3.012 Practice Problem Answers for Recitation 2 (09.20.05)

The following are not meant to be comprehensive solutions, but simply a guide for checking your answers. Please see me at office hours if you need further assistance.

Part I. Working with State Functions.

Note: Work on problem 3 only after you have completed Part II; it is less essential.

1. How would you express a free energy (G) with three degrees of freedom – T, V, and n – in partial differential notation?

$$dG = \left(\frac{\partial G}{\partial T}\right)_{V,n} dT + \left(\frac{\partial G}{\partial V}\right)_{T,n} dV + \left(\frac{\partial G}{\partial n}\right)_{T,V} dn$$

2. For the state function $P(T, V)$ that we looked at for an ideal gas, what are the mixed partial derivatives? (i.e., take the partial with respect to T, then take the partial of the result with respect to V, and vice-versa.)

Both mixed derivatives are equal to: $-R/V^2$.

3. [Do this problem last.] Consider the two two-parameter differentials below:

$$df = 2xydx + x^2dy$$
$$dg = 2x^2ydx + xy^2dy$$

Integrate each function from $[(x, y) = (0, 0)$ to $(1, 1)]$ along two paths: $y=x$ and $y=x^2$. Which differential is exact? Using what you learned in problem 2, can you think of a faster way to test for exactness?

To do this problem correctly, notice that for $y=x$, $dy=dx$, while for $y=x^2$ $dy=2xdx$.

(1) Start with df, integrate along $y=x$:

$$\int_0^1 2xydx + \int_0^1 x^2dy = \int_0^1 (2x^2dx + x^2dx) = \int_0^1 3x^2dx = \left[x^3\right]_0^1 = 1.$$

Now integrate df along $y=x^2$:

$$\int_0^1 2xy\,dx + \int_0^1 x^2 dy = \int_0^1 2x^3 dx + 2x3dx = \int_0^1 4x^3 dx = \left[x^4\right]_0^1 = 1$$

Differential df appears to be exact, since the result is path-independent.

(2) Let's try dg. First, integrate along $y=x$:

$$\int_0^1 2x^2y\,dx + xy^2 dy = \int_0^1 2x^3 dx + x^3 dx = \int_0^1 3x^3 dx = \left[\frac{3x^4}{4}\right]_0^1 = \frac{3}{4}$$

Now integrate dg along $y=x^2$:

$$\int_0^1 2x^2y\,dx + xy^2 dy = \int_0^1 2x^4 dx + 2x^6 dx = \left[\frac{2}{5}x^5 + \frac{2}{7}x^7\right]_0^1 = \frac{24}{35}$$

Since it is path-dependent, dg is an inexact differential.

Based on problem I.2 and the partial differential form of a function $F(x, y)$, we know that the partial derivative with respect to y for the dx term ($2xy$ is the dx term for df) must be equal to the partial derivative with respect to x for the dy term (x^2 for df). Indeed, for the exact differential, they are both equal to $2x$.

Part II. *PV*-work and the First Law.

Note: It is more important to fully set up the problems than to get numerical answers.

1. (after P2.4 in book) Given one mole of an ideal gas undergoing a temperature change from 100 °C to 25 °C under isobaric conditions (Pext = P = 200 kPa), how much work is performed? Is work done by the system or surroundings?

For an isobaric process, the work simply becomes $P\Delta V$, and is approximately 620 J. Work is done by the surroundings on the system since it is a compression process.

2. Now consider an isothermal process (T = 300 K) for one mole of gas being compressed from 1 to 15 atm. How much work is done? How much heat is transferred? (What is the change in *U*?) What is the entropy change?

Assume the process is reversible, and calculate the work by substituting in our favourite constitutive equation – the ideal gas law – for the pressure term before integrating. The work comes out to be 6754 J. Since the internal energy change for an isothermal process is zero, the heat q is simply $-w = -6754$ J.

Calculating entropy changes is not something we've discussed in detail yet, but it comes from the equation given in class that $dS = dq_{\text{rev}} / T$. Because the internal energy change is zero here, we can substitute the negative of the differential work $-dw = PdV$ in for the differential heat dq_{rev}. Substituting in the ideal gas equation for P and then integrating, we get:

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln\left(\frac{P_i}{P_f}\right) = -22.5 \text{ J/K}$$