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Problems for the Advanced Physical Chemistry Student
Part 4, Thermodynamics (2nd Law)

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I. SYNOPSIS

This is a set of problems that were used near the turn of the century and which will be lost when the web site they were on disappears with my demise. Because these problems are being taken from the web and are being edited, their statements and the hints/answers offered are subject to the typical editorial errors that ensue when such work is undertaken in the vacuum of a non-teaching situation. Therefore, I claim any errors for myself, and hate to note that there most likely is no point in contacting me about them for obvious reasons.

II. THERMODYNAMICS, THE 2_{nd} LAW

1. (ch5q3) The density of C_6H_6(liquid) is 0.8790 g/cc at 20^oC. Assuming that the molar volume is independent of pressure find the change in entropy (in calories) which accompanies the compression of one mole of the substance from 1 to 11 atm.

Answer and/or Hint

We need to figure out an expression for

$$\left(\frac{\partial S}{\partial p}\right)$$

which can be obtained from

$$dG = -SdT + Vdp$$

Since

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

we would have

$$\left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp = -SdT + Vdp$$

It follows that

$$\left(\frac{\partial^2 G}{\partial p \partial T}\right) = \left(\frac{\partial^2 G}{\partial T \partial p}\right)$$

Since

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

and

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

the mixed partial

$$\left(\frac{\partial \left(\frac{\partial G}{\partial T}\right)_p}{\partial p}\right)_T = \left(\frac{\partial(-S)}{\partial T}\right)_p$$

and the mixed partial

$$\left(\frac{\partial \left(\frac{\partial G}{\partial p}\right)_T}{\partial T}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p$$

Finally, we obtain

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Since we are not given the temperature dependence of volume on temperature for benzene, we can assume that at the pressure range under consideration, it is zero, i.e., $\left(\frac{\partial V}{\partial T}\right)_p = 0$ and therefore,

$$\int dS = \int \left(\frac{\partial V}{\partial T}\right)_p dp = 0$$

Had we

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

as a measured quantity, we could have done a better job.

2. For a certain ideal gas $C_v = \frac{5}{2}R\frac{cal}{(mole^oC)}$. Calculate the change in entropy (in e.u., $\frac{calories}{^oK}$) suffered by 3 moles of the gas on being heated from 300 to 600^oK at constant pressure.

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Answer and/or Hint

$C_p = \frac{7}{2}R$, so we have

$$\Delta S = 3 \times \int_{300}^{600} \frac{\left(\frac{7}{2}R\right)}{T} dT$$

3. Assuming that for $CH_4(g)$ C_p is given by the expression:

$$C_p(CH_4(g)) = 3.422 + 7.845 \times 10^{-3}T - 4.165 \times 10^{-6}T^2$$

(the overall units of the heat capacity (above) are $\frac{cal}{(mole^oK)}$) find the entropy change resulting from heating 2 moles of the gas from 300^oK to 600^oK at constant volume. Give your answer in cal/K.

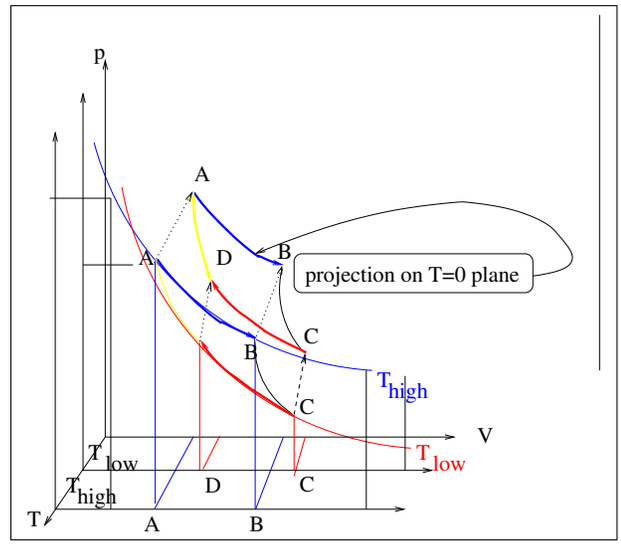

FIG. 1: The Carnot cycle int pseudo 3D and projected onto a coördinate plane. Point A in this Carnot cycle, according to our usage, is the 'corner' where the volume is smallest on the high temperature isotherm. Point B is on the same isotherm. Point C is connected to Point B by a reversible adiabatic expansion and lies on the low temperature isotherm.

Answer and/or Hint

$$\Delta S = 2\times \int_{300}^{600} \frac{\left(3.422 + 7.845 \times 10^{-3}T - 4.165 \times 10^{-6}T^2\right)}{T} dT$$

4. For a reversible Carnot engine operating between 500^oK and 0^oK, whose working fluid is two moles of a monatomic ideal gas, if V_A is exactly one-half V_B , obtain an expression for V_C in terms of V_A and assorted numerical constants.

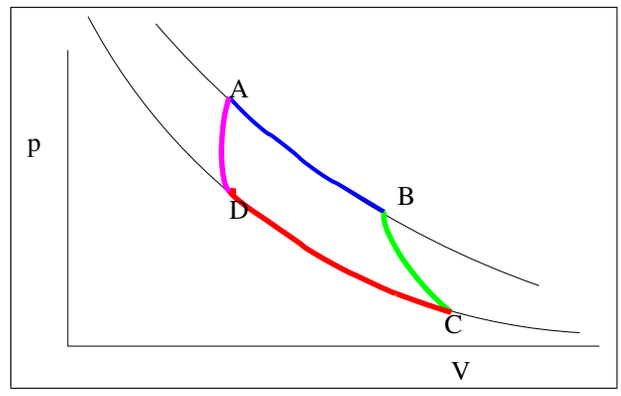

FIG. 2: The Carnot cycle.

Answer and/or Hint

We know that points A and B are connected by an isotherm, so

$$p_A V_A = p_B V_B$$

Further, we know that points B abd C are connected by a reversible adiabatic expansion, i.e.,

$$p_B \left(V_B\right)^\gamma = p_C \left(V_C\right)^\gamma$$

while at point C, $p_C V_C = nRT_C$ (with a similar expression for point B). The rest is algebra.

5. For a reversible Carnot engine operating between 500^oK and 20^oK , whose working fluid is two moles of a monatomic ideal gas, if V_A is exactly one-half V_B, obtain the value of $\Delta E_{A\to C}$, the change in energy, in going from point A to Point C. Point A in this Carnot cycle, according to our usage, is the 'corner' where the volume is smallest at 500^oK . Point B is on the same isotherm. Point C is connected to Point B by a reversible adiabatic expansion and lies on the 20^oK isotherm. Give your answer in calories.

Answer and/or Hint

From point A to point B, the change in energy is zero, as this is an isothermal. From point B to point C, we have a change in temperature, so

$$\Delta E = 2\ moles \times C_v \times (20^oK - 500^oK)$$

6. A reversible Carnot Engine operating between 500^oK and 250^oK, whose working fluid is one mole of a monatomic ideal gas, produces work (assume 100 Joules) which is entirely used in a reversible refrigerator operating between the same two temperatures, i.e., there is no net work, as the output of the Carnot engine is completely used by the refrigerator. If the efficiency of the refrigerator is 4/5 of the efficiency of the Carnot engine, what is the net flow of heat (in Joules) from the lower temperature reservoir (250^oK) to the upper temperature (500^oK) reservoir?

Answer and/or Hint

This is my preferred method of understanding the classical thermodynamics of Carnot engines and spontaneity. The usual arguments are phrased in cascades of "greater than" and "less than" symbols, leaving most of us with terrible headaches.

Here, we posit (assume) that it is possible to have a Carnot engine whose efficiency is less than expected (from the temperature formula). We conclude that this would result in heat going from a lower to a higher temperature with no external work being done, which is never observed, i.e., the original assumption must be wrong! Assume

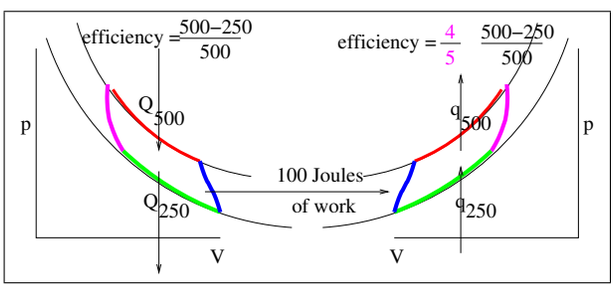

FIG. 3: The juxtaposed Carnot cycles with one operating in reverse as a refrigerator.

$Q_{500} = 200\ Joules$ so for the left Carnot cycle

$$\Delta E = 0 = q_{net} + w = 200 - Q_{250} - 100\ Joules$$

which means

$$200 - Q_{250} = 100\ Joules$$

i.e.,$Q_{250} = 100\ Joules$ while for the right hand Carnot cycle, if $q_{250} = 100\ Joules$ and efficiency

$$\zeta = \frac{250}{500} = \frac{w}{q_{high}} = \frac{T_{high} - T_{low}}{T_{high}}$$

(That's where the value of $Q_{500} = 200\ Joules$ came from.)

The refrigerator engine has efficiency

$$\zeta' = \left(\frac{4}{5}\right)\left(\frac{250}{500}\right) = \frac{w}{q_{high}} = \frac{2}{5}$$

so

$$\frac{-100\ Joules}{q} = \frac{2}{5}$$

which means $q_{500} = -250$ where the sign indicates that the heat is going into the upper (high) temperature reservoir.

Only 200 $Joules$ came down, while 250 $Joules$ went up (?!?, up and down are euphemisms for leaving or going into the high temperature reservoir).

BUT THAT's impossible!. No external work, and the high temperature reservoir gained heat (and the lower one lost heat (how much?)).

This calculation, when done abstractly, constitutes one part of the proof that all reversible Carnot engines have the same efficiency, determined solely by the temperatures of the high and low temperature reservoirs.

7. One gram of ice at 0^oC is added to 10 grams of liquid water at the boiling point. What is the entropy change accompanying this process? Assume ΔH_{fusion} of ice = 80 cal/gram, and that the heat capacity of liquid water is $1\frac{cal}{gram^oC}$. Express your answer in e.u., i.e., $\frac{cal}{^oK}$.

Answer and/or Hint

There are two parts to this problem, and the first part is fraught with peril.

The first part is determining the final temperature of the system. Why is this difficult?

It is difficult because blindly following formuli without thought will lead to possible nonsense. Let's start, but pause when the thinking is required.

The ice has to melt, and the melted ice has to warm up. Meanwhile, the water at the boiling point (100^oC) has to cool to the same temperature as the ice water, i.e., we have to arrive at the compromise temperature which corresponds to equilibrium.

The heat "gained" by the ice as it melts and warms, is balanced by the heat "lost" by the hot water in cooling.

$$1\ gram \times 80 \frac{cal}{gram} = 80\ cal$$

is the heat of melting the ice, and

$$1\ gram \times 1 \frac{cal}{gram^o C} \times (t_{final} - 0)$$

Meanwhile, the heat of cooling the hot water is

$$10\ grams \times 1 \frac{cal}{gram^o C} \times (t_{final} - 100)$$

The first source of error is here! If we blindly set these two equal to each other we obtain

$$80 + (t_{final} - 0) = 10 \times (t_{final} - 100)$$

we obtain $t_{final} =\sim 121^o C$. What's going on here? We're predicting a temperature higher than the starting temperature of the initially hot water.

Instead, we need to write

$$80 + (t_{final} - 0) = -10 \times (t_{final} - 100) \tag{2.1}$$

Now we obtain $t_{final} \sim 84^o C$. Ah Hah. The initial formulation forgot the sign conventions of thermodynamics, i.e., anything into a system is positive. The final formulation, the right one, takes into account the fact that the heat from the high temperature part of the system is going out from it.

Now, we need to start the second part of the problem, which is straightforward, except for the need to change all the temperatures to Kelvin.

$$\frac{80}{273} + \int_{273}^{273+84} \frac{C_p}{T} dT = \Delta S_{ice \to warm\ water}$$

and

$$\int_{373}^{273+84} \frac{C_p}{T} dT = \Delta S_{hot\ water \to cool\ water}$$

I mentioned that the problem is not as easy as it seems. My choice, in making up the problem, is the amount of ice and the amount of hot water. What if the amount of hot water was insufficient to melt the ice, even if the hot water cooled all the way down to 0^oC? What would you do now?

Blindly using Equation 2.1 will give (analyzable) trouble!

Another variant will mix steam with ice, so that one (steam) must condense, one (ice) must melt, and then the two must find a common temperature. Ah the joys of making up nasty problems.

8. One mole of ideal gas initially at $0^o C$ and 1 atm expands adiabatically and irreversibly against a constant pressure of 0.50 atm. Assuming that $C_v = \frac{3R}{2}$, compute the change in entropy (in $\frac{cal}{mole^o K}$) suffered by the gas.

Answer and/or Hint

$$\Delta E = q + w$$

where

$$w = -\int_{V_{initial}}^{V_{final}} 0.50 dV$$

and

$$\Delta E = C_v \left(T_{final} - T_{initial}\right)$$

so one obtains

$$\Delta E = C_v \left(T_{final} - T_{initial}\right) = -0.5 \left(V_{final} - V_{initial}\right)$$

and, of course, V_{final} is the volume of the sample at the final temperature and 0.5 atm (when the piston stops moving).

The rest is straight forward.

9. Calculate the change in entropy (of the 'universe') when one mole of Sulfur(monoclinic) at $368^o K$ is converted (using an ice-water bath at $0^o C$) to Sulfur(rhombic), where S(monoclinic) $\to$ S(rhombic) ; $\Delta H = -96.01 \frac{cal}{mol}$. Assume that the heat is withdrawn from the sulfur at $368^o K$, but is absorbed by the ice-water bath at $273^o K$. This is legal, since the process is irreversible.

Answer and/or Hint

This is a typical (difficult and contorted) problem in this subfield.

We have

$$\Delta S = \frac{-96}{368} + \frac{96}{263}$$

10. For a certain substance, the constant pressure heat capacity (C_p) has the temperature dependence:

$$C_p(T) = 8.3T/(1 + 1.4T)$$

(in $\frac{cal}{mol^oK}$) from 0^oK to 203^oK. At 203^0K the substance undergoes a phase transformation with a ΔH of transformation of +13,401 cal/(mole). The heat capacity (C_p) of the new phase is 9.4 cal/(mol^{o}K) and this phase is stable to well over 212^oC. Calculate the standard entropy of this substance at $0^oC(in\frac{cal}{mole^oK})$).

Answer and/or Hint

There are 3 parts to this question, heating to the phase transition, the phase transition, and then heating the new phase. We have

$$\Delta S_1 = \int_0^{203} \frac{8.3}{(1+1.4T)} dT$$

then

$$\Delta S_2 = \frac{13401}{203}$$

and finally

$$\Delta S_3 = \int_{203}^{212} \frac{9.4}{T} dT$$

Always check for units consistency (not like I'm following my own advice)! Typical "do as I say, not as I $\cdots$".

11. Calculate the entropy change suffered by 1 gram of supercooled liquid water at -12^oC freezing to form ice at -12^oC. ΔH (fusion (solid $\rightarrow$ liquid)) at 273^oC = 6.0095 kJ/mol, and for liquid water in this temperature range is 75.3 Joule/(mole^{o}K) and for solid water (ice) is 38.0 J/(mole^{o}K).

Answer and/or Hint

Here, we warm the ice to 0^oC, melt it, then cool the water back to -12°C, all done "reversibly".

$$\Delta S_1 = \int_{-12+273}^{273} \frac{38}{T} dT$$

and

$$\Delta S_2 = \frac{60095}{273}$$

while finally

$$\Delta S_3 = \int_{273}^{-12+273} \frac{75.3}{T} dT$$

12. 2.3 moles of an ideal gas originally at STP expands irreversibly and isothermally from point A to point B in the Carnot cycle diagram Figure 1. It then is expanded reversibly and adiabatically from B to C. What is the volume and the pressure at the point B? $p_C = 0.288\ atm$, $V_C = 143\ liter$, $C_v = 3R/2$.
a) What is the volume at point B in liters?
b) What is the entropy change of the fluid?

Answer and/or Hint

(a) We know that points A and B are connected by an isotherm, so

$$p_A V_A = p_B V_B$$

Further, we know that points B abd C are connected by a reversible adiabatic expansion, i.e.,

$$p_B (V_B)^\gamma = p_C (V_C)^\gamma$$

while at point C, $p_C V_C = nRT_C$ (with a similar expression for point B). The rest is arithmetic.

(b) The entropy change is solely that of the isothermal expansion from A to B.

III. EPILOGUE

After editing this material for weeks, and continuously finding errors, some small, some huge, I have to wrap it up and send this off. If, in the years 2008-2010 or so, you come across an error, and you e-mail me, I will try to have it corrected.

But since this material is written in LaTeX there is some doubt whether or not I'll have access to a Linux machine, and access to the digitialcommons site. You can try; we'll see what happens, if anything. Thanks to all the students over the last 45 years who've taught me Physical Chemistry.