

CHEM352: PHYSICAL CHEMISTRY I / FALL 2020  
PROBLEM SET I - DUE 25<sup>th</sup> OF SEPT, 5.00 PM

Instructor: Dr. Mateusz Marianski

Room#: HN-1321B  
email: [mmarians@hunter.cuny.edu](mailto:mmarians@hunter.cuny.edu)  
20 points total/2 points per problem

1. Simplify following relations using equation of state for ideal gas:

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (1a)$$

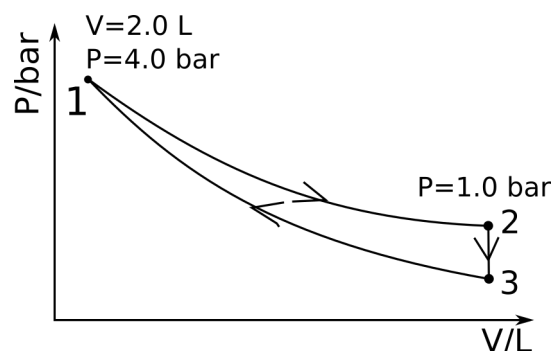
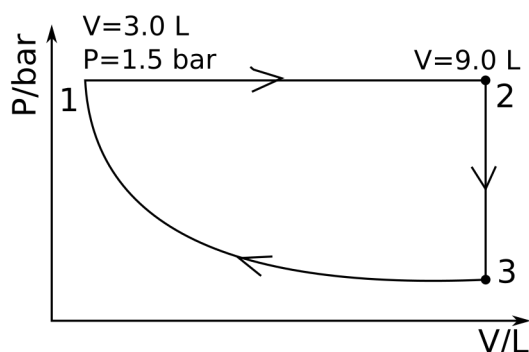
$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad (1b)$$

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \quad (1c)$$

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H = -\frac{1}{C_P} \left[ \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T + \left( \frac{\partial PV}{\partial P} \right)_T \right] \quad (1d)$$

$$\left( \frac{\partial H}{\partial P} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial P} \right)_T + V \quad (1e)$$

2. (a) Calculate work involved when one mole of an ideal gas is compressed reversibly from 2.00 to 6.00 bar at constant temperature of 275K  
(b) Calculate work involved when one mole of an ideal gas is expanded reversibly from 15.0 L to 45.0 L at constant temperature of 275K  
(c) Calculate minimum amount of work required to compress two moles of an ideal gas isothermally at 275K from volume of 20.0 L to 2.5L.
3. Calculate  $\Delta H$  and  $\Delta U$ ,  $q$  and  $w$  for:
- (a) heating of 1.25 mol of an ideal gas from 25.0°C to 375.0°C under constant volume of 2.00 L, if  $C_{V,m} = 20.8 \text{ [J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}]$ .  
(b) heating of 2.50 mol of an ideal gas from 25.0°C to 375.0°C under constant pressure of 10 atm, if  $C_{P,m}(T) = 20.9 + 0.042 \cdot T \cdot \text{K}^{-1} \text{ [J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}]$ .
4. (a) (Left diagram) A system containing 2.00 mol of an ideal gas for which  $C_{V,m} = 20.8 \text{ [J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] \simeq \frac{5}{2}R$  is taken through the cycle in the diagram following isobaric, isochoric and isothermal processes respectively. Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for each segment and the cycle, assuming that the molar heat capacity  $C_{V,m}$  is independent of temperature.  
(b) (Right diagram) A system containing 1.25 mol of a *monoatomic* ideal gas for which  $C_{V,m} = 12.47 \text{ [J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] \simeq \frac{3}{2}R$  is taken through the cycle in the diagram following isothermal, isochoric and adiabatic transitions respectively. Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for each segment and the cycle, assuming that the heat capacity is independent of temperature.



5. Using a diagram with cylinders and pistons, explain the following relations:

$$|w_{irrev}| > |w_{rev}| \quad \text{for gas compression} \quad (2a)$$

$$|w_{irrev}| < |w_{rev}| \quad \text{for gas expansion} \quad (2b)$$

6. Starting from vdW equation of state, find:

- (a) An expression for the total differential  $dP$  in terms of  $dV$  and  $dT$ .
- (b) Determine whether the  $dP$  is an exact differential.
- (c) Thermal expansion  $\beta$  and isothermal compressibility  $\kappa$  coefficients of the vdW gas.

7. (a) Explain in terms of physical processes, why heat capacity at constant pressure is always larger than the heat capacity at constant volume ( $C_{p,m}$   $C_{v,m}$ )

(b) The relation between  $C_{v,m}$  and  $C_{p,m}$  for real materials is given by  $C_{v,m} + \frac{TV\beta^2}{\kappa} = C_{p,m}$ . Show that the relation simplifies to  $C_{v,m} + R = C_{p,m}$  for the ideal gas.

(c) Why for liquids and solids  $C_{v,m} \approx C_{p,m}$ ? Prove it using equation from point 1 assuming some reasonable estimates for  $\beta$  and  $\kappa$ .

8. A 5.00 kg sample of liquid water is used to cool an engine. Calculate the heat removed from the engine when the temperature of water is raised from 275K to 425K. Take  $C_{p,m}=75.2$  [J · K<sup>-1</sup> · mol<sup>-1</sup>] for liquid water.

9. From the following data, compute the  $\Delta_f H^\circ$  of  $\text{CaC}_2(s)$  at 298 K.



The combustion enthalpies of  $\text{C}(s)$  and  $\text{C}_2\text{H}_2(g)$  are -393.5 and -1299.8 kJ/mol respectively. Next, I would suggest that you take a look at problem 4.21 in the book (involving phase transitions). It's tedious to calculate and implicitly introduces couple of assumptions, but you should know how to tackle it.

10. Given the following data for sodium, plot  $H_m(T) - H_m(0)$  against T for sodium:

- melting point 361K, boiling point 1156 K,
- $\Delta H_{fus,m}=2.60$  kJ · mol<sup>-1</sup>,  $\Delta H_{vap,m}=97.4$  kJ·mol<sup>-1</sup>,
- $C_{p,m}(g)=20.8$  J · K<sup>-1</sup> · mol<sup>-1</sup>,  $C_{p,m}(l)=32.7$  J · K<sup>-1</sup> · mol<sup>-1</sup>,  $C_{p,m}(s)=28.2$  J · K<sup>-1</sup> · mol<sup>-1</sup>.

Be careful about the numerical values and units.