Homework Assignment #1:

Due at 500 pm Friday 1 July, Drohny Mailbox #10.

1) Consider the following expression for the differential change in the heat of an ideal gas: 
\[ dq = nC_v dT + \frac{nRT}{V} dV , \]
where \( C_v, n, \) and \( R \) are constants. Using Euler’s criterion for exactness, show that \( dq \) is an inexact differential. Also, show that the function \( \frac{dq}{T} \) is exact.

Solution:

\[ dq = nC_v dT + \frac{nRT}{V} dV = M(V, T) dT + N(V, T) dV \]

\[ \frac{\partial M}{\partial V} = 0 and \frac{\partial N}{\partial T} = \frac{nR}{V} \quad \therefore \quad \frac{\partial M}{\partial V} \neq \frac{\partial N}{\partial T} \]

and \( dq \) is inexact.

\[ \frac{dq}{T} = \frac{nC_v dT}{T} + \frac{nR}{V} dV = M(V, T) dT + N(V, T) dV \]

\[ \frac{\partial M}{\partial V} = 0 and \frac{\partial N}{\partial T} = 0 \quad \therefore \quad \frac{\partial M}{\partial V} = \frac{\partial N}{\partial T} \]

and \( \frac{dq}{T} \) is exact.

2) Assume that the differential change in volume is given as the exact differential

\[ dV = \left( \frac{\partial V}{\partial T} \right)_p dT + \left( \frac{\partial V}{\partial P} \right)_T dP \]

For an ideal gas, derive the expressions

\[ \left( \frac{\partial V}{\partial T} \right)_p \]

and \[ \left( \frac{\partial V}{\partial P} \right)_T \]. Assume for an ideal gas undergoing a reversible expansion the work is expressed as \( dw = -PdV \). Using your expression for \( dV \) prove that \( dw \) is inexact...i.e. that the work is path dependent.

Solution: For an ideal gas...

\[ \left( \frac{\partial V}{\partial T} \right)_p = \frac{\partial}{\partial T} \left( \frac{nRT}{P} \right) = \frac{nR}{P} \]

and

\[ \left( \frac{\partial V}{\partial P} \right)_T = \frac{\partial}{\partial P} \left( \frac{nRT}{P} \right) = -\frac{nRT}{P^2} \]

Then 
\[ dV = \frac{nR}{P} dT - \frac{nRT}{P^2} dP \]
and the work is therefore...

\[ dw = -PdV = -P \left( \frac{nR}{P}dT - \frac{nRT}{P^2}dP \right) \]

\[ = -nRdT + \frac{nRT}{P}dP = M(P,T)dT + N(P,T)dP \]

Then \( \frac{\partial M}{\partial P} = \frac{\partial}{\partial P}(-nR) = 0 \) and \( \frac{\partial N}{\partial T} = \frac{\partial}{\partial T} \left( \frac{nRT}{P} \right) = \frac{nR}{P} \)

\[ \therefore \frac{\partial M}{\partial P} \neq \frac{\partial N}{\partial T} \]

and so \( dw \) is an inexact differential.

3) The pressure change for a gas is given by: \( dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \). The van der Waals equation of state is \( \left( P + \frac{an^2}{V^2} \right)(V-nb) = nRT \) where \( a \) and \( b \) are constants characteristic of the gas.

a) Obtain expressions for \( \left( \frac{\partial P}{\partial T} \right)_V \) and \( \left( \frac{\partial P}{\partial V} \right)_T \) for a van der Waals gas.

\[ \left( P + \frac{an^2}{V^2} \right)(V-nb) = nRT \]

\[ \therefore P = \frac{nRT}{V-nb} - \frac{an^2}{V^2} = (nRT)(V-nb)^{-1} - \frac{an^2}{V^2} \]

\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V-nb} \quad \text{and} \quad \left( \frac{\partial P}{\partial V} \right)_T = -(nRT)(V-nb)^{-2} + \frac{2an^2}{V^3} \]

\[ : dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV = \frac{nR}{V-nb}dT + \left( -\frac{2an^2}{V^3} - \frac{nRT}{(V-nb)^2} \right) dV \]

b) Calculate the change in pressure when 1 mole of ammonia increases its temperature from 500K to 600K. For ammonia \( a=4.17 \text{ atm L}^2 \text{ mol}^{-1} \) and \( b=0.0371 \text{ L mol}^{-1} \). Assume the volume is constant at 10L.

Solution:

\[ dP = \frac{nR}{V-nb}dT \text{ for } dV = 0. \] Then

\[ \Delta P = \frac{nR}{V-nb} \Delta T = \left( \frac{8.31J/K}{L \cdot \text{atm}/101J} \right) \left( 600K - 500K \right) = 0.82 \text{ atm} \]
c) Calculate the change in pressure when 1 mole of ammonia increases its volume from 10L to 20K. For ammonia a=4.17 atm L^2 mol^{-1} and b=0.0371 L mol^{-1}. Assume the temperature is constant at 500K.

\[ dP = \left( 2 \frac{an^2}{V^3} - \frac{nRT}{(V-nb)^2} \right) dV \Rightarrow \Delta P = \left( \frac{0.0821L \cdot atm / K \cdot (500K)}{V - 0.0371L} - \frac{4.17L^2}{V^2} \right)_{10L}^{20L} \]

\[ \Delta P = \frac{(41L \cdot atm)}{(20L - 0.0371L)} - \frac{(41L \cdot atm)}{(10L - 0.0371L)} - \frac{4.17atmL^2}{400L^2} + \frac{4.17atmL^2}{100L^2} \approx 2.1atm - 4.1atm = -2atm \]

4) The heat capacities and constant pressure and volume are defined as

\[ \bar{c}_p = \left( \frac{\partial H}{\partial T} \right)_p and \bar{c}_v = \left( \frac{\partial U}{\partial T} \right)_v \], respectively.

a) Using the heat capacity definitions and the definition of enthalpy

\[ H=U+PV \text{ show that } \bar{c}_p - \bar{c}_v = \left( \frac{\partial U}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_v \]

Solution:

\[ \bar{c}_p - \bar{c}_v = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v = \left( \frac{\partial [E + PV]}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v \]

\[ = \left( \frac{\partial E}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p + V \left( \frac{\partial P}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v = \left( \frac{\partial E}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v \]

b) Using the relationships

\[ dU = \left( \frac{\partial U}{\partial T} \right)_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV \text{ and } dV = \left( \frac{\partial V}{\partial T} \right)_p dT + \left( \frac{\partial V}{\partial P} \right)_T dP \]

show that \[ \left( \frac{\partial U}{\partial T} \right)_p = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + \left( \frac{\partial U}{\partial T} \right)_v \]. Hint: Substitute the dV expression into the dU expression, then differentiate with respect to T at constant P.

Solution:

\[ \left( \frac{\partial E}{\partial T} \right)_p = \left( \frac{\partial E}{\partial T} \right)_v \left( \frac{\partial T}{\partial T} \right)_p + \left( \frac{\partial E}{\partial V} \right)_T \frac{\partial}{\partial T} \left( \frac{\partial V}{\partial T} \right)_p dT + \left( \frac{\partial V}{\partial P} \right)_T dP \]

\[ = \left( \frac{\partial E}{\partial T} \right)_v + \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \]
c) Use the results from parts a and b to show that
\[
\bar{c}_p - \bar{c}_v = \left( P + \left( \frac{\partial U}{\partial V} \right)_T \right) \left( \frac{\partial V}{\partial T} \right)_P
\]

Solution:
\[
\bar{c}_p - \bar{c}_v = \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v
\]
\[
= \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_P - \left( \frac{\partial E}{\partial T} \right)_v
\]
\[
= \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\partial V}{\partial T} \right)_p \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right]
\]

d) Using your result in part c, show that for an ideal gas \( \bar{c}_p - \bar{c}_v = R \)

Solution:
\[
\bar{c}_p - \bar{c}_v = \left( \frac{\partial V}{\partial T} \right)_p \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] = \left( \frac{\partial}{\partial T} \left[ \frac{RT}{P} \right] \right)_P (P) = R
\]

5) Using the definition \( dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP \), show that \( C_p = -\left( \frac{\partial H}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_H \)

Solution:
\[
dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP \Rightarrow \left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial H}{\partial P} \right)_p \left( \frac{\partial T}{\partial P} \right)_H + \left( \frac{\partial H}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_H
\]
\[
0 = \left( \frac{\partial H}{\partial P} \right)_p + \left( \frac{\partial H}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_H \Rightarrow \left( \frac{\partial H}{\partial T} \right)_p = C_p = -\left( \frac{\partial H}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_H
\]

6) Hydrogen behaves as an ideal gas at temperatures above 200 K and at pressures below 50 atm. Assume 6.00 moles of hydrogen are initially contained in a 100 liter vessel at a pressure of 2.00 atm. The average molar heat capacity of hydrogen at constant pressure \( C_p \) is 29.3 J mol\(^{-1}\) K\(^{-1}\) in the temperature range of this problem. The gas is cooled slowly at constant pressure from its initial state to a volume of 50 liters. Calculate the following quantities for this process:

(a) Temperature of the gas in the final state, \( T_f \).

Solution:
\[
T_i = \frac{PV}{nR} = \frac{(2\text{ atm})(100\text{ L})}{(6\text{ moles})(0.0821\text{ L·atm/moles·K})} = 406K
\]
\[
T_f = \frac{V_f}{V_i} = \left( 406K \right) \frac{50\text{ L}}{100\text{ L}} = 203K
\]
(b) Work done on the gas, $w$, in Joules.

Solution:

$$ w = -P \Delta V = -(2\text{ atm})(50L - 100L) = 100L \cdot \text{atm} = 10100J = 10.1kJ $$

(c) Heat absorbed by the gas, $q$, in Joules.

$$ q = \Delta H = n \tilde{C}_p \Delta T = n \left( \tilde{C}_v + R \right) \Delta T = (6\text{ moles})(29.3 \text{ / moles} \cdot \text{K})(203K - 406K) = -3.57kJ $$

(d) Internal energy change of the gas, $\Delta U$, in Joules.

$$ \Delta U = q + w = -35.7kJ + 10.1kJ = -25.6kJ $$

(e) Enthalpy change of the gas $\Delta H$, in Joules

See part c.

7) A sample of crystalline urea $H_2NCONH_2$ weighing 1.372 g is burned in a bomb calorimeter for which the net heat capacity is 5.00 kJ K$^{-1}$. The temperature rise is from $T=294K$ to 298K. The combustion products are carbon dioxide gas, nitrogen gas, and liquid water.

a) Write the net balanced combustion reaction

Solution: If the combustion products are carbon dioxide gas, nitrogen gas, and liquid water the balanced equation has to be

$$ H_2NCONH_2(s) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + N_2(g) $$

b) Calculate $\Delta U$. Give your answer in kJ mol$^{-1}$.

Solution: The volume is constant so for 1.372 g of urea:

$$ \Delta U = q = -C \Delta T = -(5.00kJ / K)(2.95K) = -15.75kJ $$

Per mole of urea this is $\Delta U = \frac{-15.75kJ}{1.372g}(60.05g / mole) = -645.6kJ / mole$

Where the negative sign means heat flows out of the system.

c) Calculate the volume change that would have occurred if this reaction had occurred at constant pressure of 1 atm. Give your answer in liters and cubic meters.

Solution:

$$ P\Delta V = \Delta \left( nRT \right) = R\Delta \left( nT \right) $$

$$ \Delta V = \frac{R\Delta \left( nT \right)}{P} = \frac{R}{P} \left( 2 \times 297.92K - \frac{3}{2} \times 294.34K \right) = \frac{0.0821L \cdot \text{atm} / K}{1\text{atm}} \left( 595.84K - 441.51K \right) = 12.7L $$

d) How much heat would be given off to the surroundings in the constant pressure process described in c.
Solution:
\[ q = \Delta U + P\Delta V = -645.6 \text{kJ/mole} + (1 \text{atm})(12.7 \text{L})(101 \text{J/L \cdot atm}) \]
\[ = -645.6 \text{kJ/mole} + (1 \text{atm})(12.7 \text{L})(101 \text{J/L \cdot atm}) = -645,600 \text{J/mole} + 1282.7 \text{J/mole} \]
\[ = -644.3 \text{kJ/mole} \]

e) Calculate the enthalpy change for the constant pressure process.
Solution: At constant pressure \[ \Delta H = q = -644.3 \text{kJ/mole} \]

8) In stressed muscle tissue, glucose \( C_6H_{12}O_6 \) is converted to lactic acid \( CH_3CHOHCOOH \). The standard enthalpies of formation of glucose and lactic acid are -1274.45 and -694.04 kJ mol\(^{-1}\), respectively. The molar heat capacities at constant pressure of glucose and lactic acid are 218.86 and 127.6 JK\(^{-1}\)mol\(^{-1}\), respectively.

a) Calculate the enthalpy of reaction for the formation of lactic acid from glucose at 298K.

The equation is:

\[ C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH \]

\[ \therefore \Delta H \left( T_1 = 298K \right) = 2 \left( -694.04 \text{kJ/mole} \right) - \left( -1274.45 \text{kJ/mole} \right) = -113.6 \text{kJ/mole} \]

b) Calculate the enthalpy of reaction for the formation of lactic acid from glucose at 310K.

Solution:
\[ \Delta H \left( T_2 \right) = \Delta H \left( T_1 \right) + \Delta C_v^0 \Delta T = -113.6 \text{kJ/mole} + \left[ 2 \left( 127.6 \text{J/K \cdot mole} \right) - 218.9 \text{J/K \cdot mole} \right] \left( 310K - 298K \right) \]
\[ = -113.6 \text{kJ/mole} + \left[ 2 \left( 127.6 \text{J/K \cdot mole} \right) - 218.9 \text{J/K \cdot mole} \right] \left( 310K - 298K \right) \]
\[ = -113,600 \text{J/mole} + \left( 36.6 \text{J/K \cdot mole} \right) \left( 12K \right) = -113,161 \text{J/mole} \approx -113.2 \text{kJ/mole} \]

9) The respiratory system uses oxygen to degrade glucose to carbon dioxide and water.

The net equation is

\[ C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2 + 6H_2O(\ell) \]

a) Calculate the enthalpy of reaction at 298K.

Solution:
\[ C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2 + 6H_2O(\ell) \]
\[ \Delta H^0 = 6\Delta H_f^0(\text{CO}_2, g) + 6\Delta H_f^0(\text{H}_2\text{O}, \ell) - \Delta H_f^0(C_6H_{12}O_6, s) - 6\Delta H_f^0(\text{O}_2, g) \]
\[ = 6 \times \left( -393.51 \text{kJ} \right) + 6 \times \left( -285.84 \text{kJ} \right) - \left( -1274.45 \text{kJ} \right) \]
\[ = -2361.06 \text{kJ} - 1715.04 \text{kJ} + 1274.45 \text{kJ} = -2801.65 \text{kJ} \]

b) Assume respiration occurs at constant pressure. Calculate the amount of heat produced by respiration per mole of oxygen absorbed at 298K.
Solution: \( q = \frac{\Delta H^0}{6} = \frac{-2801.65kJ}{6} = -466.94kJ \)

c) An average person uses about 1.2 moles of oxygen per hour in the course of respiring. Calculate the amount of heat produced by respiration per kilogram per hour by an average person. Assume a weight of 70 kg.

Solution: \( q = \frac{(-466.94kJ/mole)(1.2mole/hr)}{70kg} = -8.00kJ/hr \cdot kg \)

d) Most of the heat produced by the body is lost. But suppose that a person were clothed in a thermally insulated suit such that all the heat from respiration were retained by the body. After 10 hours of respiration, how much would the body temperature of the person described in part c rise? Assume a heat capacity of 4.18kJ kg\(^{-1}\) mol\(^{-1}\).

\( q = (-8.00kJ/kg \cdot hr)(10hr) = -80.0kJ/kg \)

Solution: \( 80.0kJ/kg = (4.18kJ/kg \cdot K) \Delta T \Rightarrow \Delta T = 19.14K \)

10) Certain yeast can degrade glucose into ethanol and carbon dioxide in a process called alcoholic fermentation according to the equation:

\[ C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g) \]

a) Calculate the enthalpy of reaction. You can find appropriate heats of formation in your text appendices.

Solution:
\[ \Delta H^0 = 2\Delta H_f^0(C_2H_5OH, l) + 2\Delta H_f^0(CO_2, g) - \Delta H_f^0(C_6H_{12}O_6, s) \]
\[ = 2 \times (-276.98kJ) + 2 \times (-393.51kJ) - (-1274.45kJ) \]
\[ = -553.96kJ - 787.02kJ + 1274.45kJ = -66.53kJ \]

b) Calculate the amount of heat produced at constant pressure and at T=298K per mole of glucose fermented.

Solution: \( q = \Delta H^0 = -66.53kJ \)

c) Calculate the work done at constant pressure of 1 atm. And at T=298K per mole glucose fermented. Assume carbon dioxide behaves ideally.

Solution:
\[ w = -P\Delta V = -(1atm)(2)(22.4L)\left(\frac{298K}{273K}\right) = (-48.90L \cdot atm)(101J/L \cdot atm) = -4939J \]

d) Calculate the energy change \( \Delta U \) when one mole of glucose ferments at T=298K and 1 atm.

Solution: \( \Delta U = q + w = -66530J - 4939J = -71469J \)