## **Solutions to Problem Set 3**

<b>1.</b> 1 mole liquid, T, 1 atm $\rightarrow$	vapor, T, 1 atm	
Equation	Basis for the equation	Eq.
		#
$d\mathbf{U} = (\partial \mathbf{U} / \partial \mathbf{T})_{V} d\mathbf{T} + (\partial \mathbf{U} / \partial \mathbf{V})_{T} d\mathbf{V}$	U = U(T, V)	1
$\mathbf{U}(T,V)=f(T)-a/V$	Given	2
$V_{\text{liquid}} = 18 \times 10^{-3} \text{ L} \text{ mol}^{-1}$		
$V_{vapor} = 24 L \text{ mol}^{-1}$		
$a = 5.72 L^2 atm mol^{-1}$		
$U_{\text{liquid}} = f(T) - 5.72/18$	substituting values of V into Eq 2	3
$U_{vapor} = f(T) - 5.72/24$		
$\mathbf{U}_{vapor} - \mathbf{U}_{liquid} = -5.72/245.72/0.018$		4
$= 317.54 \text{ L} \text{ atm mol}^{-1}$		5
$= 7690 \text{ cal mol}^{-1}$		
$\mathbf{H}_{vapor} - \mathbf{H}_{liquid} = \mathbf{U}_{vapor} - \mathbf{U}_{liquid}$	H = U + pV Definition	
+ $p(V_{vapo}r - V_{liquid})$		
= 317.54 + 1(24-0.018)	Using Eq 5 and values of V	
$= 341.5 \text{ L} \text{ atm mol}^{-1}$		
= 8270. cal mol <sup>-1</sup>		
Answer		
This is smaller than		
$\Delta_{vap}H = 9820 \text{ cal mol}^{-1} \text{ expt}$		

**2.** 0.1 mol ideal monatomic gas  $T_1 \rightarrow T_2$  along path V = a•exp(bT)

Equation	Basis for the equation	Eq.
		#
p = 0.1RT/V	Given ideal gas equation of state, 0.1 mol	1
W = -∫p <sub>op</sub> dV	Definition	2
$p_{op} = p_{gas}$	given reversible	3
W = - ∫ 0.1RTdV/V		4
V = a∙exp(bT)	Given path	5
$dV = a \cdot exp(bT) \cdot bdT$	Taking the In	6
dV/V = bdT		7
W = -∫0.1RbTdT		8
$W = -0.1 \text{ Rb}(1/2)[T_2^2 - T_1^2]$	Note the function for work depends on the path!	9
Answer		
$q = C (T_2 - T_1)$	Note that C is neither C <sub>V</sub> nor C <sub>p</sub> because the path	
However, given it is an ideal gas,	is neither constant volume nor constant pressure.	
for which $(\partial \mathbf{U}/\partial V)_T = 0$	property of an ideal gas	10
$d\mathbf{U} = (\partial \mathbf{U}/\partial \mathbf{T})_{V} d\mathbf{T} + (\partial \mathbf{U}/\partial V)_{T} dV$	U = U(T, V)	11
$d\mathbf{U} = \mathbf{C}_{V} d\mathbf{T}$		12

$\Delta \mathbf{U} = \mathbf{C}_{\mathbf{V}}[\mathbf{T}_2 - \mathbf{T}_1]$		13
$\Delta \mathbf{U} = \mathbf{q} + \mathbf{W},  \mathbf{q} = \Delta \mathbf{U} - \mathbf{W}$	First law of thermodynamics	14
$q = C_{V}[T_2 - T_1]$		15
+ $(0.1 \text{Rb}/2) \cdot [\text{T}_2^2 - \text{T}_1^2]$		
Answer		
$T_1 = 300 \text{ K}$ $T_2 = 400 \text{ K}$ $b = 0.01 \text{ K}^{-1}$	Given	16
$W = - (0.00831451/2)(400^2 - 300^2)$	Using Eq 9 and 0.1 mol	17
W = - 291 J = -0.291 kJ <b>Answer</b>		18
$\Delta \mathbf{U} = 1.5(8.31451)[400-300] = 1247 \text{ J}$		19
= 1.247 kJ Answer		20
$q = \Delta U - W = 1.538 J$ Answer	Using Eq 14, 18 and 20	

### 3.

#### В С

1 mole ideal gas  $p_1$ ,  $T_1$ ,  $V_1 \rightarrow p_2$ ,  $T_2$ ,  $V_2 \rightarrow p_3$ ,  $T_3$ ,  $V_3 \rightarrow p_4$ ,  $T_4$ ,  $V_4$  **A** reversible heating at constant p = 1 atm, from 298 to 373 K **B** reversible isothermal expansion to  $2V_2$ 

Α

C reversible adiabatic cooling to 308 K

 $C_{p} = (5/2)R$ 

$G_p = (3/2) R$	Basis for the equation	Ea
Equation	Basis for the equation	Eq.
	Qia an	#
$p_1 = 1 \text{ atm } T_1 = 298$	Given	1
$V_1 = R298/1 \text{ atm} = 24.45 \text{ L}$	ideal gas	2
$p_2 = 1 \text{ atm } T_2 = 373$		3
$V_2 = R373/1$ atm = 30.61 L		4
$T_3 =_{T_2} = 373 V_3 = 2V_2 = 61.22 L$		5
$p_3 = R373/61.22 = 0.50 atm$		6
$T_4 = 308 \text{ K}$		7
$p_4$ , $V_4$ can be calculated but we		
actually do not need these		
$d\mathbf{U} = \mathbf{C}_{V} dT + (\partial \mathbf{U} / \partial V)_{T} dV$	$\mathbf{U} = \mathbf{U}(T,V)$ and definition of $C_{V}$	8
$(\partial \mathbf{U}/\partial \mathbf{V})_{\mathrm{T}} = 0$	property of an ideal gas	9
$d\mathbf{U} = \mathbf{C}_{V} d\mathbf{T}$		10
$d\mathbf{H} = \mathbf{C}_{\mathbf{p}}d\mathbf{T} + (\partial \mathbf{H}/\partial \mathbf{p})_{T}d\mathbf{p}$	$H = H(T,p)$ and definition of $C_p$	11
$(\partial \mathbf{H}/\partial \mathbf{p})_{\mathrm{T}} = 0$	property of an ideal gas	12
$d\mathbf{H} = C_{p}dT$		13
Step A		
∆ <b>U</b> = (3/2)R(373-298)= 935.4 J	From Eq 10 and given $C_V = (3/2)R$	14
Answer		
∆ <b>H</b> = (5/2)R(373-298)= 1559.0 J	From Eq 13 and given $C_p = C_V + R = (5/2)R$	15
Answer		
$W = -\int popdV = -1 \text{ atm } [V_2 - V_1]$	Definition and $p = constant = 1 atm$	16
= -1 [30.61 - 24.45] = - 6.16 L atm		
= - 624.2 J <b>Answer</b>		17

$\Delta \mathbf{U} = \mathbf{q} + \mathbf{W}$	First law of thermodynamics	18
$q = \Delta U - W = 935.4 + 624.2 = 1559.6 J$		19
Answer		10
Step B		20
$\Delta \mathbf{U} = 0 \text{ J} \qquad \text{Answer}$	dT = 0	20
$\Delta \mathbf{H} = 0 \mathbf{J}$ Answer	dT = 0	21
$W = -\int p_{op}dV = -\int p_{ga}sdV$	p <sub>op</sub> = p <sub>gas</sub> reversible expansion	22
$W = -\int RTdV/V = -R373 \ln(V_3/V_2)$		23
W = - R373 ln 2 = -2149 J <b>Answer</b>		24
$q = \Delta U - W$	First law of thermodynamics	25
q = 0 + 2149 J <b>Answer</b>		26
Step C		
∆ <b>U</b> = (3/2)R(308-373)= - 810.7 J	From Eq 10 and given $_{CV} = (3/2)R$	27
Answer		
∆ <b>H</b> = (5/2)R(308-373)= - 1351.1 J	From Eq 13 and given $C_p=C_V+R = (5/2)R$	
Answer		
q = 0 Answer	adiabatic	
$\Delta \mathbf{U} = \mathbf{q} + \mathbf{W} \qquad \mathbf{W} = \Delta \mathbf{U}$	First law of thermodynamics	
W = - 810.7 J <b>Answer</b>	From Eq 27	
Overall		
∆ <b>U</b> = 124.7 J		
∆ <b>H</b> = 208.8 J		
W = -3583.9		
q = 3708.6 J		
Answer		

В С 4. Α

1 mole ideal gas  $p_1,\,T_1,\,V_1\to p_2,\,T_2,\,V_2\to p_3,\,T_3,\,V_3\to p_4,\,T_4,\,V_4$  A reversible heating at constant V, from 298 to 373 K

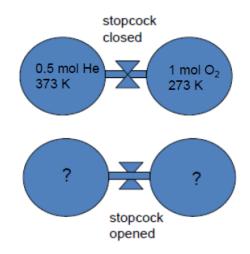
**B** Joule expansion into a vacuum to  $2V_2$ 

C reversible cooling at constant p to 298 K

Equation	Basis for the equation	Eq. #
$p_1 = ? T_1 = 298 V_1 = ?$	Given	
$p_2 = ? T_2 = 373 V_2 = V_1$		
$p_3 = ? T_3 = 373 V_3 = 2V_2$	In a Joule expansion, there is no T change	
$p_4 = p_3$ $T_4 = 298$ K $V_4 = ?$		
Step A		
$q = C_V(373-298)$		1
$W = -\int p_0 p dV = 0$ since $dV = 0$		2
$d\mathbf{U} = C_{V}dT + (\partial \mathbf{U}/\partial V)_{T}dV$	$\mathbf{U} = \mathbf{U}(T, V)$ and definition of $C_V$	3
$(\partial \mathbf{U}/\partial \mathbf{V})_{\mathrm{T}} = 0$	property of an ideal gas	4
$\Delta U = C_{V}(373-298) = q + W$ indeed		5

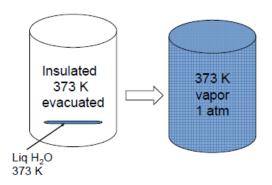
$d\mathbf{H} = \mathbf{C}_{p} \mathbf{dT} + (\partial \mathbf{H} / \partial \mathbf{p})_{T} \mathbf{dp}$	$H = H(T,p)$ and definition of $C_p$	6
$(\partial \mathbf{H}/\partial \mathbf{p})_{\mathrm{T}} = 0$	property of an ideal gas	7
$\Delta H = C_{p}(373-298)$		8
Another way,	$\mathbf{H} = \mathbf{U} + \mathbf{pV}$ definition	9
$\Delta \mathbf{H} = \Delta \mathbf{U} + \mathbf{p}_2 \mathbf{V}_2 - \mathbf{p}_1 \mathbf{V}_1$		10
= C <sub>V</sub> (373-298) + R373- R298	Using ideal gas law	11
$= C_p(373-298)$ the same	$C_p - C_V = R$ for an ideal gas	
Step B		
$W = -\int p_{op} dV$		12
$p_{op} = 0$		13
W = 0		14
$\Delta \mathbf{U} = \mathbf{C}_{\mathbf{V}} \mathbf{dT} = 0$	dT = 0 in a Joule expansion	15
$\Delta \mathbf{U} = \mathbf{q} + \mathbf{W}$		16
$q = \Delta U = 0$		17
$\Delta \mathbf{H} = \mathbf{C}_{\mathbf{p}} \mathbf{dT} = 0$		18
Step C	•	
$q = C_p(298-373)$		19
$\Delta \mathbf{U} = \mathbf{C}_{V}(298-373)$		20
$\Delta \mathbf{U} = \mathbf{q} + \mathbf{W}$		21
$W = C_V(298-373) - C_p(298-373)$		22
= - R(298 - 373)		23
Another way: W = -∫ p <sub>op</sub> dV		24
reversible pop = $p_{qas}$		
At constant pressure,		
$W = -p_3 \int dV = -p_3 (V_4 - V_3) = -R298 -$		
R373		
the same as - R(298 – 373) found		
from first law		
$\Delta \mathbf{H} = \mathbf{C}_{p} (298 - 373)$		
for the overall process		
$q = C_V(373-298) + 0 + C_p(298-373)$		
$= (C_p - C_V)298 - (C_p - C_V)373$	$C_p$ - $C_V$ = R for an ideal gas	
q = R(298-373) = -0.624  kJ		
Answer		
W = 0+0 - R(298 - 373) = + 0.624 kJ		
Answer		
$\Delta \mathbf{U} = \mathbf{C}_{\mathbf{V}}(373-298) + 0$		
+ C <sub>V</sub> (298-373)		
$\Delta \mathbf{U} = 0 \qquad \qquad \mathbf{Answer}$	Note answers do not require $C_p$ or $C_V$ values.	
$\Delta \mathbf{H} = \mathbf{C}_{p}(373-298) + 0 + \mathbf{C}_{p}(298-373)$		
$\Delta \mathbf{H} = 0$ Answer		

### 5. adiabatic process, ideal gases



Equation	Basis for the equation	Eq. #
q=0	Given adiabatic	1
W = 0	No work done to surroundings	2
$\Delta \mathbf{U} = \mathbf{q} + \mathbf{W} = 0$		3
$d\mathbf{U} = \mathbf{C}_{V}dT + (\partial \mathbf{U}/\partial V)_{T}dV$	$\mathbf{U} = \mathbf{U}(T, V)$ and Definition of $C_V$	4
$(\partial \mathbf{U}/\partial \mathbf{V})_{\mathrm{T}} = 0$	property of an ideal gas	5
$\Delta \mathbf{U} = \mathbf{C}_{V}(\mathbf{T}_{f} - \mathbf{T}_{i})$		6
$\Delta U_{\text{He}} = 0.5 (3/2) R(T_{\text{f}} - 373)$		7
$\Delta U_{02} = (5/2)R(T_f - 273)$		8
$0 = \Delta \mathbf{U}_{\text{He}} + \Delta \mathbf{U}_{\text{O2}}$	From Eq 3	9
$0 = 0.5(3/2)R(T_f - 373)$		
$+ (5/2)R(T_f - 273)$		
$T_{\rm f} = (3/4)373 + (5/2)273$	Solving for T <sub>f</sub>	
(3/4)+(5/2)		
$T_f = 296 \text{ K}$ Answer		

6. 10 L tank, ideal gas vapor, negligible volume of liquid water



Equation	Basis for the equation	Eq. #
q=0	Given insulated, no q to or from surroundings	1
W = 0	vapor formed in evacuated volume	2
Final state: water vapor		
V = 10 L, T = 373, p = 1 atm		
in equilibrium with remaining liquid		
pV = nRT	ideal gas	3
1 atm (10 L)		
= n 0.0820578 L atm mol <sup>-1</sup> K <sup>-1</sup> (373)		
n = 0.3267 mol		4
$\Delta$ <b>H</b> = 9720 cal mol <sup>-1</sup> (0.3267 mol)	given $\Delta_{vap}H$ and using moles from Eq 4	
= 3175 cal Answer		5
$\Delta \mathbf{U} = \mathbf{q} + \mathbf{W} + \mathbf{U}_{vap} - \mathbf{U}_{liq} = \Delta_{vap} \mathbf{U}$	first law	6
$\Delta \mathbf{H} = \Delta \mathbf{U} + (\mathbf{pV})_{vap} - (\mathbf{pV})_{liq}$	$\mathbf{H} = \mathbf{U} + \mathbf{pV}$ definition	7
$\Delta \mathbf{H} = \Delta_{vap} \mathbf{U} + 1 \operatorname{atm}(10 \text{ L}) - (\sim 0)$	neglecting $V_{liq}$ remaining in final state and	8
	neglecting (pV) <sub>liq</sub> at the initial state	
3175 cal = $\Delta_{vap}$ <b>U</b>	substituting value from Eq 5 into Eq 8	
+ 1atm(10 L)(1.9872/.0820578)	converting to cal from L atm	
Δ <sub>vap</sub> <b>U</b> = 3175 - 242.2 = 2933 cal		
Answer		

	<b>7. (a)</b> 10	g ice(263 K)	+ 25 g liq water	(288 K) <b>→ ?</b>	adiabatic process
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Equation	Basis for the equation	Eq. #
$      \begin{array}{l} (i) \ 10 \ g \ ice(263 \ K) \rightarrow 10 \ g \ ice \ (273 \ K) \\ (ii) \ 10 \ g \ ice(273 \ K) \rightarrow 10 \ g \ liq \ (273 \ K) \\ (iiii) \ 10 \ g \ liq(273 \ K) \rightarrow 10 \ g \ liq \ (T_f \ K) \\ (iv) \ 25 \ g \ liq \ (288 \ K) \rightarrow 25 \ g \ liq \ (T_f \ K) \\      \end{array} $	One possibility is that all ice melts and final state is all liq water at $T_f \ge 273$ . Another possibility is that only some of the ice melts and final state is some ice, some liquid water, all at 273 K The largest contribution comes from the q associated with melting of ice, so the second possibility is more likely. Nevertheless, let us try the first possibility and see what we find out.	
$\begin{array}{l} q = 0 = q_i + q_{ii} + q_{iii} + q_{iv} \\ q_i = 10g \bullet 0.5 \ cal \ K^{-1}g^{-1} \bullet (273 \cdot 263) K \\ q_{ii} = 10 \ g \bullet 80 \ cal \ g^{-1} \\ q_{iii} = 10 \ g \bullet 1.0 \ cal \ K^{-1}g^{-1} \bullet (T_f \cdot 273) K \\ q_{iv} = 25 \ g \bullet 1.0 \ cal \ K^{-1}g^{-1} \bullet (T_f \cdot 288) K \\ 0 = 50 + 800 + 10T_f \cdot 2730 + 25T_f \\ - 7200 \end{array}$	q contributions must sum to zero because it is an adiabatic process. q = $\int CdT$ , and C is independent of temperature	
Solving for $T_f$ $T_f = 259.5$ K this answer is <u><b>absurd</b></u> .	because it is lower than the freezing point of water. Therefore it is not possible that all ice melts	

$ \begin{array}{l} (i) \ 10 \ g \ ice(263 \ \text{K}) \rightarrow 10 \ g \ ice(273 \ \text{K}) \\ (ii) \ x \ g \ ice(273 \ \text{K}) \rightarrow x \ g \ liq(273 \ \text{K}) \\ (iiii) \ 25 \ g \ liq(288 \ \text{K}) \rightarrow 25 \ g \ liq(273 \ \text{K}) \\ q = 0 = q_i + q_{ii} + q_{iii} \\ q_i = 10g \bullet 0.5 \ cal \ \text{K}^{-1}g^{-1} \bullet (273 - 263) \text{K} \\ q_{iii} = x \ g \bullet 80 \ cal \ g^{-1} \\ q_{iii} = 25 \ g \bullet 1.0 \ cal \ \text{K}^{-1}g^{-1} \bullet (273 - 288) \text{K} \\ \end{array} $	Assume only some of the ice melts and the final state is some ice some liquid all at 273 K q contributions must sum to zero because it is an adiabatic process	
$\begin{array}{l} 0 = 50 + 80x - 375 \\ x = 4.06 \text{ g of ice melted} \\ \hline \text{Final state is 5.94 g ice 29.06 g liq} \\ \text{water all at 273 K} \\ \end{array}$	solve for x	

**7.** (b) 10 g ice(263 K) + 100 g liq water (288 K)  $\rightarrow$  ? adiabatic process

Equation	Basis for the equation	Eq. #
(i) 10 g ice(263 K) $\rightarrow$ 10 g ice (273 K) (ii) 10 g ice(273 K) $\rightarrow$ 10 g liq (273 K) (iii) 10 g liq(273 K) $\rightarrow$ 10 g liq (T <sub>f</sub> K) (iv) 100 g liq (288 K) $\rightarrow$ 100 g liq (T <sub>f</sub> K) q = 0 =q_i+q_{ii}+q_{iii}+q_{iv} q <sub>i</sub> = 10g•0.5 cal K <sup>-1</sup> g <sup>-1</sup> •(273-263)K q <sub>ii</sub> = 10 g•80 cal g <sup>-1</sup> q <sub>iii</sub> = 10 g•1.0 cal K <sup>-1</sup> g <sup>-1</sup> •(T <sub>f</sub> -273)K	One possibility is that all ice melts and final state is all liq water at $T_f \ge 273$ . Another possibility is that only some of the ice melts and final state is some ice, some liquid water, all at 273 K Let us try the first possibility and see what we find out. Adiabatic process	1 2 3 4 5 6 7 8 9
$\begin{array}{l} q_{iv} = 100 \ g\bullet 1.0 \ cal \ K^{-1}g^{-1}\bullet(T_f\text{-}288)K \\ 0 = 50 + 800 + 10T_f\text{-}2730 \\ & + 100T_f\text{-}28800 \\ \text{Solving for } T_f \\ T_f = \ 278.9 \ K \\ \text{The final state is } 110 \ g \ \text{liquid water at} \\ 278.9 \ K \\ \end{array}$	Substituting each term into Eq 5	10

8.	$C + H_2O(g) \rightarrow CO(g) + H_2(g)$	rxn (1)
	$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$	rxn (2)

Equation	Basis for the equation	Eq.
		#
(a) Final products are equimolar	Assuming only rxn (1) occurs	1
$CO(g) + H_2(g)$		
Combustion at 298 K, 1 atm:	Given	
$CO(g) + H_2(g) + O2 \rightarrow CO_2(g) + H_2O(g)$	Assuming all combustion products are vapor	2
$\Delta_{rxn}\mathbf{H} = \Delta_{form}\mathbf{H}[CO_2(g)] + \Delta_{form}\mathbf{H}[H_2O(g)]$	By definition, $\Delta_{form} \mathbf{H}[\mathbf{H}_2(g)] = 0$	3
- ∆ <sub>form</sub> H[CO(g)]	$\Delta_{form} \mathbf{H}[O_2(g)] = 0$	

$\Delta_{rxn}$ <b>H</b> = -393.51 -241.82 –(-110.53)	Look up $\Delta_{form}$ <b>H</b> for CO <sub>2</sub> (g) , H <sub>2</sub> O(g) and CO(g) in	4
= -524.8 kJ mol <sup>-1</sup>	textbook at 1 atm, 298 K in kJ mol <sup>-1</sup>	
For 1 L of water gas	Assume ideal behavior	5
pV = nRT	Ideal gas law	6
n =1 atm•1 L		
$/(0.0820578L \text{ atm mol}^{-1} \text{ K}^{-1} \bullet 298)$		
n = 0.0409 mol = 0.02045 mol CO	Solve for total number of moles in 1 L of gas	7
+ 0.02045 mol H <sub>2</sub>		-
$\Delta_{\text{comb}}$ <b>H</b> of 1 L of water gas		8
$= 0.02045 \text{ mol} \cdot (-524.8 \text{ kJ mol}^{-1})$	for this number of moles	
= -10.73 kJ <b>Answer</b>		
(b) Final products of water gas	95% of C appears as CO from rxn (1) and and 5%	
reaction are	as CO <sub>2</sub> from rxn (2)	
$0.95 \text{ CO}(g) + 0.05 \text{ CO}_2(g) + 1.05 \text{ H}_2(g)$		9
For 1 L of water gas, $n = 0.0409$ mol	but now consists of	
as before,	(0.95/2.05)(0.0409) mol CO	10
$= 0.01895 \text{ mol CO} + 0.0010 \text{ mol CO}_2$	+ $(0.05/2.05)(0.0409)$ mol CO <sub>2</sub>	10
+ 0.02095 mol H <sub>2</sub>	+ (1.05/2.05)(0.0409) mol H <sub>2</sub>	
20(x) + 1(0) = 00(x)	Do $\Delta_{rxn}$ <b>H</b> separately because no longer 1:1 in CO	
$CO(g) + \frac{1}{2}O_2 \rightarrow CO_2(g)$	and H <sub>2</sub>	11
$\Delta_{\rm rxn} \mathbf{H} = \Delta_{\rm form} \mathbf{H} [\rm CO_2(g)] - \Delta_{\rm form} \mathbf{H} [\rm CO(g)]$	Using $\Delta_{form}$ <b>H</b> for CO <sub>2</sub> (g) and CO(g)	11
= -393.51–(-110.53) = -282.98 kJ mol <sup>-1</sup>		
$H_2(g) + (1/2)O_2 \rightarrow H_2O(g)$	$H_{\text{sing}} \wedge H_{\text{for}} + O(a)$	12
$\Delta_{rxn}\mathbf{H} = \Delta_{form}\mathbf{H}[\mathbf{H}_2\mathbf{O}(\mathbf{g})]$ = -241.82 kJ mol <sup>-1</sup>	Using $\Delta_{form}$ <b>H</b> for H <sub>2</sub> O(g)	12
$\Delta_{\text{comb}}$ <b>H</b> of 1 L of water gas	Using the number of moles found in Eq 10	
$= 0.01895 \text{ mol} \cdot -282.98 \text{ kJ mol}^{-1}$		
+ 0.02095 mol • -241.82 kJ mol <sup>-1</sup>	Enthalpy of combustion of 1 L of water gas	
= -10.42 kJ <b>Answer</b>		

<b>9.</b> $C + \frac{1}{2}O_2(g) \rightarrow CO(g)$	rxn (1)	
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	rxn (2)	
Equation	Basis for the equation	Eq.
		#
Final products are 0.95 mol CO + 0.05	95% of $O_2$ appears in CO from rxn (1) and and	
mol $CO_2$ for every 0.5 mol $O_2$ used up,	5% in CO <sub>2</sub> from rxn (2)	
which is accompanied by 2.0 mol $N_2$ in		
the dry air used to produce the gas		
consider 1 L producer gas at 1 atm		
pV = nRT	Ideal gas law	1
n =1 atm●1 L		
$/(0.0820578L \text{ atm mol}^{-1} \text{ K}^{-1} \bullet 298)$		
n = 0.0409 mol		2
$= (0.95/3.0)(0.0409) \mod CO + .$		3

(0.05/3.0)(0.0409 mol CO <sub>2</sub> + (2.0/3.0)(0.0409) mol N <sub>2</sub>	Of the components only CO can contribute to	
or 0.01295 mol CO	heating value	
Combustion of CO in air		
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	By definition, $\Delta_{form} \mathbf{H}[O_2(g)] = 0$	4
$\Delta_{rxn}\mathbf{H} = \Delta_{form}\mathbf{H}[CO_2(g)] - \Delta_{form}\mathbf{H}[CO(g)]$	using $\Delta_{form}$ <b>H</b> for CO <sub>2</sub> (g) and CO(g) in textbook at 1 atm, 298 K in kJ mol <sup>-1</sup>	5
= -393.51-(-110.53)	atm, 298 K in kJ mol <sup>-1</sup>	6
= -282.98 kJ mol <sup>-1</sup>		
$\Delta_{comb}H$	For 1 L producer gas containing 0.01295 mol CO	7
= 0.01295 mol ● -282.98 kJ mol <sup>-1</sup>		
= 3.66 kJ per L of producer gas		
Answer		

# **10. (a)** $CH_4(g) + 2O_2(g)/air \text{ at } 293 \text{ K} \rightarrow CO_2(g) + 2H_2O(g) \text{ at } 373 \text{ K}$

Equation	Basis for the equation	Eq. #
1 mol CH <sub>4</sub> 4 mol O <sub>2</sub> 16 mol N <sub>2</sub>	given Twice the minimum amount of air is used for combustion	
At 293 K $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(I)$ $\Delta_{comb}\mathbf{H} = -212.91 \text{ kcal mol}^{-1}$	Definition of $\Delta_{comb}$ <b>H</b> is that products of combustion are CO <sub>2</sub> (g) and H <sub>2</sub> O(I) Given	1 2
$\begin{array}{c} \text{CO}_2(g) \ 293 \ \text{K} \to \text{CO}_2(g) \ 373 \ \text{K} \qquad (1) \\ 2\text{H2O} \ (l) \ 293 \ \text{K} \to 2\text{H2O} \ (l) \ 373 \ \text{K} \qquad (2) \\ 2\text{H2O} \ (l) \ 373 \ \text{K} \to 2\text{H2O} \ (g) \ 373 \ \text{K} \qquad (3) \\ 16\text{N}_2(g) \ 293 \ \text{K} \to 2\text{H2O} \ (g) \ 373 \ \text{K} \qquad (3) \\ \underline{2\text{O}_2(g) \ 293 \ \text{K} \to 2\text{O}_2(g) \ 373 \ \text{K} \qquad (4) \\ \underline{2\text{O}_2(g) \ 293 \ \text{K} \to 2\text{O}_2(g) \ 373 \ \text{K} \qquad (5) \\ \text{CH}_4(g) \ + \ 4\text{O}_2(g) \ +16\text{N2}(g) \ \text{at} \ 293 \ \text{K} \\ \to \text{CO}_2(g) \ +2\text{H}_2\text{O}(g) \ +2\text{O}_2 \ +16\text{N}_2 \\ & \text{at} \ 373 \ \text{K} \end{array}$	The CO2 product has to be heated to 373 K the liquid water has to be heated to 373 K and vaporized The $N_2$ and the unused $O_2$ have to be heated to 373 K Adding up the changes	3 4 5 6 7 8
$\Delta \mathbf{H} = \Delta_{\text{comb}} \mathbf{H} + \Delta \mathbf{H}(1) + \Delta \mathbf{H}(2) + \Delta \mathbf{H}(3) + \Delta \mathbf{H}(4) + \Delta \mathbf{H}(5) \Delta \mathbf{H}(1) = 1 \cdot 8.87 \text{ cal mol}^{-1} \text{ K}^{-1} (373-293) \Delta \mathbf{H}(2) = 2 \cdot 18 \text{ cal mol}^{-1} \text{ K}^{-1} (373-293) \Delta \mathbf{H}(3) = 2 \cdot 9720 \text{ cal mol}^{-1} \\\Delta \mathbf{H}(4) = 16 \cdot 6.96 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot (373-293) \Delta \mathbf{H}(5) = 2 \cdot 7.02 \text{ cal mol}^{-1} \text{ K}^{-1} (373-293) \Box \mathbf{H}(5) = 2 \cdot 7.02 \text{ cal mol}^{-1} \text{ K}^{-1} (373-293) \Box \mathbf{H}(5) = 2 \cdot 7.02 \text{ cal mol}^{-1} \text{ K}^{-1} (373-293) $	Using d <b>H</b> = C <sub>p</sub> dT at dp =0 Using $\Delta_{vap}$ <b>H</b> =9720 cal mol <sup>-1</sup> for water	9 10 11 12 13 14
$\Delta \mathbf{H} = -212.91 \times 10^{3} + 709.6 + 2880$ +19440 + 8909 + 1123 = -179848 cal <b>Answer</b>	Summing up terms in Eq 9 from Eq 10-14 heat liberated for 1 mol of CH <sub>4</sub> gas burned	

Equation	Basis for the equation	Eq. #
1 mol CH <sub>4</sub> 4 mol O <sub>2</sub> 16 mol N <sub>2</sub>	given Twice the minimum amount of air is used for combustion	
final state of stack gases: T such that saturated with water vapor but no condensation Composition of stack gases: $2 \mod O_2 + 16 \mod N_2 + 1 \mod CO_2$ $+ 2 \mod H_2O = 21 \mod X_{H2O} = 2/21 = 0.095$ 0.095 atm is the partial pressure of water at 1 atm total pressure	given find the mole fraction of water in the stack gases	2
or 72 mm Hg	using plot of vapor pressure of water, 72 mm Hg corresponds to 40°C or 313 K	3
same steps Eq 3-8 as in 10.(a) have to be added up except T is 313 not 373	Everything is the same as in <b>10.</b> (a) except that the temperature of the stack gases is 313 K instead of 373 K and we need to get $H_2O(g)$ from 373 K back down to 313 K	
$\Delta \mathbf{H} = \Delta_{\text{comb}} \mathbf{H} + \Delta \mathbf{H}(1) + \Delta \mathbf{H}(2) + \Delta \mathbf{H}(3) + \Delta \mathbf{H}(2a) + \Delta \mathbf{H}(4) + \Delta \mathbf{H}(5) \Delta \mathbf{H}(1) = 1 \bullet 8.87 \text{ cal mol}^{-1} \text{ K}^{-1} (313-293) \Delta \mathbf{H}(2) = 2 \bullet 18 \text{ cal mol}^{-1} \text{ K}^{-1} (373-293) \Delta \mathbf{H}(3) = 2 \bullet 9720 \text{ cal mol}^{-1} \Delta \mathbf{H}(2a) = 2 \bullet 8.03 \text{ cal mol}^{-1} \text{ K}^{-1} (313-373) \Delta \mathbf{H}(4) = 16 \bullet 6.96 \text{ cal mol}^{-1} \text{ K}^{-1} • (313-293) \Delta \mathbf{H}(5) = 2 \bullet 7.02 \text{ cal mol}^{-1} \text{ K}^{-1} (313-293)$	Using d <b>H</b> = C <sub>p</sub> dT at dp =0 Using $\Delta_{vap}$ <b>H</b> =9720 cal mol <sup>-1</sup> for water at 373 K	4 5 6 7 8 9 10
$\Delta \mathbf{H} = -212.91 \times 10^{3} + 177 + 2880$ +19440 -321 +2227 + 280 = -188227 cal <b>Answer</b>	Summing up Eq 5-10 into Eq 4 heat liberated for 1 mol of CH <sub>4</sub> gas burned to stack gases at 313 K where water in saturated vapor just fails to condense	