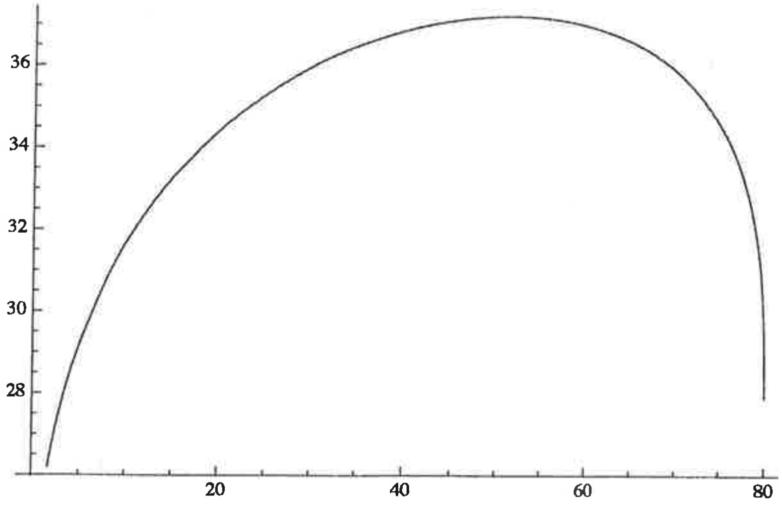
```
S[UA_] := (NA * VA * UA) ^ (1 / 3) + (NB * VB * (U - UA)) ^ (1 / 3)
```

Let's play with cases. First, spose all the energy is on the B side and none on the A side. That would be S[0], which is

```
N[S[0]]
18.5664
```

So far so good ... S[0] is a lot lower than $S_{\text{unconstrained}}$[80] = 37.3251.

Let's now plot S[U_A] to see if it is always lower than 37.3251



```
FindMaximum[S[x], {x, 55}]
{37.2087, {x → 51.8024}}
S[51.8024]
37.2087
```

Very cool. The constrained entropy is maximized by a certain partitioning of energies. Energy on A side is U_A = 51.8024 and on B side ... U_B= 80 - 51.802 = 28.198. **These energies maximize the entropy at S = 37.2087.** This is a maximum with a constraint: a diathermal wall in place. ***Notice:*** It is ever so slightly lower than the entropy of the unconstrained system where there is no wall.

QUESTION : What is the source of the difference in maximal entropy? Why is the maximum of the constrained S, which is $S = S_A + S_B = 37.2018$, less than the maximum of $S_{\text{uncostrained}} = 37.3251$? This difference isn't big. Is it even real? See below, the last part of this notebook for my answer ...

So far ... we have found that if the internal wall is made diathermal to let energy go back and forth, individual systems will come to energies such that U_A = 51.8024 and U_B = 80 - 51.8024 = 28.1976. Does this imply that the two sides come to the same temperature? For this: write derivative of S with respect to U in order to get T = $(\partial U / \partial S)_{V,N}$

```
Temp[UU_, NN_, VV_] := 3 * UU^(2 / 3) / NN^(1 / 3) / VV^(1 / 3)
Temp[51.8024, NA, VA]
6.4501
Temp[28.1976, NB, VB]
6.45009
```

Whoohoo ... $T_A = T_B$ at point in parameter space where S(U,V,N) is maximized wrt variations δU.

We could also do this: Given the form of S and that it varies the same way with U, V and N. We could do variations δV and δN to show $P_A = P_B$ if the wall can move to choose volume Similarly, we could show $\mu_A = \mu_B$ if the wall were porous to passage of particles.

ANSWER to question about entropy difference: The wall is keeping the density on side A equal to 30/9 = 5/3 which is less than side B's density of 20/4 = 5. The wall-free values of N_A and N_B would be different. Suppose we re-calculate everything assum-

*ing VA = 9, VB = 4, U = 80, and NA + NB = 50 but ... taking a guess at what would maximize entropy, the densities are as equal as we can get them. NA = 50 * 9/13 = 450/13 (not an integer! it's ok, though, for mathematical purposes) and NB = 200/13.*

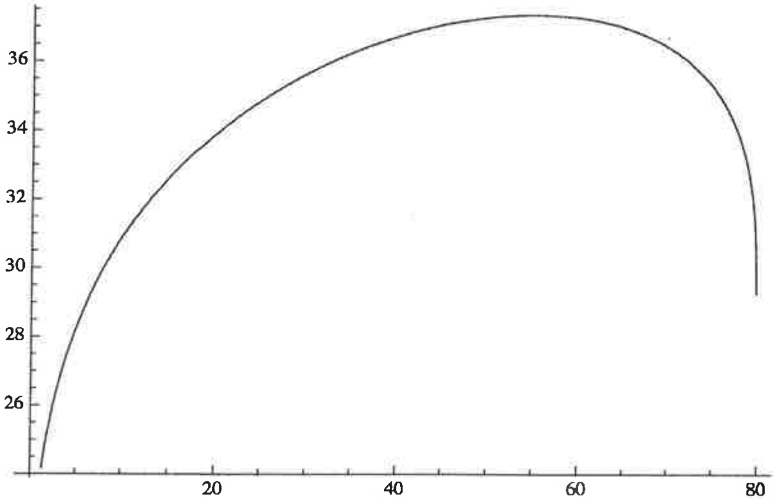
```
NA = 450 / 13; NB = 200 / 13; VA  = 9; VB = 4; U = 80;
```

```
N[S_unconstrained[80]]
```

```
37.3251
```

```
S[UA_] := (NA * VA * UA) ^ (1 / 3) + (NB * VB * (U - UA)) ^ (1 / 3)
```

```
Plot[Evaluate[S[UA]], {UA, 0, U}]
```



```
FindMaximum[S[x], {x, 55}]
```

```
{37.3251, {x → 55.3846}}
```

In conclusion: S = 37.3251 for this most recent choice of energy and density, where we have created constrained densities in A and B that are equal to each other. Thus, they are identical to unconstrained density that would exist without a wall. Also, the energies that nature chooses in order to maximize S are identical to what they would be were the wall not there. The particle numbers and the energies have the ratio

$N_A / N_B = U_A / U_B = V_A / V_B = 9/4 = 2.25$

(Note that this was *not* the ratio of the energies which maximized S when the particle numbers were set to $N_A = 30$ and $N_B = 20$, so that $N_A / N_B = 1.5$.)

The constrained and unconstrained entropies are now the same ... it doesn't matter if the wall is there or not.

Problema 13 → Callen 2.2-1

Find the three equations of state corresponding to

$$U = \underbrace{\frac{v_0\theta}{R^2}}_{\text{call me } C} \frac{S^3}{NV}$$

Definitions →

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} ; \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} ;$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Thus

$$T = \frac{3CS^2}{NV}$$

$$P = +\frac{CS^3}{NV^2}$$

$$\mu = -\frac{CS^3}{N^2V}$$

Now, we want to replace S and also (can we?) make these homog. of order 0 in extensive var's.

(Problem 13 cont')

last two ... P & μ equ's ...

$$\underline{P} = -\mu\frac{N}{V} = -\underline{\rho\mu} \quad ; \rho = \frac{N}{V}$$

$$\underline{\mu} = -P\frac{V}{N} = -\underline{P/\rho}$$

from either of these, say P one

$$S^3 = +\frac{PNV^2}{C}$$

$$S = +\frac{P^{1/3}(NV^2)^{1/3}}{C^{1/3}}$$

first equ

$$\Rightarrow \quad T = +\frac{3C}{NV}P^{2/3}\frac{(NV^2)^{2/3}}{C^{2/3}}$$

$$T = +3C^{1/3}P^{2/3}\frac{V^{1/3}}{N^{1/3}}$$

$$\underline{T = 3C^{1/3}P^{2/3}/\rho^{1/3}}$$

All are homog. of order 0 ☺