Chemistry 231 **Test 2** (16 November 2018) **Name:** ____________________

- please answer all **5 questions** in the spaces provided
- you have **two hours** to write this test
- a calculator and the equation sheets provided may be used
- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

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1. **a)** Carbon monoxide is oxidized at 25 °C and 1.00 bar: $CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$

(p constant)

Calculate q, w, ΔU and ΔH.

Data at 25 °C

$\Delta H_{fm}°(CO_2, g) = -393.509 \text{ kJ mol}^{-1}$

$\Delta H_{fm}°(CO, g) = -110.525 \text{ kJ mol}^{-1}$

$C_{pm}°(CO_2, g) = 37.11 \text{ J K}^{-1} \text{ mol}^{-1}$

$C_{pm}°(CO, g) = 29.14 \text{ J K}^{-1} \text{ mol}^{-1}$

$C_{pm}°(O_2, g) = 21.91 \text{ J K}^{-1} \text{ mol}^{-1}$

work $w = -\int p_{ext}\, dV = -p\int dV$

$= -p\Delta V = -p(V_{mCO2} - V_{mCO} - \frac{1}{2}V_{mO2})$

$$w = -p\left(\frac{RT}{p} - \frac{RT}{p} - \frac{1}{2}\frac{RT}{p}\right) = \frac{RT}{2} = \frac{(8.314 \text{ J K}^{-1}\text{mol}^{-1})(298.15 \text{ K})}{2}$$

$\boxed{W = 1240 \text{ J}}$

heat $\boxed{q = \Delta H}$ (p constant) $= \Delta H^°_{fm}(CO_2, g) - \Delta H^°_{fm}(CO, g) - \frac{1}{2}\overset{0}{\cancel{\Delta H^°_{fm}(O_2, g)}}$

$= -393.509 - (-110.525) = \boxed{-282.984 \frac{\text{kJ}}{\text{mol}}}$

internal energy $\Delta U = q + w = -282.984 \frac{\text{kJ}}{\text{mol}} + 1.240 \frac{\text{kJ}}{\text{mol}}$

$\boxed{\Delta U = -281.744 \text{ kJ mol}^{-1}}$

b) Calculate the adiabatic flame temperature if CO(g) initially at 25 °C is burned in oxygen.

$$T_f = T_i - \frac{\Delta H(T_i)}{C_p(\text{products})} = T_i - \frac{\Delta H_R^°}{C_{pm}(CO_2, g)}$$

$$= 298.15 \text{ K} - \frac{-282{,}984 \text{ J mol}^{-1}}{37.11 \text{ J K}^{-1} \text{mol}^{-1}}$$

$$= 298.15 \text{ K} + 7625 \text{ K}$$

$\boxed{T_f = 7920 \text{ K}}$

c) The flame produced by burning CO(g) in oxygen is significantly hotter than the flame produced by burning CO(g) in air. Why? Explain briefly.

air: about 4 mol N_2 per mol O_2

In air, N_2 increases C_p(products):

$CO(g) + \frac{1}{2}O_2(g) + 2N_2(g) \rightarrow CO_2(g) + 2N_2(g)$

$$T_{f(air)} = T_i - \frac{\Delta H_R^°}{C_{pm}(CO_2) + 2C_{pm}(N_2)} < T_f(\text{in pure } O_2)$$

Carnot cycle :

2. **a)** Analysis of the Carnot cycle for reversible heat engines shows $\frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$. How did this result lead to the discovery of the entropy?

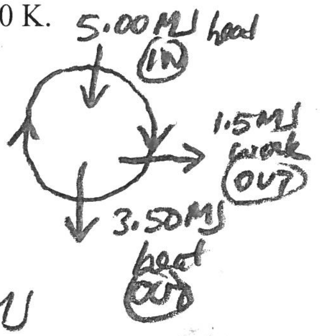
This result, generalized to $\oint \frac{dq_{rev}}{T} = 0$, suggested that $\frac{dq_{rev}}{T}$ is the differential of a new state function (Why? Because $\oint_i^i df = f_i - f_i = 0$ for state functions)

b) For a Carnot heat engine: $q_H + q_C + w = 0$. Why?

For one cycle $\oint_i^i dU = U_i - U_i = q + w$

$= q_H + q_C + w$

c) A heat engine absorbs 5.00 MJ at $T_H = 500$ K and rejects 3.50 MJ heat at $T_C = 300$ K.



i) Calculate the work is done on the surroundings.

$q_H = 5.00 \text{ MJ}$ $\quad q_C = -3.50 \text{ MJ}$

$0 = q_H + q_C + w$

$-w = q_H + q_C = 5.00 \text{ MJ} - 3.50 \text{ MJ}$

$= \boxed{1.50 \text{ MJ}}$ work done on surroundings

ii) Is the engine operating reversibly? Justify your answer.

max efficiency (if reversible) $= 1 - \frac{T_C}{T_H} = 1 - \frac{300 K}{500 K} = 0.400_{rev}$

actual efficiency $= \frac{-w}{q_H} = \frac{1.50 \text{ MJ}}{5.00 \text{ MJ}} = \boxed{\overset{\varepsilon}{0.300}} \; (< 0.400)_{rev}$

NOT REVERSIBLE

d) Give two practical applications of heat pumps.

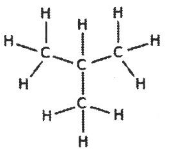
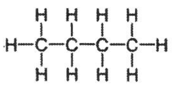
air conditioning
refrigeration

e) 1.0 MJ of electrical work is used to run a Carnot engine in reverse. If $T_C = 290$ and $T_H = 300$ K, calculate the maximum amount of heat pumped into the reservoir at $T_H = 300$ K.

work done on the engine to pump heat (nonspontaneously) from 290 K to 300 K: $w = +1.0 \text{ MJ}$

$$-\frac{w}{q_H} = 1 - \frac{T_C}{T_H} \qquad \frac{-1.0 \text{ MJ}}{q_H} = 1 - \frac{290 K}{300 K} = 0.0333$$

$$q_H = \frac{-1.0 \text{ MJ}}{0.0333} = \boxed{-30 \text{ MJ}}$$

3. Butane is found in two common forms:  and 

iso-butane **n-butane**

Data at 25 °C

$\Delta H_{fm}{}^{o}$(*iso*-butane, g) = −134.52 kJ mol^{-1}

$\Delta H_{fm}{}^{o}$(*n*-butane, g) = −126.15 kJ mol^{-1}

$S_m{}^{o}$(*iso*-butane, g) = 294.75 J K^{-1} mol^{-1}

$S_m{}^{o}$(*n*-butane, g) = 310.23 J K^{-1} mol^{-1}

a) Direct measurement of the enthalpies of formation of *iso*-butane and *n*-butane is very difficult. Why?

$4C(\text{graphite}) + 5H_2(g) \rightarrow$ n-butane or iso-butane

Big Problems: The reactions are very slow (nonexistant) at 25 °C and there are many side reactions.

b) Explain how the enthalpies of formation of *iso*-butane and *n*-butane can be calculated from measured enthalpies of combustion.

$$C_4H_{10} + 6\tfrac{1}{2}O_2 \rightarrow 4CO_2 + 5H_2O \qquad \Delta H_c$$

measure $\Delta H_c = 4\Delta H^o_{fm}(CO_2) + 5\Delta H^o_{fm}(H_2O) - \Delta H^o_{fm}(C_4H_{10})$

(known)

calculate $\Delta H^o_{fm}(C_4H_{10}) = 4\Delta H^o_{fm}(CO_2) + 5\Delta H^o_{fm}(H_2O) - \Delta H_c$

c) $S_m{}^{o}$(*iso*-butane, g) and $S_m{}^{o}$(*n*-butane, g) are absolute entropies, not entropies of formation. How are absolute entropies measured?

$$S^o_m(C_4H_{10}) = \int_0^T \frac{C^o_{pm}}{T}\,dT + \sum_i \frac{\Delta H^o_{im}}{T_i}$$

at temperature T

for $s \rightarrow l$, $l \rightarrow g$ phase changes

c) Calculate $\Delta S_R{}^{o}$ for the reaction *iso*-butane(g) → *n*-butane(g) at 25 °C. $\Delta S_R{}^{o}$ for the reaction is positive at 25 °C. Does this mean the reaction is spontaneous? Explain.

NO

$$\Delta S^o_R = S^o_m(n\text{-butane}) - S^o_m(\text{iso-butane})$$

$$= (310.23 - 294.75)\ J\ K^{-1}\ mol^{-1} = \boxed{15.48\ J\ K^{-1}\ mol^{-1}}$$

ΔS^o_R alone can't be used to decide spontaneity

system not isolated

d) To decide if the reaction *iso*-butane(g) → *n*-butane(g) is spontaneous, why not just buy some *iso*-butane and see if it reacts to form *n*-butane?

The reaction is very slow (immeasurably slow)

$(\Delta H^o_R = 8370\ J)$

e) An organic chemist argues that *n*-butane has less steric hindrance and therefore more stable than *iso*-butane. Is this correct? Use thermodynamics to decide which isomer is more stable at 25 °C.

at 25 °C, 1 bar $\Delta G_{T,p} <$ if spontaneous

Here: $\Delta G^o_R = \Delta(H - TS)^o_R = \Delta H^o_R - T\Delta S^o_R$

$= \Delta H^o_{fm}(n\text{-but}) - \Delta H^o_{fm}(\text{iso-but}) - T\Delta S^o_R$

$= -126150 - (-134520) - (298.15)(15.48) = +3755\ J$

not spont.

iso → n
$\Delta G^o > 0$
iso more stable

or $(\Delta S_{sys} + \Delta S_{surr})_{isolated} = \Delta S^o_R + \frac{-q}{T} = 15.48 + \frac{(-8370)}{298.15} = \left(-12.6\ \frac{J}{K}\right)$ impossible! (isolated)

4. **a)** The equation

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad (4.1)$$

[5]

is mathematically correct, but not very convenient for calculating energy changes. Explain.

how are $\left(\frac{\partial U}{\partial T}\right)_V$ and $\left(\frac{\partial U}{\partial V}\right)_T$ calculated?

b) Show $\left(\frac{\partial U}{\partial T}\right)_V = C_V$

$dU = dq - P_{ext}\, dV$ at constant volume $dU_V = dq_V$

$C_V = \frac{dq_V}{dT} = \frac{dU_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$

or: $dU = TdS - pdV$ $\div dT_V$

$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$ $TdS = dq_{rev}$

c) Show $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ (*hint*: use $dU = TdS - pdV$ and a Maxwell relation)

$dU = TdS - pdV$ $(\div dV_T)$

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

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

Maxwell relation:
from $dA = -SdT - pdV$
get $-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V$

d) Combining **a**, **b** and **c** gives

$$dU = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]dV \qquad (4.2)$$

Equation (4.2) is more convenient for calculating internal energy changes than equation (4.1). Why?

C_V, T, $\left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\kappa}$, p $\Longrightarrow$ all measurable or can be calculated from equations of state

e) Use equation (4.2) to show $dU = C_V dT$ for an ideal gas.

$p = \frac{nRT}{V}$

$dU = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]dV = C_V dT + \left[T\left(\frac{\partial \frac{nRT}{V}}{\partial T}\right)_V - p\right]dV$

$dU = C_V dT + \left[T\frac{nR}{V}\overset{\nearrow 1}{\cancel{\left(\frac{\partial T}{\partial T}\right)_V}} - p\right]dV = C_V dT + \overset{\nearrow 0}{\cancel{\left[\frac{nRT}{V} - p\right]}}\,dV$

$dU = C_V dT$

5. The "water gas shift reaction" $CO(g) + H_2O(g) = CO_2(g) + H_2(g)$ is used to produce hydrogen and carbon dioxide from carbon monoxide and steam at 1000 K.

Data at 1000 K		
	$\Delta G_{fm}^{o}(CO_2, g) = -395.866$ kJ mol^{-1}	$\Delta H_{fm}^{o}(CO_2, g) = -394.623$ kJ mol^{-1}
	$\Delta G_{fm}^{o}(CO, g) = -200.275$ kJ mol^{-1}	$\Delta H_{fm}^{o}(CO, g) = -111.983$ kJ mol^{-1}
	$\Delta G_{fm}^{o}(H_2O, g) = -192.590$ kJ mol^{-1}	$\Delta H_{fm}^{o}(H_2O, g) = -247.867$ kJ mol^{-1}

a) At 1000 K, show the equilibrium constant for the reaction is $K = 1.43$.

$$\Delta G_R^o = \Delta G_{fm}^o(CO_2, g) + \Delta G_{fm}^o(H_2, g) - \Delta G_{fm}^o(CO, g) - \Delta G_{fm}^o(H_2O, g)$$

$$= -395{,}866 + 0 - (-200{,}275) - (-192{,}590) = -3{,}001 \text{ J mol}^{-1}$$

$$K = \exp\left(-\frac{\Delta G_R^o}{RT}\right) = \exp\left[-\left(\frac{-3001}{8.314(1000)}\right)\right] = e^{0.3610} = 1.434$$

b) A mixture containing 5.00 mol CO(g) and 5.00 mol $H_2O(g)$ is heated to 1000 K at 1.00 bar total pressure. Calculate the number of moles of H_2 produced at equilibrium.

	CO +	H_2O =	CO_2 +	H_2O
intially:	5.00 mol	5.00 mol	0	0
equilibrium	$5.00 - x$	$5.00 - x$	x	x

$$K = 1.43 = \frac{P_{CO2} P_{H2}}{P_{CO} P_{H2O}} = \frac{\frac{n_{CO2}RT}{V} \frac{n_{H2}RT}{V}}{\frac{n_{CO}RT}{V} \frac{n_{H2O}RT}{V}} = \frac{n_{CO2} n_{H2}}{n_{CO} n_{H2O}}$$

$$K = \frac{x\,x}{(5.00 - x)(5.00 - x)}$$

$$\sqrt{K} = \frac{x}{5.00 - x} \qquad x = \frac{\sqrt{K}}{1 + \sqrt{K}}\, 5.00 \text{ mol} = \boxed{2.72 \text{ mol } H_2}$$

c) For a higher yield of H_2, should the temperature be increased? Justify your answer.

$$\Delta H_R^o = \Delta H_{fm}^o(CO_2, g) + \Delta H_{fm}^o(H_2, g) - \Delta H_{fm}^o(CO, g) - \Delta H_{fm}^o(H_2O, g)$$

$$= -394{,}623 + 0 - (-111{,}933) - (-247{,}867)$$

$$\Delta H_R^o = -34{,}823 \quad \text{exothermic} \quad \left(\frac{d \ln K}{dT} = \frac{\Delta H_R^o}{RT^2} < 0\right)$$

should decrease T for higher yield

d) For a higher yield of H_2, should the pressure be increased? Justify your answer. NO

$$H_2 \text{ yield} = \frac{\sqrt{K}}{1 + \sqrt{K}}$$

pressure has no effect on yield (assuming ideal gas behavior)