Solutions to Problem Set 6

1. non- ideal gas, 1 mol 20.0 L 300 K → 40.0 L 300 K isothermal, reversible

Equation of state: $p = RT[\bar{V}^{-1} + BV^{-2}]$

Equation	Basis for the equation	Eq. #
(a)B is a constant independent of T	Given	
$d\mathbf{U} = (\partial \mathbf{U}/\partial T)_V dT + (\partial \mathbf{U}/\partial V)_T dV$	$\mathbf{U} = \mathbf{U}(T,V)$	1
$dT = 0$	Given, isothermal	2
$d\mathbf{U} = (\partial \mathbf{U}/\partial V)_T dV$		3
$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$	Derived from first and second law of thermodynamics and using cross derivatives (see lecture notes Part 4)	4
$(\partial p/\partial T)_V = \partial\{RT[V^{-1} + BV^{-2}]\}$ $= R[V^{-1} + BV^{-2}]$ $(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$ $= T R[V^{-1} + BV^{-2}] - RT[V^{-1} + BV^{-2}]$ $= 0$	Apply to this equation of state, where B (has units of volume) is indep of T	5
$\Delta\mathbf{U} = 0$ **Answer**	From Eq 1, 2 and 5	6
$d\mathbf{H} = (\partial \mathbf{H}/\partial T)_p dT + (\partial \mathbf{H}/\partial p)_T dp$	$\mathbf{H} = \mathbf{H}(T,p)$	
We could do this: $(\partial \mathbf{H}/\partial p)_T = - T(\partial V/\partial T)_p + V$ But equation of state is too complex to derive$(\partial V/\partial T)_p$. Use another route to get $\Delta\mathbf{H}$	Derived from first and second law of thermodynamics and using cross derivatives (see lecture notes Part 4)	
$\mathbf{H} = \mathbf{U} + pV$ $\Delta\mathbf{H} = \Delta\mathbf{U} + p_fV_f - p_iV_i$	Definition	7
$p = RT/V + BRT/V^2$ $p_i = (0.0820578)(300)[(1/20.0) + (B/20.0^2)]$ $p_f = (0.0820578)(300)[(1/40.0) + (B/40.0^2)]$ $\Delta(pV) = (0.0820578)(300)B(-0.025)$	Substituting known values	8
$\Delta\mathbf{H} = 0+(0.0820578)(300)B\bullet(-0.025)$ $= (8.31451 J\ mol^{-1}K^{-1})(300)B \bullet (-0.025)$ **Answer**		9
$\Delta\mathbf{U} = q + W$	First law of thermodynamics	10
$q_{REV = -}W_{REV}$	From Eq 6 and 10	11

$W = -\int p_{op}dV$	Definition	12
$p_{op} = p_{gas}$	reversible	13
$W_{REV} = -\int [RT/V + BRT/V^2]dV$ $= -RT\ln(V_f/V_i) + 2BRT[(1/V_f)-(1/V_i)]$	Using equation of state for this gas and integrating	14
$W_{REV} = -RT[\ln(2) + 2B(-0.025)]$ $= -(8.31451 J\ mol^{-1}K^{-1})(300)\bullet$ $[\ln(2) - 0.050B]$ $= -q_{REV}$	Substituting	15
$d\mathbf{S} = \delta q_{REV}/T$ $\Delta\mathbf{S} = q_{REV}/T$	Second Law of thermodynamics reversible isothermal	16 17
$\Delta\mathbf{S} = +(8.31451 J\ mol^{-1}K^{-1})\bullet$ $[\ln(2) - 0.050B]$ **Answer**	From Eq 15 and 17	18
$\mathbf{A} = \mathbf{U} - T\mathbf{S}$	Definition	19
$\Delta\mathbf{A} = \Delta\mathbf{U} - T\Delta\mathbf{S}$	For constant T (this problem)	20
$\Delta\mathbf{A} = 0 - 300\bullet(8.31451 J\ mol^{-1}K^{-1})\bullet$ $[\ln(2) - 0.050B]$ **Answer**	From Eq 6, 18 and 20	21
$\mathbf{G} = \mathbf{H} - T\mathbf{S}$	Definition	21
$\Delta\mathbf{G} = \Delta\mathbf{H} - T\Delta\mathbf{S}$	For constant T (this problem)	22
$\Delta\mathbf{G} = 300\bullet(8.31451 J\ mol^{-1}K^{-1})\bullet$ $[-0.025B - \ln(2) + 0.050B]$ $= 300\bullet(8.31451 J\ mol^{-1}K^{-1})\bullet$ $[0.025B - \ln(2)]$ **Answer**	From Eq 9, 18 and 22	23
(b) B is dependent on T $B = a + bT + cT^2$	Given	24
$(\partial p/\partial T)_V = \partial\{RT[V^{-1} + BV^{-2}]\}$ $= R[V^{-1} + BV^{-2}] + RV^{-2}(dB/dT)$ $(\partial\mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$ $= RT[V^{-1} + BV^{-2}] - RT[V^{-1} + BV^{-2}]$ $+RTV^{-2}(dB/dT)$ $(\partial\mathbf{U}/\partial V)_T = RTV^{-2}(dB/dT)$	Just as in deriving Eq 5 but with the additional term in (dB/dT) Where $dB/dT = b + 2cT$	25
$\Delta\mathbf{U} = \int(\partial\mathbf{U}/\partial V)_T dV$ $= RT(dB/dT)\int V^{-2}dV$ $= RT(dB/dT)[(1/V_f) - (1/V_i)]$ $= (8.31451 J\ mol^{-1}K^{-1})(300)\bullet$ $(b + 600c)\bullet[-0.025]$ **Answer**	From Eq 3 and 25 Note that $\Delta\mathbf{U} \neq 0$ when B is dependent on T	26
$p = RT/V + BRT/V^2$ $p_i = (0.0820578)(300)[(1/20.0) + (B/20.0^2)]$ $p_f = (0.0820578)(300)[(1/40.0) + (B/40.0^2)]$ $\Delta(pV) = (0.0820578)(300)B(-0.025)$	The equation for $\Delta(pV)$ is the same as when B is independent of T	27

$\Delta\mathbf{H} = (8.31451\text{J mol}^{-1}\text{K}^{-1})(300)\bullet$ $(b + 600c)\bullet(-0.025)$ $+ (8.31451\text{J mol}^{-1}\text{K}^{-1})(300)B$ $\bullet (-0.025)$ $= - (8.31451\text{J mol}^{-1}\text{K}^{-1})(300)\bullet$ $0.025\bullet[a+bT+cT^2 + b + 600c]$ **Answer**	The same as in part (a) except that $\Delta\mathbf{U}$ from Eq 26 and $B = a + bT + cT^2$ are inserted.	28
$\Delta\mathbf{S} = + (8.31451\text{J mol}^{-1}\text{K}^{-1})\bullet$ $[\ln(2) - 0.050B]$ **Answer**	The equation is derived the same as in part (a) except that $B = a + bT + cT^2$ is inserted	29
$\Delta\mathbf{A} = \Delta\mathbf{U} - T\Delta\mathbf{S}$ $\Delta\mathbf{A} = (8.31451\text{J mol}^{-1}\text{K}^{-1})(300)\bullet$ $(b + 600c)\bullet(- 0.025)$ $- 300\bullet (8.31451\text{J mol}^{-1}\text{K}^{-1})\bullet$ $[\ln(2) - 0.050B]$ **Answer**	The same as in part (a) except that $\Delta\mathbf{U}$ from Eq 26 and $B = a + bT + cT^2$ are inserted.	30
$\Delta\mathbf{G} = \Delta\mathbf{H} - T\Delta\mathbf{S}$ $\Delta\mathbf{G} = - (8.31451\text{J mol}^{-1}\text{K}^{-1})(300)\bullet$ $0.025\bullet[a+bT+cT^2 + b + 600c]$ $- 300\bullet (8.31451\text{J mol}^{-1}\text{K}^{-1})\bullet$ $[\ln(2) - 0.050B]$ $\Delta\mathbf{G} = + (8.31451\text{J mol}^{-1}\text{K}^{-1})(300)\bullet$ $[0.025\bullet(a+bT+cT^2)$ $- 0.025(b + 600c) - \ln(2)]$ **Answer**	$\Delta\mathbf{H}$ from Eq 28 and $B = a + bT + cT^2$ are inserted.	31
(c) B is a constant independent of temperature and the process is carried out *irreversibly*		
$\Delta\mathbf{U} = 0$ **Answer** $\Delta\mathbf{H} =$ $- (8.31451\text{J mol}^{-1}\text{K}^{-1})(300)(0.025)B$ **Answer** $\Delta\mathbf{S} = + (8.31451\text{J mol}^{-1}\text{K}^{-1})\bullet$ $[\ln(2) - 0.050B]$ **Answer** $\Delta\mathbf{A} = - 300\bullet (8.31451\text{J mol}^{-1}\text{K}^{-1})\bullet$ $[\ln(2) - 0.050B]$ **Answer** $\Delta\mathbf{G} = 300\bullet (8.31451\text{J mol}^{-1}\text{K}^{-1})\bullet$ $[0.025B - \ln(2)]$ **Answer** But q_{IRREV} and W_{IRREV} are not the same as in part (a). $q_{\text{IRREV}} + W_{\text{IRREV}} = 0$ $q_{\text{IRREV}} < T\Delta\mathbf{S}$ $\mathbf{W}_{\text{IRREV}} > W_{\text{REV}}$ $\mathbf{W}_{\text{IRREV}} > -T\Delta\mathbf{S}$	All are exactly the same as in part (a) because these are **state functions** and **do not depend on the path** (reversible or otherwise). What do we know about the non-state functions? Because $\Delta\mathbf{U} = 0$ here because of Clausius inequality: $T\Delta\mathbf{S} > q_{\mathbf{IRREV}}$ Algebraic relation! Remember W is a signed quantity. Negative value means work is done by system <u>on</u> the surroundings. Less work than maximum work appears in the surroundings for irreversible process	

2. non- ideal gas, 2 mol 10 atm 600 K → 5 atm 300 K *irreversible*

Equation of state: $pV = nRT + nBp$ $B = 0.035$ L mol^{-1}

$C_p = 52.675 + 1.561\times10^{-2}T$ J mol^{-1} K^{-1}

Equation	Basis for the equation	Eq. #
$d\mathbf{U} = (\partial\mathbf{U}/\partial T)_V dT + (\partial\mathbf{U}/\partial V)_T dV$	$\mathbf{U} = \mathbf{U}(T,V)$	1
$(\partial\mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$	Derived from first and second law of thermodynamics and using cross derivatives (see lecture notes Part 4)	2
$p = nRT/(V-nB)$	Given equation of state	3
$(\partial p/\partial T)_V = nR/(V-nB)$ $(\partial\mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$ $= nRT/(V-nB) - nRT/(V-nB)$ $= 0$	Apply to this equation of state, where B (has units of volume) is independent of T	4
$d\mathbf{U} = C_V dT + 0$	From Eq 1 and 4	5
$C_p - C_V = [p + (\partial U/\partial V)_T]\,(\partial V/\partial T)_p$	General relation derived from $\mathbf{U} = \mathbf{U}(T,V)$ and the first law of thermodynamics (see lecture notes Part 2)	6
$V-nB = nRT/p$ $(\partial V/\partial T)_p = nR/p$	Rearrange equation of state and differentiate	7
$C_p-C_V = [p +0](nR/p) = nR$	From Eq 6, 7 and 4	8
$C_V = C_p - nR = n[52.675 + 1.561\times10^{-2}T - 8.31451]$ J mol^{-1}K^{-1} $C_V = 2\ \text{mol}\bullet(44.361 + 1.561\times10^{-2}T)$ J mol^{-1}K^{-1}	From Eq 8 and given C_p	9
$\Delta\mathbf{U} = 2\ \text{mol}\bullet \int(44.361 + 1.561\times10^{-2}T)dT$	Integrating Eq 5 and using given C_V	10
$\Delta\mathbf{U} = 2\{44.361(T_2-T_1) + (1/2)1.561\times10^{-2}(T_2^2-T_1^2)\}$ $= 2\{(44.361(300 - 600) + (1/2)1.561\times10^{-2}(300^2-600^2)\}$ $= 2\{-13308.3 -2107.3\}$ $= - 30830$ J **Answer**	Integrating Eq 5 and using given C_V	11
$d\mathbf{H} = (\partial\mathbf{H}/\partial T)_p dT + (\partial\mathbf{H}/\partial p)_T dp$	$\mathbf{H} = \mathbf{H}(T,p)$	12
$(\partial\mathbf{H}/\partial p)_T = - T(\partial V/\partial T)_p + V$	Derived from first and second law of thermodynamics and using cross derivatives (see lecture notes Part 4)	13
$(\partial V/\partial T)_p = nR/p$ and $V = nRT/p +nB$ $(\partial\mathbf{H}/\partial p)_T = nB$	From Eq 7 and Equation of state substituted into Eq 13	14
$d\mathbf{H} = C_p dT + nB\,dp$ $\Delta\mathbf{H} = \int n(52.675 + 1.561\times10^{-2}T)dT + \int nB dp$	From Eq 12 and 14	15

$\Delta\mathbf{H} = 2\{52.675(T_2-T_1)$ $+ (1/2)1.561\times10^{-2}(T_2^2-T_1^2)\}$ $+2\bullet 0.035\ \mathrm{L\ mol^{-1}}\ [p_2-p_1]$ $= 2\{(52.675(300 - 600)$ $+ (1/2)1.561\times10^{-2}(300^2-600^2)\}$ $+2\bullet 0.035[5-10]$ $\bullet 8.31451/0.0820578$ $= 2\{-15802.5 -2107.3 - 17.7 \}$ $= - 35850$ J **Answer**	Integrating and substituting known values We would have obtained the same answer by using H = U+pV $\Delta\mathbf{H} = \Delta\mathbf{U} + \Delta(pV)$ It happens that dV=0 here	8
$d\mathbf{S} = (\partial\mathbf{S}/\partial T)_p dT + (\partial\mathbf{S}/\partial p)_T dp$	$\mathbf{S} = \mathbf{S}(T,p)$	12
$(\partial\boldsymbol{S}/\partial p)_T = -(\partial V/\partial T)_p$	Derived (see lecture notes Part 4) starting from $d\boldsymbol{U} = \text{đ}q_{rev} - p dV = T d\boldsymbol{S} - p dV$ and use of cross derivatives	13
$d\mathbf{S} = (C_p/T)dT - nRdp/p$	Using Eq 7 and 2 into Eq 12	14
$\Delta S = \int n(52.675/T + 1.561\times10^{-2})dT$ $- nR\int dp/p$	Using Eq 7 and 2 into Eq 12	15
$\Delta\mathbf{S} = 2\{$ $52.675\ln(T_2/T_1)+1.561\times10^{-2} (T_2-T_1)$ $- 8.31451\ln(p_2/p_1)\}$ $\Delta\mathbf{S} = 2\{ 52.675\ln(300/600)$ $+1.561\times10^{-2} (300-600)$ $- 8.31451\ln(5/10) \}$ $\Delta\mathbf{S} = - 52.12\ \mathrm{J\ K^{-1}}$ **Answer**	Integrating and substituting given values We would have obtained the same answer by using $d\mathbf{S} = (\partial\mathbf{S}/\partial T)_V dT + (\partial\mathbf{S}/\partial V)_T dV$ $(\partial\mathbf{S}/\partial V)_T = (\partial p/\partial T)_V$ but it happens that dV=0 here, so $\Delta\mathbf{S} = \int C_V dT/T$ = same answer	16
$\mathbf{A} = \mathbf{U} - T\mathbf{S}$ $\Delta\mathbf{A} = \Delta\mathbf{U} - \Delta(T\mathbf{S})$ $\mathbf{S}_{abs,f} = \mathbf{S}_{abs,i} + \Delta\mathbf{S}$ $\Delta(T\mathbf{S}) = 300\mathbf{S}_{abs,i} - 600[\mathbf{S}_{abs,i} + \Delta\mathbf{S}]$ $\Delta\mathbf{A} = - 30830$ J $- 300\mathbf{S}_{abs,i} - 600[\mathbf{S}_{abs,i} - 52.12]$	Definition We already have $\Delta\mathbf{U}$. Since dT is not zero for this problem, it requires that we know absolute entropy. We have to have either the absolute entropy for the gas at the initial state or at the final state in order to calculate $\Delta\mathbf{A}$. If we are given data to calculate $\mathbf{S}_{abs,i}$, then we can do it.	
$\mathbf{G} = \mathbf{H} - T\mathbf{S}$ $\Delta\mathbf{G} = \Delta\mathbf{H} - \Delta(T\mathbf{S})$ $\mathbf{S}_{abs,f} = \mathbf{S}_{abs,i} + \Delta\mathbf{S}$ $\Delta(T\mathbf{S}) = 300\mathbf{S}_{abs,i} - 600[\mathbf{S}_{abs,i} + \Delta\mathbf{S}]$ $\Delta\mathbf{G} = - 35850$ J $- 300\mathbf{S}_{abs,i} - 600[\mathbf{S}_{abs,i} - 52.12]$	Definition We already have $\Delta\mathbf{H}$. As from above argument, we have to use the absolute entropy for the gas at the initial state and at the final state in order to calculate $\Delta\mathbf{G}$	

3. non- ideal gas, 2 mol p_i =1 atm T_i =300 K → p_f =11 atm T_f =300 K
$V_i = a + RT_i/p_i$ $V_f = a + RT_f/p_f$
Equation of state: $pV = RT + ap$ $a = a(T)$

Equation	Basis for the equation	Eq. #
$d\mathbf{U} = (\partial \mathbf{U}/\partial T)_V dT + (\partial \mathbf{U}/\partial V)_T dV$	$\mathbf{U} = \mathbf{U}(T,V)$	1
$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$	Derived from first and second law of thermodynamics and using cross derivatives (see lecture notes Part 4)	2
$pV = RT + ap$ $p = RT/(V-a),\ a=a(T)$	Given equation of state	3
$(\partial p/\partial T)_V$ $= R/(V-a) + RT(da/dT)/(V-a)^2$ $(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$ $= p + RT^2(da/dT)/(V-a)^2 - p$ $(\partial \mathbf{U}/\partial V)_T = RT^2(da/dT)/(V-a)^2$ **Q.E.D.**	Apply to this equation of state Using Eq 2	4 5
$d\mathbf{H} = (\partial \mathbf{H}/\partial T)_p dT + (\partial \mathbf{H}/\partial p)_T dp$	$\mathbf{H} = \mathbf{H}(T,p)$	6
$(\partial \mathbf{H}/\partial p)_T = - T(\partial V/\partial T)_p + V$	Derived from first and second law of thermodynamics and using cross derivatives (see lecture notes Part 4)	7
$V = RT/p + a$ $(\partial V/\partial T)_p = R/p + da/dT$	From Equation of state (Eq 3)	8
$(\partial \mathbf{H}/\partial p)_T = - T(\partial V/\partial T)_p + V$ $= -RT/p - T(da/dT) + RT/p + a$ $(\partial \mathbf{H}/\partial p)_T = a - T(da/dT)$ **Q.E.D.**	Substituting Eq 8 into Eq 7	9
$a = 0.02 + 0.005\times10^{-2}(T-300)$ L mol^{-1} $(da/dT) = 0.005\times10^{-2}$ L mol^{-1}K^{-1}	We will need da/dT in Eq 5 and Eq 9 The given 3 values of a(T) changes linearly with T by 0.005 per 100 K increment	10
$d\mathbf{U} = (\partial \mathbf{U}/\partial T)_V dT + (\partial \mathbf{U}/\partial V)_T dV$	$\mathbf{U} = \mathbf{U}(T,V)$	1
$d\mathbf{U} = C_V dT + RT^2(da/dT)/(V-a)^2 dV$ In this problem $dT = 0$	Substituting Eq 5 into Eq 1	11
$\Delta\mathbf{U} = 2\ \text{mol}\bullet$ $RT^2(da/dT) \int (V-a)^{-2}\, dV$ $= 2\ \text{mol}\bullet RT^2(da/dT) \bullet (-1)(V-a)^{-1}\|_i^f$ $= -2\ \text{mol}\bullet RT^2(da/dT) \bullet p/RT\ \|_i^f$ $= -2\ \text{mol}\bullet T(da/dT) \bullet [p_f - p_i]$ $\Delta\mathbf{U} = -2\ \text{mol}\bullet (300\ K)(0.005\times10^{-2}\ L\ mol^{-1}K^{-1}) \bullet [11 - 1]\ atm$ $\Delta\mathbf{U} = -0.30$ L atm or -30.4 J **Answer**	Integrating Eq 11 Using equation of state to express $(V-a)^{-1}$ substituting values Using conversion factor 8.31451 J / 0.0820578 L atm	12 13 14
$d\mathbf{H} = (\partial \mathbf{H}/\partial T)_p dT + (\partial \mathbf{H}/\partial p)_T dp$	$\mathbf{H} = \mathbf{H}(T,p)$	6
$d\mathbf{H} = 0 + \{a - T(da/dT)\}dp$	Using $dT = 0$ and Eq 9 into Eq 6	15

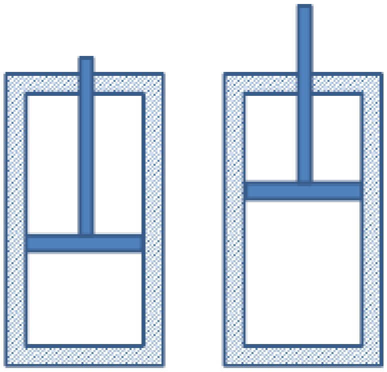
$\Delta\mathbf{H} = 2\ \text{mol}\bullet$ $\{0.02\ \text{L mol}^{-1} - (300\ \text{K})(0.005\times10^{-2}\ \text{L mol}^{-1}\text{K}^{-1})\} \bullet [p_f - p_i]$ $\Delta\mathbf{H} = 2\ \text{mol}\bullet 0.005\ \text{L mol}^{-1} \bullet [11 - 1]\ \text{atm}$ $\Delta\mathbf{H} = +0.10\ \text{L atm}$ or $+10.1\ \text{J}$ **Answer**	Integrating Eq 15 Substituting values	16
$W = -\int p_{op}dV$ $W_{max} = -\int p_{gas}dV$ $= -2\ \text{mol} \int RT\ (V-a)^{-1}dV$ $= -2\ \text{mol RT ln } [(V_f - a)/(V_i - a)]$ $= -2\ \text{mol RT ln } (p_i/(p_f)$ $W_{max} = -2\ \text{mol}\bullet$ $(8.31451\ \text{J mol}^{-1}\ \text{K}^{-1})(300\text{K})\ln(1/11)$ $W_{max} = +11963\ \text{J}$ **Answer**	Maximum work is obtained by carrying out the process reversibly, in which case $p_{op} = p_{gas}$ Integrating Using the equation of state Substituting values	17 18
$d\mathbf{G} = Vdp - \mathbf{S}dT$	one of the fundamental equations of thermodynamics (Lecture notes Part 5)	19
dT = 0 for this process $\Delta\mathbf{G} = \int Vdp = 2\ \text{mol}\bullet \int (RT/p + a)dp$ $\Delta\mathbf{G} = 2\ \text{mol}\bullet\{ RT\ln(p_f/pi) + a[p_f - pi] \}$ $= 2\ \text{mol}\bullet$ $\{(8.31451\ \text{J mol}^{-1}\text{K}^{-1})(300\text{K}) \bullet \ln(11/1) + 0.02\ \text{L mol}^{-1}[11-1]\ \text{atm} \bullet 8.31451\text{J}/0.0820578\ \text{L atm}\}$ $\Delta\mathbf{G} = +11963\ \text{J} + 20.26\ \text{J}$ $\Delta\mathbf{G} = +11983\ \text{J}$ **Answer**	Using the equation of state Integrating	
$d\mathbf{A} = -pdV - \mathbf{S}dT$	one of the fundamental equations of thermodynamics (Lecture notes Part 5)	
dT = 0 for this process $\Delta\mathbf{A} = -\int pdV = -\int RTdV/(V-a)$ $= -2\ \text{mol RT ln } [(V_f - a)/(V_i - a)]$ $= -2\ \text{mol RT ln } (p_i/(p_f)$ $\Delta\mathbf{A} = -2\ \text{mol}\bullet$ $(8.31451\ \text{J mol}^{-1}\ \text{K}^{-1})(300\text{K})\ln(1/11)$ $\Delta\mathbf{A} = +11963\ \text{J}$ **Answer**	Integrating Using the equation of state Substituting the values Note that $\Delta\mathbf{A} = W_{max}$, as it should be	

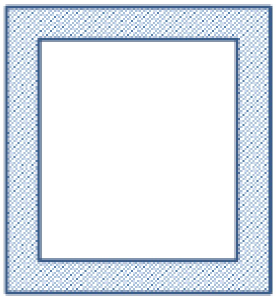
4. 0.5 mol $CH_4(g)$ at 298 K is burned in excess O_2 under adiabatic conditions. $\mathbf{T_{final} = ?}$

The reaction at 298 K $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Standard enthalpy of combustion at 298 K $= \Delta_{comb}\mathbf{H}_{298}^{\ominus}$

$= 2\Delta_{form}\mathbf{H}_{298}^{\ominus}(H_2O(l)) + \Delta_{form}\mathbf{H}_{298}^{\ominus}(CO_2(g)) - \Delta_{form}\mathbf{H}_{298}^{\ominus}(CH_4(g)) - 2\Delta_{form}\mathbf{H}_{298}^{\ominus}(O_2(g))$

Equation	Basis for the equation	Eq. #
$\Delta_{comb}\mathbf{H}_{298}^{\ominus} = 2\Delta_{form}\mathbf{H}_{298}^{\ominus}(H_2O(l))$ $+\Delta_{form}\mathbf{H}_{298}^{\ominus}(CO_2(g))$ $-\Delta_{form}\mathbf{H}_{298}^{\ominus}(CH_4(g))$ $= 2(-285.83)+(-393.51)-(-74.81)$ kJ mol^{-1} $\Delta_{comb}\mathbf{H}_{298}^{\ominus} = -890.36$ kJ mol^{-1}	$\Delta_{form}\mathbf{H}_{298}^{\ominus}$ for the elements in their standard state is defined as zero Using $\Delta_{form}\mathbf{H}_{298}^{\ominus}$ given in the provided table for $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ all at 298 K	1 2
(a) at constant pressure ~ 1 bar  0.5 mol CH_4 0.5 mol $CO_2(g)$ 10 mol O_2 [10-1] mol $O_2(g)$ 0.5(2) mol $H_2O(g)$ 298 K $T_f = ?$	$q_p = 0$ adiabatic (insulated container and piston)	
$d\mathbf{H} = (\partial\mathbf{H}/\partial T)_p dT + (\partial\mathbf{H}/\partial p)_T dp$	$\mathbf{H} = \mathbf{H}(T,p)$	3
$d\mathbf{H} = C_p dT + 0$ $\Delta\mathbf{H} = q_p$ $q_p = 0$	Given dp = 0 Given adiabatic	4 5 6
$\Delta\mathbf{H} = \frac{1}{2}\Delta_{comb}\mathbf{H}_{298}^{\ominus}$ $+ 0.5\int_{298}^{T_f} C_p(CO_2 g)dT$ $+ 9\int_{298}^{T_f} C_p(O_2 g)dT$ $+ 1\int_{298}^{373} C_p(H_2O liq)dT$ $+ 1 \bullet \Delta_{vap}\mathbf{H}_{373}(H_2O)$ $+ 1\int_{373}^{T_f} C_p(H_2O g)dT = 0$	Need to sum up all the contributions to $\Delta\mathbf{H}$	7

$0.5(-890.36\times10^3)$ $+ 0.5(37.11)(T_f - 298)$ $+ 9(29.355)(T_f - 298)$ $+1(75.291)(373-298)$ $+ 1(40.656\times10^3)$ $+ 1(33.58)(T_f - 373) = 0$	Substitute values of $\Delta\mathbf{H}$ in J mol^{-1} from Eq 2 and into Eq 7 and look up C_p in J mol^{-1}K^{-1} for CO_2(g), O_2(g), H_2O(liq) and H_2O(g) in given table	8
$T_f = 1567$ K **Answer**	Solving Eq 8 for T_f	9
(b) at constant volume  initial final 0.5 mol CH_4 0.5 mol CO2(g) 10 mol O_2 [10-0.5] mol O2(g) 0.5(2) mol H_2O(g) 298 K T_f = ?	adiabatic (insulated container) with rigid walls	
$d\mathbf{U} = (\partial\mathbf{U}/\partial T)_V dT + (\partial\mathbf{U}/\partial V)_T dV$	$\mathbf{U} = \mathbf{U}(T,V)$	10
$d\mathbf{U} = (\partial\mathbf{U}/\partial T)_V dT + 0$ $\Delta\mathbf{U} = q_V$ $q_V = 0$	Given dV = 0 Given adiabatic	11 12 13
$\Delta\mathbf{U} = ½\, \Delta_{comb}\mathbf{U}_{298}^{\ominus}$ $+ 0.5\int_{298}^{Tf} C_V(CO_2g)dT$ $+ 9\int_{298}^{Tf} C_V(O_2g)dT$ $+ 1 \int_{298}^{373} C_V(H_2Oliq)dT$ $+ 1\bullet\Delta_{vap}\mathbf{U}_{373}\ (H_2O)$ $+ 1 \int_{373}^{Tf} C_V(H_2Og)dT = 0$	Need to sum up all the contributions to $\Delta\mathbf{U}$	14
$\mathbf{H} = \mathbf{U} + pV$	Definition	15
$\Delta\mathbf{H} = \Delta\mathbf{U} + \Delta(pV)$		16
$\Delta_{comb}\mathbf{H}_{298}^{\ominus} = \Delta_{comb}\mathbf{U}_{298}^{\ominus}$ $+(pV)_{products} - (pV)_{reactants}$	Apply Eq 16 to the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ at 298 K	17
$(pV)_{products} = (298\ R)\ 1$ $(pV)_{reactants} = (298\ R)\ 3$ $(pV)_{products} - (pV)_{reactants} = -2(298\ R)$ $= -2(298)(8.31451)$ $(pV)_{products} - (pV)_{reactants} =$ -4955 J mol^{-1}	Assuming ideal gas behavior for reactants and products, neglecting pV for liquid	18 19
$\Delta_{comb}\mathbf{U}_{298}^{\ominus} = -890.36\times10^3$ $-(-4955)$ $= -885.40\times10^3$ J mol^{-1}	Substituting the values from Eq 2 & 19 into Eq 17	20 21

$\Delta_{vap}\mathbf{H}_{373}^{\ominus} = \Delta_{vap}\mathbf{U}_{373}^{\ominus} + (pV)_{gas} - (pV)_{liq}$ $\Delta_{vap}\mathbf{U}_{373}^{\ominus} = \Delta_{vap}\mathbf{H}_{373}^{\ominus} - \Delta(pV)$	Apply Eq 16 to vaporization	22 23
$\Delta(pV) = (373R) = 3101\ \text{J mol}^{-1}$	Assuming ideal gas behavior for gas and neglecting pV for liquid	24
$\Delta_{vap}\mathbf{U}_{373}^{\ominus} = (40.656\times10^3) - 3101 = 37.554\times10^3\ \text{J mol}^{-1}$	Substituting the values	25
$\Delta\mathbf{U} = ½(-885.40\times10^3)$ $+ 0.5(28.8)(T_f - 298)$ $+ 9(21.0)(T_f - 298)$ $+1(75.2)(373-298)$ $+ 1(37.554\times10^3)$ $+ 1(25.3)(T_f - 373) = 0$	Using values for Eq 21 & 25 into Eq 14 and looking up C_V values in J mol^{-1}K^{-1} for CO_2(g), O_2(g), H_2O(liq) and H_2O(g) in given table	26
$T_f = 2053$ K **Answer**	Solving Eq 26 for T_f	
Note that this is a higher final temperature than the final temperature reached in doing the combustion at constant pressure.	This is because all of the chemical energy released by the reaction at *constant volume* went into raising the temperature of the products, whereas, some of the chemical energy released by the reaction at constant pressure went into Work against p_{op} = 1 bar.	

5. The formation of H_2O(g) at 298 K $H_2(g) + ½O_2(g) \rightarrow H_2O(g)$
given $\Delta_{form}\mathbf{H}^{\ominus}_{298} = -241.82\ \text{kJ mol}^{-1}$

Initial	Final
1 mol H_2(g)	$(1-x)$ mol H_2(g)
10 mol O_2(g)	$(10-½x)$ mol O_2(g)
	x mol H_2O(g)
T = 298	T = 2000 K

constant pressure

Equation	Basis for the equation	Eq. #
set up the problem as shown above	Recognize that the reaction is that for the formation of H_2O(g)	
$d\mathbf{H} = (\partial\mathbf{H}/\partial T)_p dT + (\partial\mathbf{H}/\partial p)_T dp$	$\mathbf{H} = \mathbf{H}(T,p)$	1
$d\mathbf{H} = C_p dT + 0$ $\Delta\mathbf{H} = q_p$	Given dp = 0	2 3
$q_p = 0$	Assume that all the $\Delta_{rxn}\mathbf{H}$ is accounted for by the final temperature of 2000 K, i.e., as if H_2 was burned in an insulated cylinder/piston at ~ 1 atm or 1 bar.	4
$\Delta\mathbf{H} = x\ \Delta_{form}\mathbf{H}_{298}^{\ominus}$ $+ (1-x)\int_{298}^{2000} C_p(H_2g)dT$ $+ (10-½x)\int_{298}^{2000} C_p(O_2g)dT$ $+ x\int_{298}^{2000} C_p(H_2Og)dT = 0$	Need to sum up all the contributions to $\Delta\mathbf{H}$	5

$x\,(-241.82\times10^{3})$ $+\ (1-x)(28.824)(2000-298)$ $+\ (10-\tfrac{1}{2}x)(29.355)(2000-298)$ $+\ x\,(33.58)(2000-298) = 0$	Substitute value of $\Delta_{\text{form}}\mathbf{H}_{298}^{\ominus}$ in J mol^{-1} into Eq 5 and look up C_p in J mol^{-1}K^{-1} for $H_2(g)$, $O_2(g)$, and $H_2O(g)$ in given table	6
$x = 0.47$ **Answer** fraction of original H_2 that had undergone combustion	Solving Eq 6 for x	7

6. f/p of ethane as a function of pressure at 600 K

Equation	Basis for the equation	Eq. #
$Z = 1.0000$ $-\ 0.000612\,(p/1\text{ bar})$ $+\ 2.661\times10^{-6}(p/1\text{bar})^{2}$ $-\ 1.390\times10^{-9}\,(p/1\text{bar})^{3}$ $-\ 1.077\times10^{-13}(p/1\text{bar})^{4}$	Given at 600 K	1
$\ln(f/p) = \int_0^p[(Z-1)/p]_T\,dp$	which we derived in class (see lecture notes Part 5)	2
$(Z-1)/p = -\ 0.000612$ $+\ 2.661\times10^{-6}(p/1\text{ bar})$ $-\ 1.390\times10^{-9}\,(p/1\text{bar})^{2}$ $-\ 1.077\times10^{-13}(p/1\text{bar})^{3}$	From Eq 1	3
$\ln(f/p) = \int_0^p[(Z-1)/p]_T\,dp$ $= -\ 0.000612\,(p/1\text{ bar})$ $+\tfrac{1}{2}\bullet\ 2.661\times10^{-6}\,(p/1\text{bar})^{2}$ $-\ (1/3)\bullet1.390\times10^{-9}\,(p/1\text{bar})^{3}$ $-\ (1/4)\bullet1.077\times10^{-13}(p/1\text{bar})^{4}$	Substituting Eq 3 into Eq 2 and integrating	4
$(f/p) =$ $\exp\{-\ 0.000612\,(p/1\text{ bar})$ $+\tfrac{1}{2}\bullet\ 2.661\times10^{-6}\,(p/1\text{bar})^{2}$ $-\ (1/3)\bullet1.390\times10^{-9}\,(p/1\text{bar})^{3}$ $-\ (1/4)\bullet1.077\times10^{-13}(p/1\text{bar})^{4}\}$ at 600 K **Answer**	Rearranging Eq 4	5

7. Distribution of a real gas in a gravity field

Equation	Basis for the equation	Eq. #
$F = mg$ $F_{z+dz} + dF = F_z$	See lecture notes Part 1 for starting this problem Pressure at any height z is determined by the column of fluid above that height. Start withforce arising from the weight of fluid in the column at z (F_z) and compare that with the force arising from the weight of the fluid in the column at z+dz.	1 2
Let ρ be the density at height z The mass of fluid in the column between z and z+dz is ρAdz $dF = (\rho Adz)g$	A is the cross sectional area of the column	3
The pressure: p at height z = F_z/A p + dp at height z+dz = F_{z+dz}/A $A(p+dp) + dF = Ap$ $dF = -Adp$	Substituting Eq 4&5 into Eq 2 Rearranging	4 5 6
$dp = -\rho gdz$	Substituting Eq 6 into Eq 3	7
$\rho = M/V$	where M is the molar mass and V is the molar volume	
$dp = -(M/V)\,gdz$	substituting for ρ in Eq 7	8
$dp/p = -(M/ZRT)\,gdz$	Using $Z = pV/RT$ or $V = ZRT/p$ into Eq 8	9
$\int_{p0}^{p}(dp/p) = -(M/ZRT)\,g\int_0^z dz$ $\ln(p/p_0) = -(Mg/ZRT)\,z$ $p = p_0 \exp[-(Mg/ZRT)\,z]$	Integrating between z = 0 and z	10 11
(a) if $Z > 1$, $\exp[-(Mg/ZRT)z] > \exp[-(Mg/RT)z]$ That is, need to go to larger height to drop from p_0 (at the surface) to the same pressure p it would have been had the gas been ideal. This means the gas distribution is broader when $Z > 1$. (b) if $Z < 1$, $\exp[-(Mg/ZRT)z] < \exp[-(Mg/RT)z]$ That is, don't need to go as high to drop from p_0 to the same pressure p it would have been had the gas been ideal. This means the gas distribution is narrower $Z < 1$.	Comparing with ideal case where Z = 1	
If $Z = 1+Bp$ $dp/p = -[M/(1+Bp)RT]\,gdz$	Substitute this into Eq 9	12
$\{(1+Bp)/p\}\,dp = -[Mg/RT]\,dz$	Rearranging	

$\int_{p0}^{p}(dp/p) + B\int_{p0}^{p} dp$ $= - (Mg/RT) \int_0^z dz$ $\ln(p/p_0) + B(p-p_0)$ $= - (Mg/RT)\, z$ **Answer**	Integrating between z = 0 and z to be compared with the ideal case: $\ln(p/p_0) = - (Mg/RT)\, z$	

8. Fugacity of a gas

Equation	Basis for the equation	Eq. #
$Z = 1 + [b-(a/RT)](p/RT)$ $(Z-1)/p = [b-(a/RT)]/RT$	Given Rearranging	1 2
$\ln(f/p) = \int_0^p[(Z-1)/p]_T\, dp$	which we derived in class (see lecture notes Part 5)	3
$\ln(f/p) = \int_0^p \{b-(a/RT)]/RT\}_T\, dp$ $= [b-(a/RT)]/RT\}_T\, p$	Substituting Eq 2 into Eq 3 Integrating	
$(f/p) = \exp[(p/RT)[b-(a/RT)]$ $f = p \exp[(p/RT)[b-(a/RT)]$ **Answer**		

9.

Equation	Basis for the equation	Eq. #
The actual chemical potential is $\mu(T,p) = \mu^{\ominus}(T) + RT\ln(f/1bar)$	Recall that the standard state for a gas corresponds to a fictitious state of an ideal gas at 1 bar and temperature T for which the chemical potential is $\mu^{\ominus}(T)$	1
$\frac{\mu(T,p)}{T} = \frac{\mu^{\ominus}(T)}{T} + R\ln(f/1bar)$	Dividing Eq 1 by T	2
$(1/n)\frac{\mathbf{G}}{T} = (1/n)\frac{\mathbf{G}^{\ominus}}{T} + R\ln(f/1bar)$	Recall that for a substance $\mu = \mathbf{G}/n$ where n is the number of moles	3
$(1/n)[\partial/\partial T(\mathbf{G}/T)]_p =$ $(1/n)[\partial/\partial T(\mathbf{G}^{\ominus}/T)]_p$ $+ R\partial\ln(f/1bar)/\partial T]_p$	Take the derivative of both sides with respect to T at constant p	4
$[\partial/\partial T(\mathbf{G}/T)]_p = - \mathbf{H}/T^2$	The ***Gibbs-Helmholtz equation*** (see lecture notes Part 5)	5
$- \mathbf{H}/T^2 = - \mathbf{H}^{\ominus}/T^2 + R\partial\ln(f/1bar)/\partial T]_p$	Substitute Eq 5 into Eq 4, where **H** and $\mathbf{H}^{\ominus}$ are now molar quantities	6
$\mathbf{H} = \mathbf{H}^{\ominus} - R\, T^2\partial\ln(f/1bar)/\partial T]_p$ **Q.E.D.**	$\mathbf{H}^{\ominus}$ is $\mathbf{H}_{ideal}{}^{\ominus}$ since the standard state at temperature T corresponds to a fictitious gas behaving ideally at 1 bar, whereas **H** is the molar enthalpy of the real gas.	7