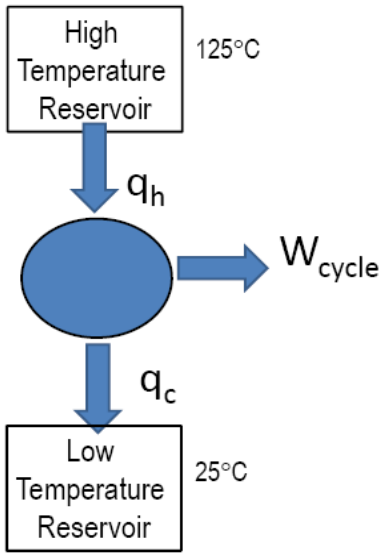
Solutions to Problem Set 4

1. (a) heat engine



Develop the equations you need:

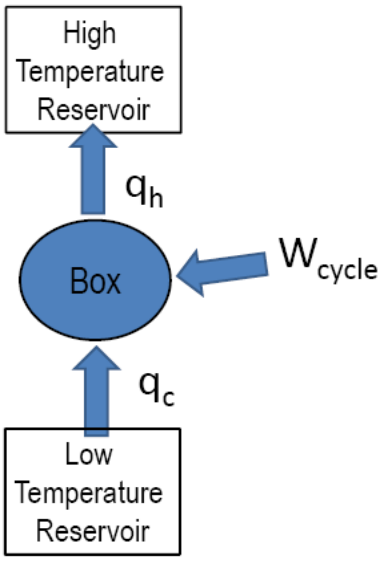
Equation	Basis for the equation	Eq. #
$\varepsilon = -W_{cycle} / q_h$	Efficiency of any heat engine based on 2 thermal reservoirs is the ratio of the work produced in the surroundings to the quantity of heat transferred from the high temperature reservoir	1
$-W_{cycle} = R(T_h - T_c) \ln(V_B/V_A)$ $q_h = RT_h \ln(V_B/V_A)$ ε rev cycle $= (T_h - T_c) / T_h$	For the Carnot cycle operating reversibly using an ideal gas (see lecture notes Part 3) efficiency is given by this equation.	2
ε rev cycle = ε rev cycle'	For all engines based on 2 thermal reservoirs and operating reversibly using any gas, efficiency is the same. (See lecture notes Part 3.) This is the maximum possible efficiency.	3
$(T_h - T_c) / T_h = (125-25)/(125+273) = 0.251$	Given t_c and t_h are 25 deg and 125 deg respectively	4
ε rev cycle = 0.251 **Answer**	Maximum possible efficiency for this problem	5

Maximum possible efficiency of heat engine is for ideal, reversible conditions, i.e., no frictional loss.

(b) Given T_c and T_h are 4 K and 20K respectively, efficiency of a reversible engine working between heat reservoirs at these temperatures is $(T_h - T_c) / T_h = (20-4)/(20) = 0.80$

(c) Given efficiency = 0.80 and T_c = 300 K, $(T_h - 300) / T_h = 0.80$, therefore T_h = 1500K

2. Refrigerator:

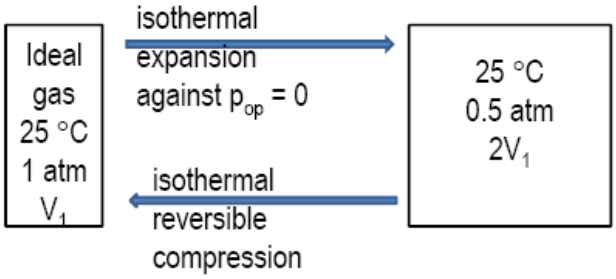


Develop the equations you need:

Equation	Basis for the equation	Eq. #
$\beta = q_c/W_{cycle}$	Definition of coefficient of performance of a refrigerator	1
$d\mathbf{U} = \delta q + \delta W$	First Law of Thermodynamics	2
For a cycle: $\Delta\mathbf{U} = 0$	**U** is a state function	3
$0 = q_{cycle} + W_{cycle}$ $0 = q_c + q_h + W_{cycle}$ $W_{cycle} = - q_c - q_h$	From Eq 2 and 3	4
$-W_{cycle} = R(T_h - T_c) \ln(V_B/V_A)$ $q_c = - RT_c \ln(V_B/V_A)$ $W_{cycle} = R(T_h - T_c) \ln(V_B/V_A)$ $q_c = RT_c \ln(V_B/V_A)$	For the Carnot cycle operating reversibly using an ideal gas (see lecture notes Part 3, but *change signs for reverse direction* of cycle)	5 6
β rev cycle $= T_c/(T_h - T_c)$	From Eq. 1 and 6 ideal coeff of performance is given by this equation.	7
$q_c/W_{cycle} = (0.75) \bullet [T_c/(T_h-T_c)]$ $q_c = W_{cycle} \bullet (0.75) \bullet [T_c/(T_h-T_c)]$	Given: not ideal, actual is 75% of ideal	8
$W_{cycle} = (1/4)(10.688$ kcal/min)	Given, for 1 min	9
$T_c = - 20+273$, $T_h = 35+273$	Given: t_c and t_h are -20 deg and 35 deg respectively	10
$q_c = (1/4)(10.688$ kcal/min) $\bullet (0.75) \bullet [253/(308-253)]$	From Eq 8, 9,10	11
$q_c = 6.9138$ kcal/min **Answer**	Solving Eq 10	12

The heat removed from the low temperature reservoir, if motor runs continuously, is 6.9138 kcal/min. Therefore, can tolerate a maximum heat leak into the box by an amount 6.9138 kcal/min.

3. 1 mole



(a)

Equation	Basis for the equation	Eq. #
$d\mathbf{U} = \delta q + \delta W$	First Law of Thermodynamics	1
$\Delta\mathbf{U}_1 = 0$	For an ideal gas, $\mathbf{U} = \mathbf{U}(T)$ only	2
$\delta W = - p_{op} dV$ $p_{op} = 0$ $\delta W_1 = 0$	Definition of pV work Given	3 4
$\delta q_1 = 0$; $q_1 = 0$	From Eq 1, 2 and 4	5
$\int \delta q_1/T = 0$	From Eq 5	6
$p_{op} = p_{gas}$ $p_{gas} = (1)RT/V$ $\delta W_2 = - RTdV/V$	Step 2 is reversible ideal gas equation of state, 1 mole	7 8 9
$\delta q_2 = RTdV/V$	From Eq 1 and 9	10
$\int \delta q_2/T = \int RdV/V = R\ln(V_1/2V_1)$	From Eq 10	11
$\int \delta q_2/T = - R\ln(2)$	Evaluating Eq 11	12
$\int_{cycle} \delta q/T = \int \delta q_1/T + \int \delta q_2/T$ $= - R\ln(2)$	From Eq 5 and 12	13
$\oint \delta q_{irrev}/T < 0$	As it should be, according to Clausius inequality.	14

(b)

Equation	Basis for the equation	Eq. #
$\Delta\mathbf{S} = \int \delta q_{REV}/T$	Second Law of Thermodynamics	15
$\Delta\mathbf{S}_2 = \int \delta q_2/T = - R\ln(2)$ $= - (1\ mol)\ 8.314\ J\ mol^{-1}K^{-1}\ (0.693)$ $= - 5.76\ J\ K^{-1}$ **Answer**	Step 2 is reversible and Eq 12	16

(c)

Equation	Basis for the equation	Eq. #
$\Delta\mathbf{S}_{cycle} = 0$	S is a state function	17
$\Delta\mathbf{S}_{cycle} = \Delta\mathbf{S}_1 + \Delta\mathbf{S}_2$	S is a state function	18

$0 = \Delta \mathbf{S}_1 - 5.76\ \text{J K}^{-1}$	Use Eq 16	19
$\Delta \mathbf{S}_1 = +5.76\ \text{J K}^{-1}$ **Answer**	Solving Eq 19	20

(d)

Equation	Basis for the equation	Eq. #
$q_1 = 0,\ \ q_1/T = 0$	From Eq 5	21
$\Delta \mathbf{S}_1 = +5.76\ \text{J K}^{-1} \neq 0$ **Answer**	As it should be; since step 1 is not reversible, $\Delta \mathbf{S}_1 \neq q_1/T$	21

4. Given $T_1 = 10$ K, $T_2 = 300$ K for one mol of an ideal gas, $C_V = (3/2)R$

Equation	Basis for the equation	Eq. #
(a) $dV = 0$	Given	1
$d\mathbf{S} = (\partial \mathbf{S}/\partial T)_V dT + (\partial \mathbf{S}/\partial V)_T dV$	$\mathbf{S} = \mathbf{S}(T,V)$	2
$(\partial \mathbf{S}/\partial T)_V = C_V/T$ $(\partial \mathbf{S}/\partial V)_T = (1/T)\{p + (\partial \mathbf{U}/\partial V)_T\} = (\partial p/\partial T)_V$	Derived (see lecture notes Part 4) starting from $d\mathbf{U} = \eth q_{rev} - p dV = T d\mathbf{S} - p dV$	3 4
$d\mathbf{S} = (C_V/T)dT$ $\Delta \mathbf{S} = \int (3/2)R dT/T$	From Eq 1, 2 and 3	5
$\Delta \mathbf{S} = (1\ \text{mol})(3/2)(8.314\ \text{J mol}^{-1}\text{K}^{-1})$ • $\ln(300/10) = 42.4\ \text{J K}^{-1}$ **Answer**	Integrating Eq 5	6
(b) $dp = 0$	Given	7
$d\mathbf{S} = (\partial \mathbf{S}/\partial T)_p dT + (\partial \mathbf{S}/\partial p)_T dp$	$\mathbf{S} = \mathbf{S}(T,p)$	8
$(\partial \mathbf{S}/\partial T)_p = C_p/T$ $(\partial \mathbf{S}/\partial p)_T = -(\partial V/\partial T)_p$	Derived (see lecture notes Part 4) starting from $d\mathbf{U} = \eth q_{rev} - p dV = T d\mathbf{S} - p dV$ and use of cross derivatives	9 10
$C_p - C_V = R$	For an ideal gas	11
$d\mathbf{S} = (C_p/T)dT$ $\Delta \mathbf{S} = \int (5/2)R dT/T$	From Eq 7, 8 and 9 From Eq 11 and 12	12 13
$\Delta \mathbf{S} = (1\ \text{mol})(5/2)(8.314\ \text{J mol}^{-1}\text{K}^{-1})$ • $\ln(300/10) = 70.7\ \text{J K}^{-1}$ **Answer**	Integrating Eq 13	14
(c) 3 moles	Given	15
$\Delta \mathbf{S}$ = multiplied by factor of 3 **Answer**	Substituting 3 mol for 1 mol in Eq 6 and 14	16

5. (a) Given 1 mol liquid water T_1 = 0+273 K, T_2 = 100+273 K, constant pressure, C_p = 18.0 cal deg^{-1} mol^{-1}.

Equation	Basis for the equation	Eq. #
dp = 0	Given	1
$d\mathbf{S} = (\partial\mathbf{S}/\partial T)_p dT + (\partial\mathbf{S}/\partial p)_T dp$	$\mathbf{S} = \mathbf{S}(T,p)$	2
$(\partial\mathbf{S}/\partial T)_p = C_p/T$ $(\partial\mathbf{S}/\partial p)_T = -(\partial V/\partial T)_p$	Derived (see lecture notes Part 4) starting from $d\boldsymbol{U} = \eth q_{rev} - p dV = T d\boldsymbol{S} - p dV$ and use of cross derivatives	3 4
C_p =18.0 cal deg^{-1} mol^{-1}.	Given	5
$d\mathbf{S} = (C_p/T)dT$	From Eq 1, 2 and 3	6
$\Delta\mathbf{S}$ = (1 mol)(18.0 cal $mol^{-1}K^{-1}$) • ln(373/273) = 5.62 cal K^{-1} **Answer**	Integrating Eq 6 and using Eq 5	7

(b) ice (0°C, 1 atm) → steam (100°C, 1 atm). $\Delta\mathbf{S}$ **= ?**

Devise reversible steps which lead from same initial state to same final state, to calculate any state function change for the given process.

ice (0°C, 1 atm) → liq water (0°C, 1 atm) step (1) $\Delta\mathbf{S}_1$
liq water (0°C, 1 atm) → liq water (100°C, 1 atm) step (2) $\Delta\mathbf{S}_2$
liq water (100°C, 1 atm) → steam (100°C, 1 atm) step (3) $\Delta\mathbf{S}_3$
$\Delta\mathbf{S} = \Delta\mathbf{S}_1 + \Delta\mathbf{S}_2 + \Delta\mathbf{S}_3$

Equation	Basis for the equation	Eq. #
dp = 0	Given	1
$d\mathbf{S} = (\partial\mathbf{S}/\partial T)_p dT + (\partial\mathbf{S}/\partial p)_T dp$	$\mathbf{S} = \mathbf{S}(T,p)$	2
$(\partial\mathbf{S}/\partial T)_p = C_p/T$ $(\partial\mathbf{S}/\partial p)_T = -(\partial V/\partial T)_p$	Derived (see lecture notes Part 4) starting from $d\boldsymbol{U} = \eth q_{rev} - p dV = T d\boldsymbol{S} - p dV$ and use of cross derivatives	3 4
C_p =18.0 cal deg^{-1} mol^{-1}.	Given	5
q_p = 1.4363 kcal mol^{-1} at (0°C,1 atm)	Given. This is $q_{REV,\ fusion}$ at these conditions	6
q_p = 9.7171 kcal mol^{-1} at (100°C,1 atm)	Given. This is $q_{REV,\ vaporizn}$ at these conditions	7
C_p =18.0 cal deg^{-1} mol^{-1}.	Given	8
$d\mathbf{S} = (\delta q_{REV}/T)$ $\Delta\mathbf{S} = q_{REV}/T$ for constant T	Second Law of thermodynamics	9 10
step (1): $\Delta\mathbf{S}_1 = q_{REV}/T$	Eq 10 and using Eq 6	11

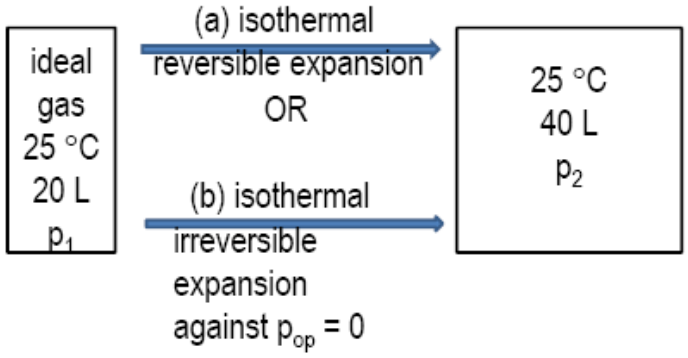
= (1 mol)(1436.3 cal mol^{-1}) /273 $\Delta \mathbf{S}_1$ = 5.26 cal K^{-1}	Evaluating Eq 11	
step (2): $d\mathbf{S} = (C_p/T)dT$ $\Delta \mathbf{S}_2$ = (1 mol)(18.0 cal deg^{-1} mol^{-1}) • ln(373/273) =5.62 cal K^{-1}	Eq 1, 2, 3 Integrating Eq 12 and using Eq 8 Already done in part (a) of this problem	12 13
step (3): $\Delta \mathbf{S}_3 = q_{REV}/T$ = (1 mol)(9717.1 cal mol^{-1}) /373 $\Delta \mathbf{S}_3$ = 26.05 cal K^{-1}	Eq 10 and using Eq 7 Evaluating Eq 14	14
$\Delta \mathbf{S} = \Delta \mathbf{S}_1 + \Delta \mathbf{S}_2 + \Delta \mathbf{S}_3$ = 5.26 + 5.62 + 26.05 = 36.93 cal K^{-1} **Answer**	**S** is a state function	15

6. (a) sulfur(s, rhombic) $\rightarrow$ sulfur(s, monoclinic) T_{trans} = 95.4+273 K, $q_{REV,trans}$ = 0.09 kcal mol^{-1} $\Delta \mathbf{S}_a$ **=?**

(b) sulfur(s, monoclinic) $\rightarrow$ sulfur(liquid) T_{trans} = 119+273 K, $q_{REV,trans}$ = 0.293 kcal mol^{-1} $\Delta \mathbf{S}_b$**=?**

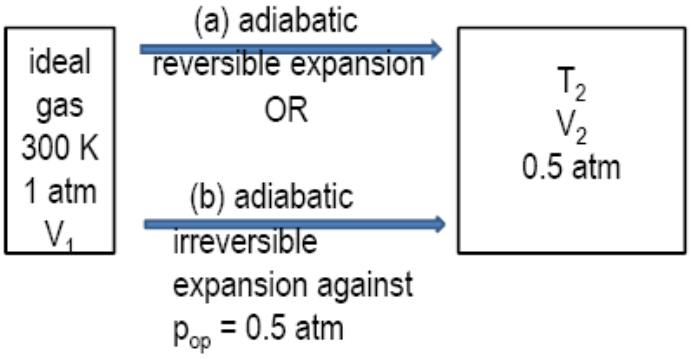
Equation	Basis for the equation	Eq. #
dp = 0	Given (understood, 1 atm)	1
$q_p = q_{REV,trans}$ = 0.09 kcal mol^{-1} at (95.4°C, 1 atm)	Given. This is $q_{REV, trans}$ at these conditions, for 1 mol = 32 g	2
$q_p = q_{REV, fusion}$ = 0.293 kcal mol^{-1} at (119°C, 1 atm)	Given. This is $q_{REV, fusion}$ at these conditions, for 1 mol = 32 g	3
$d\mathbf{S} = (\delta q_{REV}/T)$ $\Delta \mathbf{S} = q_{REV}/T$ for constant T	Second Law of thermodynamics	4 5
step (a): $\Delta \mathbf{S}_a = q_{REV}/T$ = (90 cal K^{-1} mol^{-1}) /(273+95.4) $\Delta \mathbf{S}_a$ = 0.244 cal K^{-1} mol^{-1} **Answer**	Eq 5 and using Eq 2 Evaluating Eq 6	6
step (b): $\Delta \mathbf{S}_b = q_{REV}/T$ = (293 cal K^{-1} mol^{-1}) /(273+119) $\Delta \mathbf{S}_b$ = 0.747 cal K^{-1} mol^{-1} **Answer**	Eq 5 and using Eq 3 Evaluating Eq 7	7
$\Delta \mathbf{S}_a = q_{REV}/T$ = (8x90 cal K^{-1} mol^{-1}) /(273+95.4) $\Delta \mathbf{S}_b = q_{REV}/T$ = (8x293cal K^{-1} mol^{-1}) /(273+119) $\Delta \mathbf{S}_a$ = 1.95 cal K^{-1} mol^{-1} $\Delta \mathbf{S}_b$ = 5.98 cal K^{-1} mol^{-1} **Answer**	If unit is not S atom but S_8 molecule, then I mole = 32x8 g not 32 g, making $q_{REV,trans}$ = 8x0.09 kcal mol^{-1} $q_{REV, fusion}$ = 8x0.293 kcal mol^{-1} Trouton's rule applies to vaporization, not these types of transitions.	7

7.



Equation	Basis for the equation	Eq. #
$d\mathbf{U} = \delta q + \delta W$	First Law of Thermodynamics	1
$\Delta\mathbf{U} = 0$ for both (a) and (b) **Answer**	For an ideal gas, $\mathbf{U} = \mathbf{U}(T)$ only	2
$\delta W = - p_{op} dV$	Definition of pV work	3
(a) $p_{op} = p_{gas}$ $p_{gas} = (1)RT/V$ $\delta W_a = - RTdV/V$ $W_a = - (8.314 \text{ J mol}^{-1}\text{K}^{-1})(298) \bullet \ln(40/20) = -1717 \text{ J mol}^{-1}$ **Answer**	Expansion (a) is reversible Ideal gas equation of state, 1 mole Integrating Eq 6	4 5 6 7
$\delta q_{a,REV} = - \delta W_a = RTdV/V$ $q_a = 1717 \text{ J mol}^{-1}$ **Answer**	From Eq 1, 2 and 6 From Eq 7	8 9
$\Delta\mathbf{S}_a = \int \delta q_{a,REV}/T$ $\Delta\mathbf{S}_a = \int RdV/V = R\ln(40/20)$	Second law of thermodynamics From Eq 8 and 10	10 11
$\Delta\mathbf{S}_a = (8.314 \text{ J mol}^{-1}\text{K}^{-1}) \bullet \ln(2)$ $= 5.76 \text{ J mol}^{-1}\text{K}^{-1}$ **Answer**	Evaluating Eq 11	12
(b) $p_{op} = 0$ $\delta W_b = 0$ $W_b = 0$ **Answer**	Given From Eq 3	13 14 15
$\delta q_b = 0$ $q_b = 0$ **Answer**	From Eq 1 and 2 From Eq 14	16 17
$\Delta\mathbf{S}_b = \Delta\mathbf{S}_a$ $\Delta\mathbf{S}_b = 5.76 \text{ J mol}^{-1}\text{K}^{-1}$ **Answer**	S is a state function (same initial &final states) From Eq 12	18
$\Delta\mathbf{S}_a = q_{a,REV}/T$ while $\Delta\mathbf{S}_b \neq q_{b,IRREV}/T$ **Answer**		

8.



Equation	Basis for the equation	Eq. #
d**U** = δq + δW	First Law of Thermodynamics	1
q = 0 for both (a) and (b) **Answer**	Definition of adiabatic	2
d**U** = δW Δ**U** = W for both (a) and (b)	From Eq 1 and 2	3
δW = - p_{op}dV	Definition of pV work	4
part (a) $p_{op} = p_{gas}$	Expansion (a) is reversible	5
p_{gas} = (1)RT/V V_1 = (1 mol)(0.08205 L atm mol^{-1})•(300)/(1 atm) = 24.61 L	Ideal gas equation of state, 1 mole	6
δW_a = - RTdV/V	Integrating Eq 6	7
d**U** = C_VdT + $(\partial U/\partial V)_T$dV	**U** = **U**(T,V)	8
d**U** = C_VdT	For an ideal gas, $(\partial U/\partial V)_T = 0$	9
C_VdT = - RTdV/V	From Eq 3, 7 and 9	10
$\int C_V dT/T = -R\int dV/V$ Cv ln(T_2/T_1) = -R ln (V_2/V_1)	Integrating Eq 10	11
Cv ln(T_2/T_1) = -R ln (T_2p_1/T_1p_2)	Using Eq 6	12
(C_V+R) ln(T_2/T_1) = R ln(p_2/p_1)	Rearranging Eq 12	13
(1.5R+R) ln(T_2/300) = R ln (0.5/1)	Substituting given values into Eq 13	14
T_2 = 227 K	Solving Eq 14 for the unknown T_2	15
V_2 = (1 mol)(0.08205 L atm mol^{-1})•(227)/(0.5 atm) = 37.25 L	Solving Eq 6 for the unknown V_2, using the value of T_2	15
Δ$\mathbf{U}_a$ = 1.5(8.314 J $mol^{-1}K^{-1}$)• (227-300) = 910.4 J mol^{-1} **Answer**	Integrating Eq 9 and substituting values	16
W_a = Δ$\mathbf{U}_a$ = 910.4 J mol^{-1} **Answer**	From Eq 3	17
Δ$\mathbf{S}_a$ = $\int \delta q_{a,REV}/T$ = 0 **Answer**	Second law of thermodynamics Since $\delta q_{a,REV}$ = 0 (adiabatic)	18 19
part (b) p_{op} = 0.5	Given	20
W_b = - $\int p_{op}$dV = - 0.5 atm(V_2-V_1)	From Eq 4 and 20, integrating	21
(b)		
Δ$\mathbf{U}_b$ = $\int C_V$dT = 1.5R(T_2-T_1)	Integrating Eq 9	22

$\Delta \mathbf{U}_b = 1.5[(0.5\ atm)V_2 - (1\ atm)V_1]$	Substituting ideal gas equation of state	23
$W_b = \Delta \mathbf{U}_b$	From Eq 3	3
$-0.5\ atm(V_2-V_1) = 1.5\ [(0.5\ atm)V_2 - (1\ atm)V_1]$ $-0.5\ (V_2-24.61) = 1.5\ [0.5V_2 - 24.61]$	Substituting Eq 21 and 23 into Eq 3 From Eq 6, $V_1 = 24.61$ L	25 26
$V_2 = 39.38$ L	Solving Eq 26 for V_2	27
$W_b = -0.5\ atm(39.38-24.61)$ $= -7.385\ L\ atm$ $\bullet(8.314\ J/0.08205\ L\ atm)$ $= -748.3 J$ **Answer**	Substituting V_2 into Eq 21	
$\Delta \mathbf{U}_b = -748.3\ J$ **Answer**	From Eq 3	28
$d\mathbf{S} = (\partial \mathbf{S}/\partial T)_p dT + (\partial \mathbf{S}/\partial p)_T dp$	$\mathbf{S} = \mathbf{S}(T,p)$	29
$(\partial \mathbf{S}/\partial T)_p = C_p/T$ $(\partial \mathbf{S}/\partial p)_T = -(\partial V/\partial T)_p$	Derived (see lecture notes Part 4) starting from $d\boldsymbol{U} = \eth q_{rev} - p dV = T d\boldsymbol{S} - p dV$ and use of cross derivatives	30 31
$-(\partial V/\partial T)_p = -R/p$	Differentiating ideal gas equation of state	32
$d\mathbf{S} = C_p\ dT/T - R dp/p$	Substitution of Eq 30 & 32 into Eq. 29	33
$\Delta \mathbf{S}_b = 2.5R\ \ln(T_2/T_1) - R\ \ln(p_2/p_1)$	Integrating Eq 33	34
$\Delta \mathbf{S}_b = 2.5R\ \ln[0.5 \bullet 39.38/(1 \bullet 24.61)] - R\ \ln(0.5/1) = (8.314\ J\ mol^{-1}K^{-1}) \bullet (2.5\ \ln 0.80 - \ln 0.50)$ $= 1.125\ J\ mol^{-1}K^{-1}$ **Answer**	Substitution of known values into Eq 34 and evaluating	

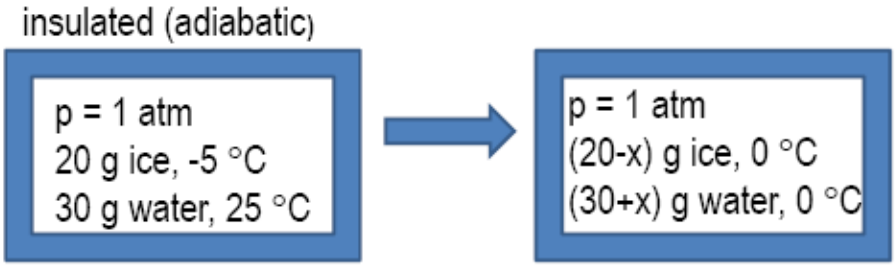
9.

$q_{total} = 0$ (adiabatic) ; this is also q_p because pressure is constant in this problem.

$q = \int C\ dT$ = mass• heat capacity• $(t_{final} - t_{initial})$ when heat capacity is a constant

except for a phase change where need to use instead: q = mass• $(\Delta \mathbf{H}_{phase\ change}\ cal\ g^{-1})$

$\Delta \mathbf{H} = q_p$, which is 0 because adiabatic.



Assume that final state is at 0 °C with both ice and water present.

1	20 g ice, - 5 °C → 20 g ice, 0°C	$q_1 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(0 - -5)$
2	30 g water, 25 °C → 30 g water, 0 °C	$q_2 = 30\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25)$
3	x g ice, 0°C → x g water, 0°C	$q_3 = x\ g\ (80\ cal\ g^{-1})$

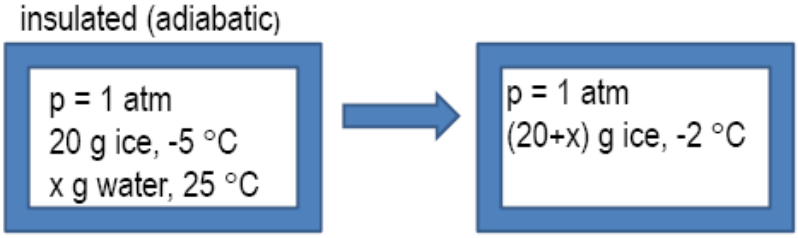
$q_{total} = 0 = q_1 + q_2 + q_3$

$0 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(0 - -5) + 30\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25) + x\ g\ (80\ cal\ g^{-1})$
$0 = 50 - 750 + 80\ x$
Solving for x,
$x = 700/80 = 8.75\ g$
Final state is 11.25 g ice and 38.75 g water, all at 0°C
If we had found a negative value for x then the final state would be some of the water will have turned to ice instead. This could happen if we had either less water or lower temperature of water to begin with.

To calculate $\Delta\mathbf{S}$, we use for each step, either $\Delta\mathbf{S} = q_{REV,trans}/T_{trans}$, or else use $\Delta\mathbf{S} = C_p \ln(T_{final}/T_{initial})$ from $\mathbf{S} = \mathbf{S}(T,p)$ and $dp = 0$ and C_p is given independent of T in these cases.
$\Delta\mathbf{S} = \Delta\mathbf{S}_1 + \Delta\mathbf{S}_2 + \Delta\mathbf{S}_3$
$= 20(0.5) \ln(273/268) + 30(1) \ln(273/298) + 8.75(80)/273$
$= 0.1848 - 2.6287 + 2.5641 = +0.1202\ cal\ K^{-1}$. We expected $\Delta\mathbf{S} > 0$ for a spontaneous process such as this one.

10. Just like problem 9, but four different amounts of water, ending in 4 different final states.
For all cases:
$q_{total} = 0$ (adiabatic) ; this is also q_p because pressure is constant in this problem.
$q = \int C\ dT$ = mass• heat capacity• $(t_{final} - t_{initial})$ when heat capacity is a constant
$\Delta\mathbf{H} = q_p = 0$
To calculate $\Delta\mathbf{S}$, we use for each step, either $\Delta\mathbf{S} = q_{REV,trans}/T_{trans}$, or else use $\Delta\mathbf{S} = C_p \ln(T_{final}/T_{initial})$ from $\mathbf{S} = \mathbf{S}(T,p)$ and $dp = 0$ and because C_p is given independent of T in this problem.

(a)



1	20 g ice, - 5 °C → 20 g ice, - 2°C	$q_1 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(-2 - -5)$
2	x g water, 25 °C → x g water, 0 °C	$q_2 = x\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25)$
3	x g water, 0°C → x g ice, 0°C	$q_3 = x\ g\ (-80\ cal\ g^{-1})$
4	x g ice, 0 °C → x g ice, - 2°C	$q_4 = x\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(-2 - 0)$

$q_{total} = 0 = q_1 + q_2 + q_3 + q_4$

$0 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(-2 - -5) + x\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25) + x\ g\ (80\ cal\ g^{-1}) + x\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(-2 - 0)$

$0 = 30 - 25x - 80x - x$

Solving for x,

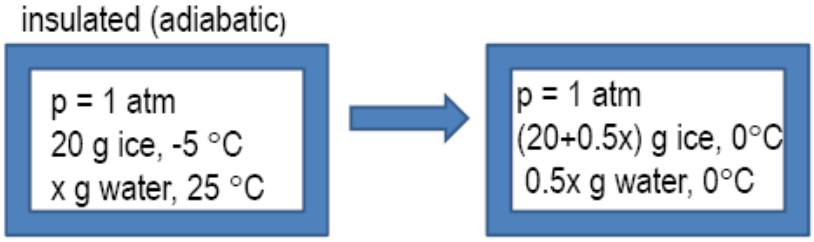
$x = 30/106 = 0.28$ g of water to start with **Answer**

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$

$= 20(0.5)\ \ln(271/268) + 0.28(1)\ \ln(273/298) + 0.28(-80)/273 + 0.28(0.5)\ \ln(271/273)$

$= 0.1113 - 0.0245 - 0.0820 - 0.0010 = 0.0038\ cal\ deg^{-1}$ **Answer**

(b)



1	20 g ice, - 5 °C → 20 g ice, 0°C	$q_1 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(0 - -5)$
2	x g water, 25 °C → x g water, 0 °C	$q_2 = x\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25)$
3	0.5x g water, 0°C → 0.5x g ice, 0°C	$q_3 = 0.5x\ g\ (-80\ cal\ g^{-1})$

$q_{total} = 0 = q_1 + q_2 + q_3$

$0 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(0 - -5) + x\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25) + 0.5x\ g\ (-80\ cal\ g^{-1})$

$0 = 50 - 25x - 40x$

Solving for x,

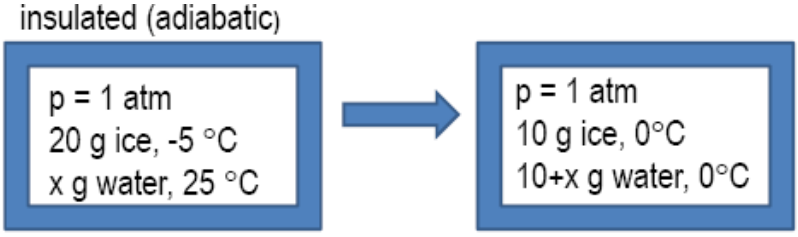
$x = 50/65 = 0.77$ g of water to start with **Answer**

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$= 20(0.5)\ \ln(273/268) + 0.77(1)\ \ln(273/298) + 0.385(-80)/273$

$= 0.1848 - 0.0675 - 0.1128 = 0.0045\ cal\ deg^{-1}$ **Answer**

(c)



1	20 g ice, - 5 °C → 20 g ice, 0°C	$q_1 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(0 - -5)$
2	x g water, 25 °C → x g water, 0 °C	$q_2 = x\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25)$
3	10 g ice, 0°C → 10 g water, 0°C	$q_3 = 10\ g\ (80\ cal\ g^{-1})$

$q_{total} = 0 = q_1 + q_2 + q_3$

$0 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(0 - -5) + x\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25) + 10\ g\ (80\ cal\ g^{-1})$

$0 = 50 - 25x + 800$

Solving for x,

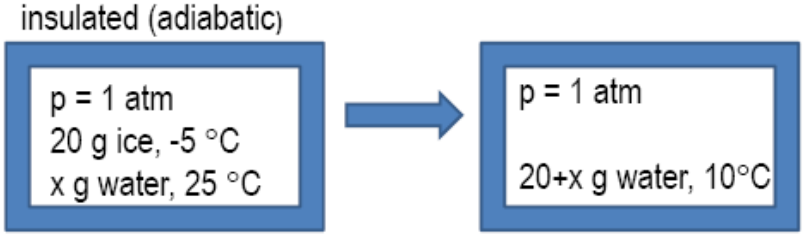
$x = 850/25 = 34$ g of water to start with **Answer**

$\Delta \mathbf{S} = \Delta \mathbf{S}_1 + \Delta \mathbf{S}_2 + \Delta \mathbf{S}_3$

$= 20(0.5)\ \ln(273/268) + 34(1)\ \ln(273/298) + 10(80)/273$

$= 0.1845 - 2.9791 + 2.9304 = 0.136\ cal\ deg^{-1}$ **Answer**

(d)



1	20 g ice, - 5 °C → 20 g ice, 0°C	$q_1 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(0 - -5)$
2	x g water, 25 °C → x g water, 0 °C	$q_2 = x\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25)$
3	20 g ice, 0°C → 20 g water, 0°C	$q_3 = 20\ g\ (80\ cal\ g^{-1})$
4	(20+x) g water, 0 °C → (20+x) g water, 10°C	$q_4 = (20+x)\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(10 - 0)$

$q_{total} = 0 = q_1 + q_2 + q_3 + q_4$

$0 = 20\ g\ (0.5\ cal\ deg^{-1}\ g^{-1})(0 - -5) + x\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(0 - 25) + 20\ g\ (80\ cal\ g^{-1})$
$+ (20+x)\ g\ (1.0\ cal\ deg^{-1}\ g^{-1})(10 - 0)$

$0 = 50 - 25x + 1600 + (20+x)10$

Solving for x,

$x = 1850/15 = 123.$ g of water to start with **Answer**

$\Delta \mathbf{S} = \Delta \mathbf{S}_1 + \Delta \mathbf{S}_2 + \Delta \mathbf{S}_3 + \Delta \mathbf{S}_4$

$= 20(0.5)\ \ln(273/268) + 123(1)\ \ln(273/298) + 20(80)/273 + 143(1)\ \ln(283/273)$

$= 0.1845 - 10.7775 + 5.8608 + 5.1444 = 0.412\ cal\ deg^{-1}$ **Answer**