Chemistry Education Materials   Department of Chemistry

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Advanced Physical Chemistry Problems (III), Gases and Thermodynamics (1st Law)

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Problems for the Advanced Physical Chemistry Student
Part 3, Gases, Thermodynamics (1st 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. GASES

1. Assuming that dry air contains 79% N_2 and 21% O_2 by volume, calculate the density (in grams/liter) of moist air at 25^oC and 1 atm pressure when the relative humidity is 60%. The vapor pressure of water at 25^oC is 23.76 mm Hg.

Answer and/or Hint

The relative humidity measures the partial pressure of water vis-à-vis what it would be if the air was "saturated" i.e., when the partial pressure of water was equal to the vapor pressure of liquid water, thereby being the highest possible value of partial pressure at the given temperature. In our case, we know that the partial pressure of water in the vapor is

$$0.6 \times 23.76 mm \text{ Hg}$$

which means that the pressure of the rest of the gases in this wet air was

$$(760 - 0.6 \times 23.76)\, mm \text{ Hg}$$

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Therefore, the partial pressure of the N_2 must be

$$(0.79 \times (760 - 0.6 \times 23.76))\, mm \text{ Hg}$$

and the partial pressure of O_2 must be

$$(0.21 \times (760 - 0.6 \times 23.76))\, mm \text{ Hg`}$$

so, in one liter we know the number of moles of N_2, O_2 and H_2O using the ideal gas law (we ignore the contradiction that water could not be an ideal vapor and still have liquid possible). From the number of moles of each, we compute the mass of each, and then add them, divide by the volume (1 liter) and obtain the density.

2. The composition of a mixture of gases in percentage by volume is 21% nitrogen, 45.2% carbon monoxide, 11.55% hydrogen, and the rest oxygen. Calculate the density of the mixture at STP in grams/liter.

Answer and/or Hint

After computing the percent O_2 in the mixture, we convert the percents to partial pressures and proceed as before.

3. Find the mass of helium gas necessary to fill a balloon whose capacity is 1.92×10^6 liters at 1 atm pressure and 25^oC, and then, using this information calculate (and report below) the total lifting power (in kilograms) of this balloon in air whose density is 0.89 grams/liter.

Answer and/or Hint

The first part of the problem is a simple ideal gas law problem.

It is the second part which is interesting. Knowing the mass of He in the balloon, we can add a

mass (m_{load}) such that the density of the "balloon" would be

$$\rho_{balloon} = \frac{mass\ \text{He} + m_{load}}{1.92 \times 10^6}$$

which has to equal 0.89. This provides an equation for m_{load}.

4. Write an expression for the thermal coëfficient of expansion (α) defined as

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

for one mole of a van der Waals gas,

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

This is a fun exercise for juniors, since they often are mystified when they can not solve for v in the van der Waals equation so as to carry out the differentiation explicitly.

Some then remember implicit differentiation, which was a tiny topic in first year calculus, whose applicability was invisible at the time of learning (how typical).

$$dp = \left(\frac{R}{v-b}\right)dT - \left(\frac{RT}{(v-b)^2}\right)dv + 2\left(\frac{a}{v^3}\right)dv \to 0$$

where $dp = 0$ is another way of saying that one is holding p constant.

$$\left(\frac{R}{v-b}\right)dT = \left(\frac{RT}{(v-b)^2} - 2\frac{a}{v^3}\right)dv$$

which allows us to form $\frac{dv}{dT}$ by division of both sides by dT, which leads to our ultimate answer.

5. Given that the fraction of molecules with speeds between v and $v + dv$ is

$$dN = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{mv^2}{2kT}} dv$$

calculate (approximately) the fraction of molecules of $N_2(g)$ at 100^oK in a flask containing exactly 1 mole of gas, whose velocities (speeds) are in the range 500.0 to 500.1 meters/second.

$$dN \sim 4\pi(500.05)^2 \left(\frac{\frac{28}{6\times 10^{23}}}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{\frac{28}{6\times 10^{23}}(500.05)^2}{2kT}} \overset{0.1}{dv}$$

6. In two dimensions, the fraction of molecules whose speed is between v and $v + dv$ is

$$dN = 2\pi v \left(\frac{m}{2\pi kT}\right) e^{\frac{mv^2}{2kT}} dv$$

so the fraction of molecules whose speed is greater then v_0 is

$$\int_{v_0}^{\infty} dN$$

Calculate the fraction of molecules of (in two dimensions) at 25^oC whose speed are greater than 18 meters/second.

Contrary to the case in three dimensions, in two dimensions the integrals are tractable (and trivial, see the next problem).

7. In two dimensions, the fraction of molecules whose speed is between v and $v + dv$ is

$$dN = 2\pi v \left(\frac{m}{2\pi kT}\right) e^{\frac{mv^2}{2kT}} dv$$

so the fraction of molecules whose speed is greater then v_0 is

$$\int_{v_0}^{\infty} dN$$

and the fraction of molecules whose speed is between v_0 and v_1 is

$$\int_{v_0}^{v_1} dN$$

Calculate the fraction of molecules of (in two dimensions) at 25^oC whose speed are in the range from 5.0 to 6.0 meters/second.

The integrals are of the form

$$\int_a^b (vdv)e^{-\kappa v^2}$$

where κ is a constant. Such integrals can be done by elementary means, changing variables from v to $u \equiv v^2$.

8. 2.12 grams of (gaseous) ethane and 3 grams of $O_2(g)$ are contained in a 5.37 liter (fixed) vessel at 50^oC . A spark ignites the mixture, and the resultant box of gases (assume combustion is to CO_2 and H_2O) is cooled back to the original temperature. Assuming the vapor pressure of water at 50^oC is 220 mm Hg, calculate the mole % carbon dioxide in the gaseous part of the final mixture. Make standard assumptions (ideal gases, relative sizes of liquids and gases at the same pressure and temperature, etc.).

Answer and/or Hint

After doing the stoichiometry, you need to ask yourself the question "is there liquid water present, or is it all vapor?". The answer has to do with the tentative value of the partial pressure of water computed via the ideal gas laws, compared to the vapor pressure of water at the final temperature. If the computed water pressure is greater than the vapor pressure, then the computed water pressure is <u>wrong</u>, and there is liquid water present (of ignorable volume) and water vapor at the vapor pressure.

Once the above has been deciphered you're ready to proceed to the actual problem.

9. The fraction of molecules whose velocity components are between v_x and $v_x + dv_x, v_y$ and $v_y + dv_y, v_z$ and $v_z + dv_z$ is given by a Maxwell distribution of the form

$$Ne^{\frac{mc^2}{2kT}} dv_x dv_y dv_z$$

($c = \sqrt{v_x^2 + v_y^2 + v_z^2}$ where N is a normalization constant. What fraction of molecules are traveling with velocity vectors within 10° of the z-axis (almost straight 'up')?
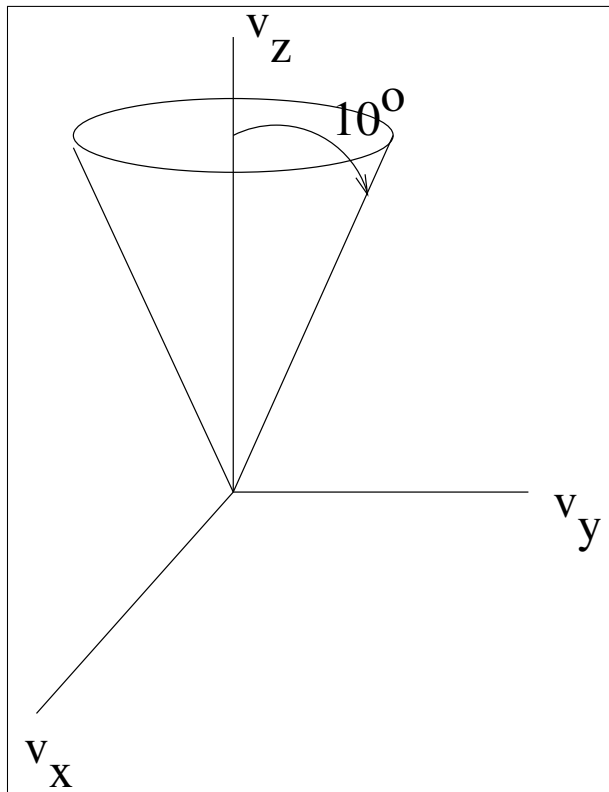

Answer and/or Hint

FIG. 1: Velocity space with cone of 10° of v_z-axis.

This question requires that we change coördinate systems to "spherical polar", since the radial velocity can be anything, and we are asking about a direction in space which constitutes a cone of inclusion. If velocity vectors are inside that cone, they are counted, otherwise they aren't. In Spherical Polar coördinates we have

$$Ne^{\frac{mv^2}{2kT}} v^2 dv \sin \vartheta d\vartheta d\varphi$$

(c and v are the same). So we are interested in integrating over all speeds, but only from 0 to 10° on ϑ and from 0 to 2π on φ.

Remember that the integrals are standard, and listed in all Physical Chemistry texts.

10. The fraction of molecules whose velocity components are between v_x and $v_x + dv_x, v_y$ and $v_y + dv_y, v_z$ and $v_z + dv_z$ is given by a Maxwell distribution of the form

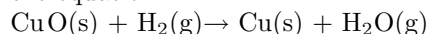$$Ne^{\frac{1}{2}\frac{m\left(v_x^2+v_y^2+v_z^2\right)}{kT}} dv_x dv_y dv_z$$

where N is a normalization constant.

We wish to construct a cone which has the v_z axis as its axis of symmetry, such that 30% of all molecules are contained therein. What angle (from the v_z axis) should this cone subtend? Give your answer in degrees.
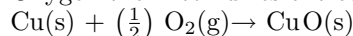

Here, again in Spherical Polar coördinates, our integration limits are over all speeds and all values of φ, but from 0 to "the answer" such that the fraction of molecules whose velocity vectors lie inside the "cone" constitutes 0.3 times the total number of molecules in the sample.

11. A mixture of oxygen and hydrogen is analyzed by passing it over hot copper oxide and through a drying tube. Hydrogen reduces the CuO according to the equation
$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$
Oxygen then reoxidizes the copper formed:
$Cu(s) + \left(\frac{1}{2}\right) O_2(g) \rightarrow CuO(s)$
104 cm^3 of the mixture measured at 22°C and 743 mm Hg yields 80.08 cm^3 of dry oxygen measured at the same temperature and pressure after passing over CuO and the drying agent. What is the mole fraction of oxygen in the original mixture? (This problem was taken from Castellan, Physical Chemistry.)

This is one of the great, I repeat, great, problems. It illustrates a command of freshman chemistry and parts of algebra provided that the student can do it at first crack which, to my mind, insures that s/he will succeed in physical chemistry. On the other hand $\cdots$.

I have two solutions [1] which are equally valid, but I caution you to not look at them until you've tried this problem on your own. Castellan offers it in his zeroth chapter, i.e., this is freshman chemistry, and you should, I repeat, should, be able to do it!

All right, here we go.

(a) If the total pressure is 743 mm Hg at 22°C is a mixture of x moles of H_2 and y moles of O_2 then

$$\left(\frac{743}{760}\right) 0.104 \; liters = (x+y)R(273+22)$$

All the H_2 is consumed, so $\frac{x}{2}$ of O_2 are also consumed. This means that the final O_2 volume, 80.08 cm^3, are carried through inviolate. Therefore

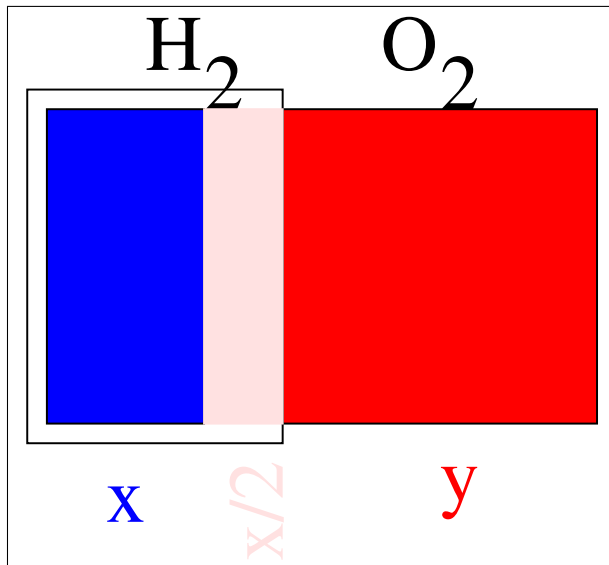$$y - \frac{x}{2} = moles \; O_2 \; remaining$$

FIG. 2: All the H_2 (blue) is consumed, so half the number of moles of H_2 figured as numbers of moles of O_2 consumedi (pink), leaves the residual O_2 (red).

(b) An alternative view combines the two equations: $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$
$Cu(s) + \left(\frac{1}{2}\right) O_2(g) \rightarrow CuO(s)$
to become $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$

The rest is obvious from the earlier treatment.

12. Assume that dry air contains 79% N_2 and 21% O_2 by volume. Consider a piston cylinder arrangement, initially at 25°C which contains a (large) bowl of water and some air. The total pressure is 1.01 atm. The vapor pressure of water at 25°C is 23.76 mm Hg. The vapor pressure of water at 37°C is 47.07 mm Hg. The original volume of the wet air sample is 20.3 liters. The piston cylinder is heated to 37°C and expanded to 25.93 liters. What is the final pressure?

At the lower temperature, we need to compute the number of moles of gas which are not water, so that we can use the ideal gas law to obtain their partial pressures at the higher temperature. The water vapor pressure at the higher temperature has to be added back in, provided there is still liquid water sitting in the bottom of the piston.

At the lower temperature

$$n_{H_2O} = \frac{\frac{23.76}{760} \times 20.3}{0.082 \times 298}$$

and, for example

$$n_{N_2} = \frac{0.79 \times 1.01 - \left(\frac{23.76}{760} \times 20.3\right)}{0.082 \times 298}$$

where I'll let you work out the units.

Once all the oxygen and nitrogen is known, these two gases are brought to the final state, and the water is added back in at its new vapor pressure (assuming there's still liquid water in the big bowl of liquid water sitting inside the piston-cylinder).

III. FIRST LAW OF THERMODYNAMICS

1. A mass of 1000 grams falls freely to a platform from a height of 10 meters. What amount (magnitude) of heat (in calories) will be evolved when the mass strikes the platform?

Answer and/or Hint

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10 meters high means that the potential energy of this mass before release is

$$mgh = 1000 \ grams \ \times 980 \frac{cm}{sec^2} \times 1000 \ cm$$

which is $9.8 \times 10^8 \ ergs$. Assuming that the mass gives up all its potential energy as heat upon impact,

$$q = 9.8 \times 10^8 \ ergs \times \frac{1.987 \ cal}{8.314 \ Joule} \times \frac{1 \ Joule}{10^5 \ erg}$$

2. A piston whose area is 60 square cm expands through a distance of 20 cm against a constant pressure of 3 atm. Calculate the work done by the cylinder-piston in Joules.

Answer and/or Hint

$$w = -\int_{x}^{x+20} \left(3 \ atm \times 60 \ cm^2\right) dz$$

where z is a measure of the position of the piston. Thus

$$w = -3 \ atm \times 60 \ cm^2 (\not{x} + 20 - \not{x}) \ cm$$

which is $-3 \times 60 \times 20 \ cm^3 \times \frac{1 \ liter}{1000 \ cm^3}$ gets us to liter-atm, and from there we can get anywhere since

$$R = 8.314 \frac{joules}{mole - ^o K} = 0.083 \frac{liter \ atm}{mole - ^o K}$$

3. A gas, in expanding against a constant pressure of 2.03 atm from 10.9 to 20.02 liters, absorbs 341.7 cal of heat (q). What is the change in the internal energy of the gas (in calories)

Answer and/or Hint

$$\Delta E = q + w$$

where

$$w = -2.03 \times (20.02 - 10.9) \ell iters$$

and q is given. The units have to be adjusted.

4. A gas expands against a variable opposing pressure given by $p = \frac{10.1}{V}$ atm, where V is the volume (in liters) of the gas at each stage of the expansion. Further, in expanding from 10.4 to 105.3 liters, the gas undergoes a change in internal energy of E = 307 cal. How much heat (in liter atmospheres) is absorbed by the gas during the process?

Answer and/or Hint

$$\Delta E = q + w$$

is the first law, and w is computable. ΔE is given; solve for q.

To get the work, we write

$$w = -\int_{start}^{finish} p_{resisting} dV$$

which, in our case becomes

$$w = -\int_{10.4}^{105.3} \frac{10.1}{V} dV$$

which is easily integrated and evaluated.

5. For a certain ideal gas $C_v = 2.98 \frac{cal}{mole\_^o C}$. If 12.4 moles of the gas are heated from 1.4 to 104.8 $^o C$, what will be ΔH for the process?

Answer and/or Hint

Given C_v we compute C_p, since it is R larger (for ideal gases). Then

$$\Delta H = 12.4 \int_{1.4}^{104.8} C_p dT = 12.4 \int_{1.4}^{104.8} (R + 2.98)dT$$

6. Two liters of an ideal gas (N_2) at 0^oCC and 5 atm pressure are expanded against a constant pressure of 1 atm until the pressure of the gas is also 1 atm and the temperature is again 0^oC. Assuming the gas to be ideal what is ΔH for the process?

Answer and/or Hint

Zero!

Why?

7. Calculate the work (in liter-atm) done by 5.8 moles of an ideal gas during expansion from 59.3 atm at 28 C to 5.2 atm at 54 C, against a constant pressure of 0.57 atm

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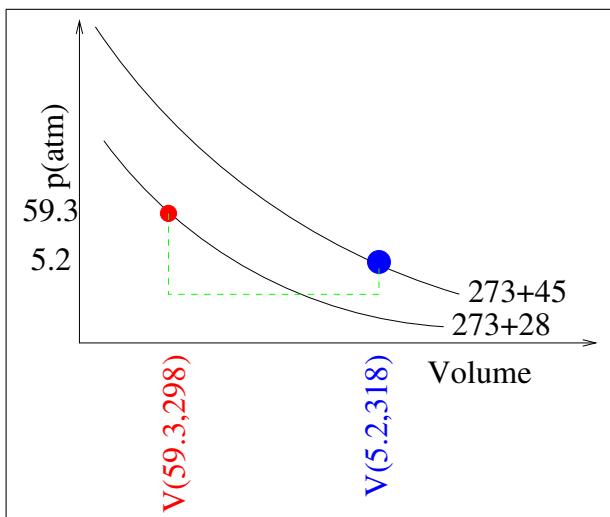
Answer and/or Hint

FIG. 3: The irreversible path for this problem.

We have

$$w = - \int_{\frac{5.8R(298)}{59.3}}^{\frac{5.8R(273+45)}{5.2}} 0.57 \; dV$$

8. 3.2 moles of an ideal gas at 1 atm pressure and 23^oC are heated at a constant pressure until the final temperature is 81^oC. For the gas $= C_p = (7.50+0.0032T)\frac{cal}{mole^oC}$. How much heat is involved in the process?

Answer and/or Hint

$$\Delta H = \int_{23+273}^{81+273} C_p dT$$

which is

$$\Delta H = \int_{23+273}^{81+273} (7.5 + 0.0032T) \, dT$$

where the answer (so far) will be in calories.

9. Assuming carbon dioxide to be an ideal gas, calculate the heat generated or absorbed by 10.0 g of carbon dioxide in expanding isothermally and reversibly from a volume of 5.0 liters to 10.0 liters at 27.0C. Give your answer in calories (R = 1.987 cal/(mol-K)).

Answer and/or Hint

Give me a break, this is too easy!

10. Calculate the minimum work necessary to compress 20 g CO_2 of (treated as an ideal gas) from 10 to 5 liters at 0^oC (in Joules).

Answer and/or Hint

Isothermal means, for ideal gases, $\Delta E = 0$.

The work is then

$$w = -\frac{20}{44} \int_5^{10} \frac{RT}{V} dV$$

which is logarithmic.

11. Two liters of N_2 at 0^oC and 5 atm pressure are expanded isothermally and reversibly until the confining pressure is 1 atm. Assuming the gas to be ideal, calculate q (in Joules) for the expansion.

$$\left(p + \frac{n^2 a}{V^2}\right) \times (V - nb) = nRT$$

can be solved for p and used in the formula

$$w = -\int_4^{40} \left(\frac{nRT}{V - nb} - \frac{n^2 a}{V^2}\right) dV$$

which gives a logarithm and a second term.

15. 1.2 moles of a gas which happens to follow the equation of state pV = nRT, expands against an opposing pressure given by

$$p_{resisting} = 10.1 \times e^{-0.032V}$$

(here p is in atm, and V is in liters), from a pressure of 6 atm at a volume of 22 liters. At the end of the expansion, the gas pressure is exactly equal to the resisting pressure, and the volume is found to be 45 liters. During the expansion, 38 Joules of heat are lost by the gas to its surroundings. What is the value of C_v for this gas?

What is the volume at the end?

$$\frac{5 \ atm \times 2 \ liters}{273} = \frac{1 \ atm \times V_f \ liters}{273}$$

so

$$w = -\int_2^{V_f} \frac{nRT}{V} dV$$

12. Calculate the work (in liter-atm) done by 5 moles of an ideal gas during expansion from 5 atm at $25^o C$ to 2 atm at $50^o C$ against a constant pressure of 0.5 atm. Assume that $C_v = 5.0 \frac{cal}{mole^o K}$.

$$w = -0.5 \times \left(\frac{R(273 + 50)}{2} - \frac{R(273 + 25)}{5}\right)$$

assuming that the gases, no matter what, are brought to thermal equilibrium before and after the expansion.

13. Three moles of an ideal gas at 1 atm pressure and $20^o C$ are heated at constant pressure until the final temperature is $80^o C$. For the gas $C_v = 7.50 + (3.2 \times 10^{-3}) * T \left(\frac{cal}{mole \ ^o K}\right)$. Calculate the change in internal energy (U or E).

We need to find the integral of pdV as usual, but the limits are a problem. We have

$$w = -\int_{22}^{45} 10.1 \times e^{-0.032V} dV$$

We need the final temperature. We know

$$\frac{1.2RT_{start}}{22} = 6$$

at the beginning, and

$$\frac{1.2RT_{final}}{45} = 10.1 \times e^{-0.032 \times 45}$$

so,

$$\Delta E = 1.2 C_v (T_{final} - T_{start}) = 38 Joules + w$$

16. A gas expands against a variable opposing pressure given by

$$p_{resisting} = 12.5 \ell n V (atm)$$

where V is the volume (in liters) of the gas at each stage of the expansion. Further, in expanding from 4.1 to 40.1 liters, the gas undergoes a change in internal energy of $E = 304$ cal. How much heat (in liter atmospheres) is absorbed by the gas during the process? (You will need to calculate the Energy change and the work to obtain the heat.)

$$\Delta E = 3 \int_{273+20}^{273+80} \left(7.50 + (3.2 \times 10^{-3}) * T + R\right) dT$$

14. For a certain gas the van der Waals constants are $a = 6.69 atm \times \left(\frac{liter}{mole}\right)^2$ and $b = 0.057 \frac{liter}{mole}$. What will be the maximum work performed in the expansion of 2 moles of the gas from 4 to 40 liters at $300^o K$? Give you answer in liter atm.

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.

Answer and/or Hint

$$w = -\int_{4.1\ell}^{40.1\ell} (12.5\ell nV)\, dV$$

IV.   EPILOGUE

After editing this material for weeks, and continuously finding errors, some small, some huge, I have to wrap it

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.

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[1] My daughter, a 7th grade teacher, tells me that the difference between being a user and a teacher is that a user can "do the problem", but the teacher can give at least three different approaches to the problem to help diverse students in their understanding. Offering only two approaches here tells me that I'm not as good a teacher as I thought I was.