due Mar. 9

Chemistry 342

Problem Set 6

In each problem, determine whether it is theoretically possible to carry out the calculations with the given data (some data are symbolic, such as a, b, c, etc., but given, nevertheless), if so, derive the required expressions for the problem and carry through the calculations, if not, explain which pieces of unstated information are required in order to do so.

You may assume independent of temperature the following data:

	C_p J mol^{-1} K^{-1}	C_V J mol^{-1} K^{-1}
H_2(g)	28.824	20.5
O_2(g)	29.355	21.0
H_2O(g)	33.58	25.3
H_2O(l)	75.291	75.2
CO_2(g)	37.11	28.8
CH_4(g)	35.31	27.0

Also you may use the following values at 298 K

$\Delta_{\text{form}}H^{\ominus}$ for the formation of	$\Delta_{\text{form}}H^{\ominus}$ kJ mol^{-1}
H_2O(g)	-241.82
H_2O(l)	-285.83
CO_2(g)	-393.51
CH_4(g)	-74.81

and the following value at 373 K: $\Delta_{\text{vap}}H^{\ominus}$ for H_2O = 40.656 kJ mol^{-1}

1. One mole of a non-ideal gas is expanded isothermally and reversibly at 300 K from 20.0 L to twice its volume. The equation of state is given by

$$p = RT\,[V^{-1} + BV^{-2}].$$

Find the molar change in U, H, S, A, and G

(a) if B is a constant (independent of temperature)

(b) if $B = a + bT + cT^2$ where a, b, c are constants

(c) if B is a constant (independent of temperature) and the expansion is carried out irreversibly

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2. Two moles of a non-ideal gas undergo an irreversible process which takes the gas from T_i = 600 K, p_i = 10 atm to T_f = 300 K, p_f = 5 atm. The equation of state is given by

$$pV = nRT + nBp$$

where B= 0.035 L mol^{-1} and the molar heat capacity of the gas is given in J mol^{-1} K^{-1} by

$$C_p = 52.675 + 1.561\times10^{-2}T$$

Find the change in U, H, S, A, and G for the process.

3. Two moles of a gas whose equation of state is $pV = RT + ap$ where a = 0.020 L mol^{-1} at 300 K, 0.025 L mol^{-1} at 400 K, 0.030 L mol^{-1} at 500 K, undergoes isothermal compression at 300 K from 1 atm to 11 atm. First derive the equations that are appropriate for this equation of state. Calculate $\Delta\mathbf{U}$ and $\Delta\mathbf{H}$ for the gas. What is the maximum work for this change in state? Calculate $\Delta\mathbf{G}$ and $\Delta\mathbf{A}$ for the gas.

4. One-half mole of methane at 25°C is exploded in a large excess, ten moles of oxygen, burning completely to carbon dioxide and water. Calculate the final temperature under adiabatic conditions, (a) assuming the explosion to be at constant pressure, (b) assuming the explosion to be at constant volume.

5. The temperature of a hydrogen-oxygen flame is found to be 2000 K. Assuming constant pressure conditions and that oxygen is initially present in a ten-fold molar excess over hydrogen (that is, 10:1 mole ratio) calculate the degree of combustion of the hydrogen to water.

6. The compressibility factor for ethane at 600 K can be fit to the expression

$$Z = 1.0000 - 0.000612\,(p/1\text{ bar}) + 2.661\times10^{-6}(p/1\text{bar})^2 - 1.390\times10^{-9}\,(p/1\text{bar})^3 - 1.077\times10^{-13}(p/1\text{bar})^4$$

for p between 0 and 600 bar. Use this expression to determine the fugacity coefficient f/p of ethane as a function of pressure at 600 K.

7. Show how non-ideal behavior of a gas this affects the equation for the distribution of the gas in a gravity field as follows. From the differential equation for the distribution, show that if $Z > 1$ the distribution is broader for the real gas than for the ideal gas and that the converse is true if $Z < 1$. Let $Z = 1+B(T)p$, integrate the equation and evaluate the constant of integration to obtain the explicit form of the distribution function.

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8. The compressibility factor of a gas is $pV/RT = 1 + [b-(a/RT)](p/RT)$. Calculate the fugacity of this gas

9. From the definition of fugacity and the Gibbs-Helmholtz equation, show that the molar enthalpy $\mathbf{H}$ of a real gas is related to the molar enthalpy of the ideal gas by $\mathbf{H}_{real} = \mathbf{H}_{ideal}^{\ominus} - RT^2(\partial \ln f/\partial T)_p$.