

Homework #3 Problems (#11-#16)

11. E&R #2.11 (a,b)

c. **part c.** Also calculate the total ΔU and ΔH (sum of the two chambers).
ALL ANSWERS SHOULD BE IN UNITS OF kJ (or J) AND degrees K

12. Derive the following for any closed system, with only P-V work:

$$C_V = - \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_U$$

13. * . E&R P3.23

Note: treat $\left(\frac{\partial U}{\partial \bar{V}} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_{\bar{V}} - P$ as a 'given' equation

(we will prove this relationship very soon)

14. (from *Basic Chemical Thermodynamics*, by J. Waser, published by Benjamin Cummings)

Indicate whether each of the following statements is true or false. If the statement is not true, indicate in what way it is false (or give a counter example) and whether it could be made into a true statement by a slight change in wording. If the statement is true but unnecessarily restricted, indicate what qualifying words or phrases could be omitted [assume that in each example we are referring to a **closed system** (closed with respect to exchange of material or change of phase)]:

- a. The work done by the system on the surroundings is never greater than the decrease in the energy of the system.
- b. The enthalpy of a system cannot change during an adiabatic process.
- c. When a system undergoes a given isothermal change (an isothermal change between specific initial and final states), its enthalpy does not depend on the process involved.
- d. For any process, the change in enthalpy of the system must be equal and opposite to that of the surroundings ($\Delta H_{\text{sys}} = - \Delta H_{\text{surr}}$).
- e. A spontaneous change is always accompanied by a decrease in the energy of the system.
- f. The equation $\Delta U = q + w$ is applicable to any change in a closed system when no electrical work is done by the system on the surroundings.

- g. For any change in an isolated system $\Delta U = 0$ and $\Delta H = 0$.
- h. For any constant pressure process, the increase in enthalpy equals the heat absorbed whether electrical work is done during the process or not.
- i. When a real gas expands into a vacuum (against $P_{\text{ext}}=0$), it does work since the molecules of the gas have to be separated from one another against attractive (van der Waals) forces.

15. In lecture we showed that for an ideal gas undergoing a reversible, adiabatic volume

change (compression/expansion)

$$T_2^{\bar{C}_V} V_2 = T_1^{\bar{C}_V} V_1 \quad (\text{i.e. } T^{\bar{C}_V} V = \text{constant along path})$$

Show that also:

$$\text{a. } \frac{T_2^{\bar{C}_P}}{P_2} = \frac{T_1^{\bar{C}_P}}{P_1} \quad (\text{i.e. } \frac{T^{\bar{C}_P}}{P} = \text{constant along the path})$$

and

$$\text{b. } P_2 V_2^\gamma = P_1 V_1^\gamma \quad \text{where } \gamma = \frac{\bar{C}_P}{\bar{C}_V} \quad (\text{i.e. } PV^\gamma = \text{constant along the path})$$

16. E&R #4.20

If 3.365 g of ethanol $\text{C}_2\text{H}_5\text{OH}(\ell)$ is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 99.472 kJ.

- a. Calculate $\Delta H_{\text{combustion}}^0$ for ethanol at 298.15 K.
- b. Calculate ΔH_f^0 of ethanol at 298.15 K.
[for part b. use Appendix A (4.1) only; **no peeking** at A(4.2) !!]