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Problems for the Advanced Physical Chemistry Student
Part 6, Free Energies

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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. GIBBS AND HELMHOLTZ FREE ENERGIES

1. The molar volume of benzene (liquid) is 88.9 cc at 20^oC and 1 atm pressure. Assuming the volume to be constant, find ΔG (Change in Gibbs Free Energy) for compression of 1 mole of the liquid from 1 to 100 atm (in calories/mole).

Answer and/or Hint

This problem asks you to remember (or derive) the pressure dependence of the Gibbs Free Energy. Here is a micro derivation:

$$dE = TdS - pdV$$

$$dA = -TdS - Sdt + TdS - pdV$$

$$dG = -Sdt - pdV + pdV + Vdp$$

so

$$dG = -Sdt + Vdp$$

implying

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

and integrating, we have

$$\int_{p=1\ atm}^{p=100\ atm} dG = \int_1^{100} Vdp$$

where $V = 0.0889\ \ell$ iters (per mole) so

$$G(p = 100\ atm) - G(p = 1\ atm) = 0.0889(100 - 1)$$

where the r.h.s. is in ℓiter-atm, which can be converted to any alternate desired units.

2. Two moles of an ideal gas are compressed isothermally and reversibly at 100^oC from a pressure of 10 to 25 atm. Find the change in the Helmholtz Free Energy (in calories) for this process.

Answer and/or Hint

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

so

$$\int dA = -2\int_{10}^{25} \frac{RT}{V} dV$$

and the rest is left to the interested reader.

3. Three moles of an ideal gas are allowed to expand freely at 300^oK from a volume of 100 to 1000 liters. What is the change in Gibbs Free Energy for this process?

Answer and/or Hint

This is done exactly the way the previous problem was done, except the r.h.s. integral is over dp.

$$\int dG = 3\int_{\frac{3RT}{100}}^{\frac{3RT}{1000}} \frac{RT}{p} dp$$

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4. Calculate the magnitude of the difference between the Gibbs and the Helmholtz free energies at 25°C for the reaction

$$\mathrm{H_2}(g, 1\ atm) + \frac{1}{2}\mathrm{O_2}(g, 1\ atm) -> \mathrm{H_2O}(liq, 1\ atm)$$

of liquid water.

Answer and/or Hint

$$\Delta G = \Delta A + \Delta(pV)$$

and

$$\Delta(pV) = \Delta nRT$$

where Δn is the change in the number of moles of gaseous materials (liquids and solids generally don't count). Therefore

$$\Delta(pV) = -(3/2) * R * 298.15$$

which is what was asked for, depending on the units desired for R.

5. For a certain process the Gibbs Free Energy change

$$\Delta G = 13,580 + 16.1 * T * \ell n(T) - 72.59 * T$$

Find ΔS for the process at 25°C.

Answer and/or Hint

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

so,

$$\Delta S = 16.1 \ell n 298 + 16.1 - 72.59$$

This is an appropriate time to discuss units in thermodynamics. When you see something like ℓnT you know there's something wrong. One can't have a unit inside a logarithm. Instead, we should have had $\ell n \frac{T}{T_{std}}$, and this goes for sines, cosines, error functions, etc., i.e., the argument should have been rendered unit-free by use of some standard state of standard comparative value which established the correct unit to use (via cancellation)!

6. Given the reaction at 25°C:

$$\mathrm{H_2O}(\ell, 23.76\ mm\ Hg) \rightarrow \mathrm{H_2O}(gas, 23.76\ mm\ Hg)$$

what is $\Delta G^o(25^oC)$ (in kJ/mole) for the reaction

$$\mathrm{H_2O}(\ell,\ atm) \rightarrow \mathrm{H_2O}(gas, 1\ atm)$$

at the same temperature. (The vapor pressure of liquid water is 23.76 mm Hg at 25°C.) Assume that the Gibbs free energy of liquid water is independent of pressure.

Answer and/or Hint

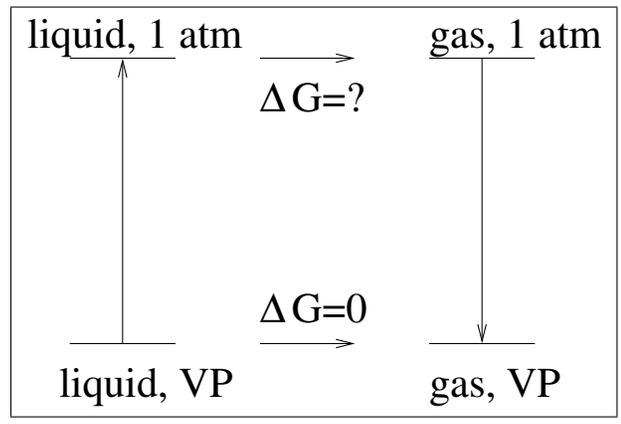

FIG. 1: Raising the pressure on a liquid to standard state, evaporating it there, and lowering the pressure on the resultant gas (vapor) back to the vapor pressure value.

We have

$$\Delta G(\ell, VP \rightarrow \ell, 1\ atm) = \int_{\frac{23.76}{760}}^{1} \frac{18\frac{grams}{mole}}{1\frac{grams}{cc}} dp$$

and

$$\Delta G(g, 1\ atm \rightarrow g, VP) = \int_{1}^{\frac{23.76}{760}} \frac{RT}{p} dp$$

which can be combined to form the ΔG we desire.

7. At the melting point of KF, the standard molar entropy of the liquid is 163.582 J/(moleK), and that of the solid is 139.536 (in the same units). The molar heat of fusion at 1131°K is 27.196 kJ/mol Assuming that the entropy of both liquid and solid do not change appreciably with temperature, calculate the molar Gibbs free energy of fusion for KF at 1131°K. (in Joules).

Answer and/or Hint

$$\Delta G = 27,196 - 1131(163 - 139)$$

8. At 25°C the standard (p = 1 atm) Gibbs free energy of formation of H_2S(g) is -33.56kJ/mole. Calculate the pressure (in atm) at which the Gibbs free energy of the reaction

$$\mathrm{H_2}(g, 1atm) + \mathrm{S}(s) \rightarrow \mathrm{H_2S}(g, P)$$

would be zero.

Answer and/or Hint

$$\mathrm{H_2}(g, 1\ atm) + \mathrm{S}(s) \rightarrow \mathrm{H_2S}(g, 1\ atm); \Delta G^o = -33.56kJ$$

so

$$0 \leftarrow \Delta G = \Delta G^o + RT\ell n\frac{p}{1\ atm}$$

As a continuation of the comments on units, notice that here I've explicitly made the argument of the logarithm unit-free by specifying the unit system and standard state (1 atm) (Of course, we could have used any other unit system and the standard states are just conventions we've all "agreed" to).

9. The density of graphite is 2.25 gm/(cc) and that of diamond is 3.51 gm/(cc). If the standard Gibbs free energy of transformation from graphite to diamond (at 25°C) is 2.9 kJ/mole, determine the pressure (in atm) at which graphite and diamond are in equilibrium.

Answer and/or Hint

Here, we have something of the likes of

$$2900\ J = \int_1^p \Delta V dp; \quad (\ell - atm)$$

$$2900\ J\frac{8.314J}{0.082\ell - atm} = \int_1^p \left(\frac{12}{2.25} - \frac{12}{3.51}\right) dp$$

At this point, I always tease my students about "diamonds are forever", and ask the women whether or not they believe the "I will love you forever" statements of beaus. If diamonds decay to graphite, to what does love decay?

10. The standard molar Gibbs free Energy of reaction for a certain substance's liquid to be transformed into vapor at 1 atm pressure, when the temperature is 25°C, is 14.8 kJ/mole. What is the vapor pressure of this substance (in mm Hg) at this temperature?

$$A(\ell, 1\ atm) \rightarrow A(vap, 1\ atm); \Delta G = \Delta G^o = 14.8kJ/mole$$

$$A(\ell, 1\ atm) \leftarrow A(\ell, v\ p); \Delta G \sim 0$$

$$A(\ell, v\ p) -> A(vap, v\ p); \Delta G = ?$$

Answer and/or Hint

$$\Delta G(g, 1\ atm \rightarrow g, VP) = \int_1^{\frac{p}{760}} \frac{RT}{p} dp$$

per mole, and then (See Figure 1), we have $\Delta G = \Delta G^o = 14.8kJ$ and

which can be combined to form the ΔG we desire.

11. At 25°C, $\Delta H^o = -92,300\frac{Joule}{mole}$, and $\Delta G^o = -95,200\frac{Joules}{mol}$. Assuming that ΔH^o is constant, i.e., independent of temperature over the temperature range in this question, calculate ΔG^o at 50°C. Give your answer in kJ/mole.

Answer and/or Hint

We know that

$$\frac{\Delta G^o(T)}{T} - \frac{\Delta G^o(T_{std})}{T_{std}} = -\int_{T_{std}}^T \frac{\Delta H^o}{T^2} dT$$

the infamous Gibbs-Hlemholtz equation. Knowing the ΔH^o is constant over the temperature domain in question helps in integrating the r.h.s. of the G-H equation, leading to

$$\frac{\Delta G^o(T)}{T} - \frac{\Delta G^o(T_{std})}{T_{std}} = \left.\frac{\Delta H^o}{T}\right|_{T_{std}}^T$$

where $T_{std} = 298^o K$ and $T = 273 + 50^o K$. The rest is an exercise.

It is interesting to ask what happens if ΔH^o is not constant over the temperature domain? The answer leads to nested integrals, i.e.,

$$\frac{\Delta G^o(T)}{T} - \frac{\Delta G^o(T_{std})}{T_{std}} = -\int_{T_{std}}^{T} \frac{\Delta H^o(T_{std}) + \int_{T_{std}}^{T} \Delta C_p dT}{T^2} dT$$

which we re-write in a manner less confusing:

$$\frac{\Delta G^o(T)}{T} - \frac{\Delta G^o(T_{std})}{T_{std}} = -\int_{T_{std}}^{T} \frac{\Delta H^o(T_{std}) + \int_{T_{std}}^{y} \Delta C_p dz}{y^2} dy$$

We note in passing that the internal nested integral concerning $C_p's$ can be more complicated if, in fact, these heat capacities are themselves temperature dependant, i.e., functions of T, i.e., $C_p(T)$ represented herein as $C_p(z)$.

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.