Midterm Exam I
CHM 3410, Dr. Mebel, Fall 2018

1. (20 pts.) What mass of Ar gas is present in a 30-liter container at 273 K under 15 atm of Ar pressure if

(a) the gas is perfect;

(b) the gas obeys the following virial equation of state, $pV = nRT\left(1 + \frac{nB}{V}\right)$. The second virial coefficient B for Ar at 273 K is -21.7 $cm^3\ mol^{-1}$.

(a) $$n = \frac{pV}{RT} = \frac{15\,atm \cdot 30L}{8.20574\cdot10^{-2}\,L\cdot atm\cdot K^{-1}\cdot mol^{-1}\cdot 273K}$$

$$n = 20.088\ mol$$

$$m = n\cdot M = 20.088\,mol\cdot 28\,\frac{g}{mol} = \underline{\underline{803.5\,g}}$$

(b) $$pV = nRT\left(1 + \frac{nB}{V}\right)$$

$$\underbrace{\frac{RTB}{V}}_{a} n^2 + \underbrace{RT}_{b} n \underbrace{-pV}_{c} = 0$$

$$a = \frac{8.20574\cdot10^{-2}\cdot 273\cdot(-21.7\cdot10^{-3})}{30} = -0.0162\ \frac{L\cdot atm}{mol^2}$$

$$b = 8.20574\cdot10^{-2}\cdot 273 = 22.4\ \frac{L\cdot atm}{mol}$$

$$c = -15\cdot 30 = -450\ L\cdot atm$$

$$D = b^2 - 4ac = 472.67 \qquad \sqrt{D} = 21.74$$

$$n = \frac{-b \pm \sqrt{D}}{2a} = 20.388\ mol \ /\ 13\cancel{62}.1$$

$$m = n\cdot M = \underline{\underline{815.5\,g}}$$

2. (20 pts.) One mole of N_2 at 25°C and 1 bar pressure is allowed to expand reversibly to a volume of 50 L (a) isothermally and (b) adiabatically. Assuming perfect gas behavior, calculate the final pressure, temperature, q, w, ΔU, and ΔH in each case.

$$V_i = \frac{8.31447\ J\,K^{-1}\,mol^{-1} \cdot 298.15K \cdot 1mol}{10^5\ Pa}$$

$$V_i = 24.79 \cdot 10^{-3} m^3 = 24.79\ L$$

a) $p_i V_i = p_f V_f \qquad p_f = p_i \frac{V_i}{V_f} = 1bar\ \frac{24.79L}{50L} =$

$p_f = \underline{0.496\ bar} \qquad T_f = \underline{298.15\ K}$

$\underline{\Delta U = \Delta H = 0}$

$w = -nRT \ln \frac{V_f}{V_i} = \underline{-1.74\ kJ} \qquad q = \underline{+1.74\ kJ}$

b) $p_i V_i^{\gamma} = p_f V_f^{\gamma} \qquad p_f = p_i \left(\frac{V_i}{V_f}\right)^{\gamma}$

$\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.4 \qquad p_f = \underline{0.374\ bar}$

$T_f = \frac{p_f V_f}{nR} = \underline{225.2\ K}$

$w = C_V (T_f - T_i) = \underline{-1.52\ kJ} \qquad q = \underline{0}$

$\Delta U = w = \underline{-1.52\ kJ}$

$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T = \underline{-2.12\ kJ}$

3. (20 pts) A 1:3 mixture of CO and H_2 is passed through a catalyst to produce methane at 500 K.

$$CO(g) + 3\,H_2(g) \rightarrow CH_4(g) + H_2O(g)$$

How much heat is liberated in producing a mole of methane? How does this compare with the heat obtained from combustion of a mole of methane at this temperature?

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$$

	$\Delta_f H^\ominus$	$C_{p,m}$
$CO(g)$	-110.5	29.1
$H_2(g)$	0	28.8
$CH_4(g)$	-74.6	35.7
$H_2O(g)$	-241.8	33.6
$H_2O(l)$	-285.8	75.3
$CO_2(g)$	-393.5	37.1
$O_2(g)$	0	29.4

$$\Delta_r H^\ominus(298\text{ K}) = -205.9\ \text{kJ mol}^{-1}$$

$$\Delta_r C_p = -46.2\ \text{J K}^{-1}\text{mol}^{-1}$$

$$\Delta_r H^\ominus(500\text{ K}) = -205.9 + (-46.2\cdot 10^{-3})(500-298)$$

$$= \underline{\underline{-215.2\ \text{kJ mol}^{-1}}}$$

Combustion reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

$$\Delta_r H^\ominus(298\text{ K}) = -890.5\ \text{kJ mol}^{-1}$$

$$\Delta_r C_p = 93.2\ \text{J K}^{-1}\text{mol}^{-1}$$

$$\Delta_r H^\ominus(500\text{ K}) = -890.5 + 93.2\cdot 10^{-3}(500-298)$$

$$= \underline{\underline{-871.7\ \text{kJ mol}^{-1}}}$$

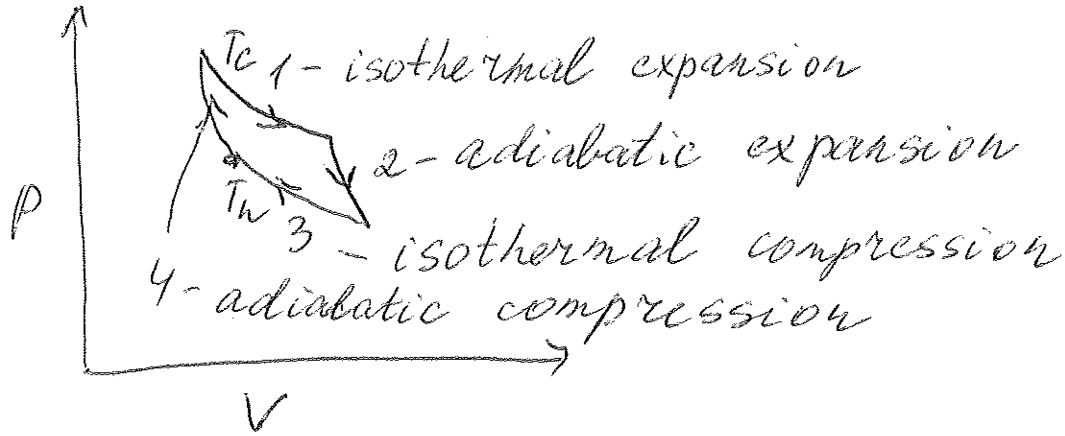
4. (20 pts.) (a) Describe the Carnot cycle.

(b) What is the efficiency of an engine using the Carnot cycle and how it is related to the Second Law of thermodynamics?

(c) Explain why absolute zero of temperature cannot be achieved.

(d) What is the entropy change ΔS in the Carnot cycle?

a)



b) $\varepsilon = 1 - \dfrac{|q_c|}{|q_h|}$

Second Law: $|q_c| > 0 \Rightarrow \varepsilon < 1$

c) $\varepsilon = 1 - \dfrac{T_c}{T_h}$ Because $\varepsilon < 1$, $T_c > 0$

d) $\Delta S = 0$

5. (20 pts) Derive an expression for the internal pressure, π_T, of a gas that obeys the Berthelot equation of state,

$$p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$$

Use the fact that π_T is related to p, V, and T by the following formula:

$$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_m - b} + \frac{a}{T^2 V_m^2}$$

$$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \cancel{\frac{RT}{V_m - b}} + \frac{a}{TV_m^2} - \cancel{\frac{RT}{V_m - b}} + \frac{a}{TV_m^2} = \frac{2a}{TV_m^2}$$