

Chem 401—Physical Chemistry
Chapter 3 Homework Solutions

P3.6

	q	w	$\Delta U = \Delta H$	ΔS	ΔS_{sur}	ΔS_{tot}
Path (a)	2.74 kJ	-2.74 kJ	0	9.13 J K ⁻¹	-9.13 J K ⁻¹	0
Path (b)	1.66 kJ	-1.66 kJ	0	9.13 J K ⁻¹	-5.53 J K ⁻¹	3.60 J K ⁻¹

Path (a)

$$\begin{aligned}
 w &= -nRT \ln \left(\frac{V_f}{V_i} \right) [3.13] = -nRT \ln \left(\frac{p_i}{p_f} \right) \text{ [Boyle's law]} \\
 &= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \ln \left(\frac{3.00 \text{ atm}}{1.00 \text{ atm}} \right) = -2.74 \times 10^3 \text{ J} \\
 &= \boxed{-2.74 \text{ kJ}}
 \end{aligned}$$

$$\Delta H = \Delta U = \boxed{0} \text{ [isothermal process in perfect gas]}$$

$$q = \Delta U - w = 0 - (-2.74 \text{ kJ}) = \boxed{+2.74 \text{ kJ}}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ [isothermal]} = \frac{2.74 \times 10^3 \text{ J}}{300 \text{ K}} = \boxed{+9.13 \text{ J K}^{-1}}$$

$$\Delta S_{\text{tot}} = \boxed{0} \text{ [reversible process]}$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sur}} = \Delta S_{\text{tot}} - \Delta S = 0 - 9.13 \text{ J K}^{-1} = \boxed{-9.13 \text{ J K}^{-1}}$$

Path (b)

$$\begin{aligned}
 w &= -p_{\text{ex}}(V_f - V_i) = -p_{\text{ex}} \left(\frac{nRT}{p_f} - \frac{nRT}{p_i} \right) = -nRT \left(\frac{p_{\text{ex}}}{p_f} - \frac{p_{\text{ex}}}{p_i} \right) \\
 &= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1}) \times (300 \text{ K}) \times \left(\frac{1.00 \text{ atm}}{1.00 \text{ atm}} - \frac{1.00 \text{ atm}}{3.00 \text{ atm}} \right) \\
 &= -1.66 \times 10^3 \text{ J} = \boxed{-1.66 \text{ kJ}}
 \end{aligned}$$

$$\Delta H = \Delta U = \boxed{0} \text{ [isothermal process in perfect gas]}$$

$$q = \Delta U - w = 0 - (-1.66 \text{ kJ}) = \boxed{+1.66 \text{ kJ}}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ [isothermal]} = \frac{2.74 \times 10^3 \text{ J}}{300 \text{ K}} = \boxed{+9.13 \text{ J K}^{-1}}$$

(Note: One can arrive at this by using q from Path (a) as the reversible path, or one can simply use ΔS from Path (a), realizing that entropy is a state function.)

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}} = \frac{-q}{T_{\text{sur}}} = \frac{-1.66 \times 10^3 \text{ J}}{300 \text{ K}} = \boxed{-5.53 \text{ J K}^{-1}}$$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{sur}} = (9.13 - 5.53) \text{ J K}^{-1} = \boxed{+3.60 \text{ J K}^{-1}}$$

COMMENT. Both $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ changed little over 100 K for this reaction. This is not an uncommon result.

P3.14 Draw up the following table and proceed as in Problem 3.11.

T/K	14.14	16.33	20.03	31.15	44.08	64.81
$(C_{p,m}/T) (\text{J K}^{-2} \text{mol}^{-1})$	0.671	0.778	0.908	1.045	1.063	1.024

T/K	100.90	140.86	183.59	225.10	262.99	298.06
$(C_{p,m}/T) (\text{J K}^{-2} \text{mol}^{-1})$	0.942	0.861	0.787	0.727	0.685	0.659

Plot $C_{p,m}$ against T (Figure 3.2(a)) and $C_{p,m}/T$ against T (Figure 3.2(b)), extrapolating to $T = 0$ with $C_{p,m} = aT^3$ fitted at $T = 14.14 \text{ K}$, which gives $a = 3.36 \text{ mJ K}^{-1} \text{ mol}^{-1}$. Integration by determining the area under the curve then gives

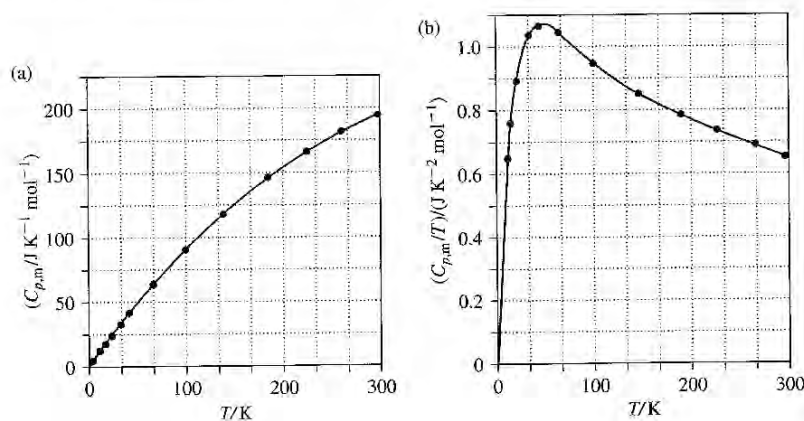


Figure 3.2

$$H_m^\ominus(298 \text{ K}) - H_m^\ominus(0) = \int_0^{298 \text{ K}} C_{p,m} dT = \boxed{34.4 \text{ kJ mol}^{-1}}$$

$$S_m(298 \text{ K}) = S_m(0) + \int_0^{298 \text{ K}} \frac{C_{p,m}}{T} dT = S_m(0) + \boxed{243 \text{ J K}^{-1} \text{ mol}^{-1}}$$

P3.16 The Gibbs–Helmholtz equation [3.52] may be recast into an analogous equation involving ΔG and ΔH , since

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \left(\frac{\partial G_f}{\partial T}\right)_p - \left(\frac{\partial G_i}{\partial T}\right)_p$$

and $\Delta H = H_f - H_i$

Thus,

$$\begin{aligned} \left(\frac{\partial}{\partial T} \frac{\Delta_r G^\ominus}{T} \right)_p &= -\frac{\Delta_r H^\ominus}{T^2} \\ d \left(\frac{\Delta_r G^\ominus}{T} \right) &= \left(\frac{\partial}{\partial T} \frac{\Delta_r G^\ominus}{T} \right)_p dT \text{ [constant pressure]} = -\frac{\Delta_r H^\ominus}{T^2} dT \\ \Delta \left(\frac{\Delta_r G^\ominus}{T} \right) &= -\int_{T_c}^T \frac{\Delta_r H^\ominus}{T^2} dT \\ &\approx -\Delta_r H^\ominus \int_{T_c}^T \frac{dT}{T^2} = \Delta_r H^\ominus \left(\frac{1}{T} - \frac{1}{T_c} \right) \quad [\Delta_r H^\ominus \text{ assumed constant}] \end{aligned}$$

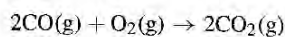
Therefore, $\frac{\Delta_r G^\ominus(T)}{T} - \frac{\Delta_r G^\ominus(T_c)}{T_c} \approx \Delta_r H^\ominus \left(\frac{1}{T} - \frac{1}{T_c} \right)$

$$\Delta_r G^\ominus(T) = \frac{T}{T_c} \Delta_r G^\ominus(T_c) + \left(1 - \frac{T}{T_c} \right) \Delta_r H^\ominus(T_c)$$

and so

$$= \tau \Delta_r G^\ominus(T_c) + (1 - \tau) \Delta_r H^\ominus(T_c) \quad \text{where } \tau = \frac{T}{T_c}$$

For the reaction



$$\begin{aligned} \Delta_r G^\ominus(T_c) &= 2\Delta_f G^\ominus(\text{CO}_2, \text{g}) - 2\Delta_f G^\ominus(\text{CO}, \text{g}) \\ &= [2 \times (-394.36) - 2 \times (-137.17)] \text{ kJ mol}^{-1} = -514.38 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r H^\ominus(T_c) &= 2\Delta_f H^\ominus(\text{CO}_2, \text{g}) - 2\Delta_f H^\ominus(\text{CO}, \text{g}) \\ &= [2 \times (-393.51) - 2 \times (-110.53)] \text{ kJ mol}^{-1} = -565.96 \text{ kJ mol}^{-1} \end{aligned}$$

Therefore, since $\tau = 375/298.15 = 1.258$

$$\begin{aligned} \Delta_r G^\ominus(375 \text{ K}) &= \{(1.258) \times (-514.38) + (1 - 1.258) \times (-565.96)\} \text{ kJ mol}^{-1} \\ &= \boxed{-501 \text{ kJ mol}^{-1}} \end{aligned}$$

P3.18

A graphical integration of $\ln \phi = \int_0^p \left(\frac{Z-1}{p} \right) dp$ [3.60] is performed. We draw up the following table

p/atm	1	4	7	10	40	70	100
$10^3 \left(\frac{Z-1}{p} \right) / \text{atm}^{-1}$	-2.9	-3.01	-3.03	-3.04	-3.17	-3.19	-3.13

The points are plotted in Figure 3.3. The integral is the shaded area, which has the value -0.313 , so at 100 atm

$$\phi = e^{-0.313} = 0.73$$

and the fugacity of oxygen is $100 \text{ atm} \times 0.73 = \boxed{73 \text{ atm}}$

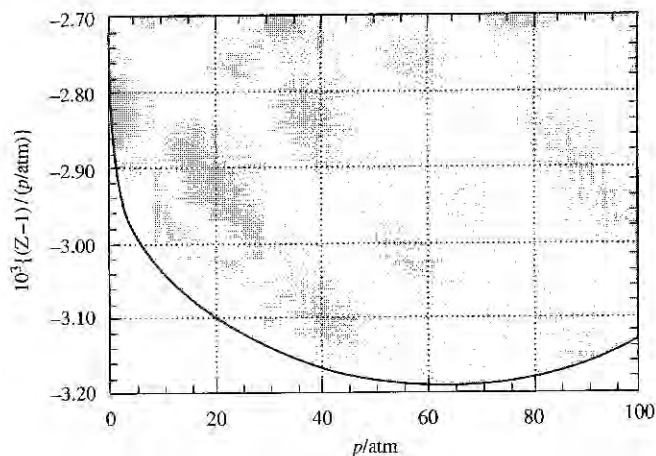


Figure 3.3

Solutions to theoretical problems

- P3.20** Paths A and B in Figure 3.4 are the reversible adiabatic paths which are assumed to cross at state 1. Path C (dashed) is an isothermal path which connects the adiabatic paths at states 2 and 3. Now go round the cycle (1 → 2, step 1; 2 → 3, step 2; 3 → 1, step 3).

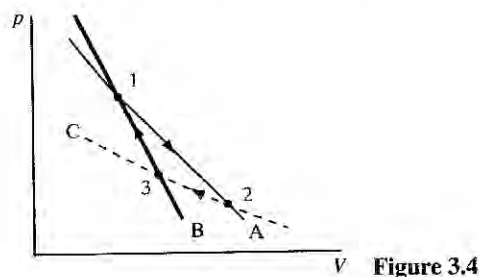


Figure 3.4

$$\text{Step 1} \quad \Delta U_1 = q_1 + w_1 = w_1 \quad [q_1 = 0, \text{adiabatic}]$$

$$\text{Step 2} \quad \Delta U_2 = q_2 + w_2 = 0 \quad [\text{isothermal step, energy depends on temperature only}]$$

$$\text{Step 3} \quad \Delta U_3 = q_3 + w_3 = w_3 \quad [q_3 = 0, \text{adiabatic}]$$

$$\text{For the cycle } \Delta U = 0 = w_1 + q_2 + w_2 + w_3 \text{ or } w(\text{net}) = w_1 + w_2 + w_3 = -q_2$$

$$\text{But, } \Delta U_1 = -\Delta U_3 \quad [\Delta T_1 = -\Delta T_3]; \text{ hence } w_1 = -w_3, \text{ and } w(\text{net}) = w_2 = -q_2, \text{ or } -w(\text{net}) = q_2.$$

Thus, a net amount of work has been done by the system from heat obtained from a heat reservoir at the temperature of step 2, without at the same time transferring heat from a hot to a cold reservoir. This violates the Kelvin statement of the Second Law. Therefore, the assumption that the two adiabatic reversible paths may intersect is disproven.

Question. May any adiabatic paths intersect, reversible or not?

P3.22

$$V = \left(\frac{\partial G}{\partial p} \right)_T \quad [3.50] = \boxed{\frac{RT}{p} + B' + C'p + D'p^2}$$

which is the virial equation of state.

P3.24

We start from the fundamental relation

$$dU = T dS - p dV \quad [3.43]$$

But, since $U = U(S, V)$, we may also write

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

Comparing the two expressions, we see that

$$\left(\frac{\partial U}{\partial S} \right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V} \right)_S = -p$$

These relations are true in general and hence hold for the perfect gas. We can demonstrate this more explicitly for the perfect gas as follows. For the perfect gas at constant volume

$$dU = C_V dT$$

and

$$dS = \frac{dq_{rev}}{T} = \frac{C_V dT}{T}$$

$$\text{Then } \left(\frac{dU}{dS} \right)_V = \left(\frac{\partial U}{\partial S} \right)_V = \frac{C_V dT}{\left(\frac{C_V dT}{T} \right)} = T$$

For a reversible adiabatic (constant-entropy) change in a perfect gas

$$dU = dW = -p dV$$

$$\text{Therefore, } \left(\frac{\partial U}{\partial V} \right)_S = -p$$

P3.26

$$\alpha = \left(\frac{1}{V} \right) \times \left(\frac{\partial V}{\partial T} \right)_p \quad [3.8]; \quad \kappa_T = - \left(\frac{1}{V} \right) \times \left(\frac{\partial V}{\partial p} \right)_T \quad [3.14]$$

$$\begin{aligned}
 \text{(a)} \quad \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \quad \text{[Maxwell relation]} \\
 \left(\frac{\partial p}{\partial T}\right)_V &= -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T \quad \text{[Euler chain relation, Further information 2.2]} \\
 &= -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \quad \text{[reciprocal identity, Further information 2.2]} \\
 &= -\frac{\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T} = \boxed{+\frac{\alpha}{\kappa_T}} \\
 \left(\frac{\partial V}{\partial S}\right)_p &= \left(\frac{\partial T}{\partial p}\right)_S \quad \text{[Maxwell relation]} \\
 \left(\frac{\partial T}{\partial p}\right)_S &= -\left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T \quad \text{[Euler chain]} = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} \quad \text{[reciprocal]}
 \end{aligned}$$

First treat the numerator:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad \text{[Maxwell relation]} = -\alpha V$$

As for the denominator, at constant p

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT \quad \text{and} \quad dS = \frac{dq_{\text{rev}}}{T} = \frac{dH}{T} = \frac{C_p dT}{T} \quad [dq_p = dH]$$

$$\text{Therefore, } \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad \text{and} \quad \left(\frac{\partial V}{\partial S}\right)_p = \boxed{\frac{\alpha TV}{C_p}}$$

$$\begin{aligned}
 \text{(b)} \quad \left(\frac{\partial p}{\partial S}\right)_V &= -\left(\frac{\partial T}{\partial V}\right)_S \quad \text{[Maxwell relation]} \\
 -\left(\frac{\partial T}{\partial V}\right)_S &= \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial S}\right)_T} \quad \text{[Euler chain]} = \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} \quad \text{[reciprocal]}
 \end{aligned}$$

$$\begin{aligned}
&= \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V} \text{ [Maxwell relation]} = \frac{-\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V} \text{ [Euler chain]} \\
&= \frac{-\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial U}{\partial T}\right)_V} \text{ [reciprocal identity, twice]} = \boxed{\frac{\alpha T}{\kappa_T C_V}} \left[\left(\frac{\partial U}{\partial S}\right)_V = T \right]
\end{aligned}$$

P3.28 First use an identity of partial derivatives that involves a change of variable

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_S$$

We will be able to identify some of these terms if we examine an expression for dH analogous to the fundamental equation [3.43]. From the definition of enthalpy, we have:

$$dH = dU + p dV + V dp = T dS - p dV [3.43] + p dV + V dp = T dS + V dp$$

Compare this expression to the exact differential of H considered as a function of S and p :

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

$$\text{Thus, } \left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_S = V \text{ [dH exact]}$$

$$\text{Substitution yields } \left(\frac{\partial H}{\partial p}\right)_T = T \left(\frac{\partial S}{\partial p}\right)_T + V = \boxed{-T \left(\frac{\partial V}{\partial T}\right)_p + V} \text{ [Maxwell relation]}$$

(a) For $pV = nRT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}, \text{ hence } \left(\frac{\partial H}{\partial p}\right)_T = \frac{-nRT}{p} + V = \boxed{0}$$

(b) For $p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$ [Table 1.7]

Because we cannot express V in closed form as a function of T , we solve for T as a function of V and evaluate

$$\left(\frac{\partial H}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p + V = \frac{-T}{\left(\frac{\partial T}{\partial V}\right)_p} + V \text{ [reciprocal identity]}$$

$$T = \frac{p(V - nb)}{nR} + \frac{na(V - nb)}{RV^2}$$

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V - nb)}{RV^3}$$

Therefore, $\mu_{\text{J}}C_V = p - \frac{\alpha T}{\kappa_T}$

P3.32

$$\kappa_S = -\left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V\left(\frac{\partial p}{\partial V}\right)_S}$$

The only constant-entropy changes of state for a perfect gas are reversible adiabatic changes, for which

$$pV^\gamma = \text{const}$$

$$\text{Then, } \left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial}{\partial V} \frac{\text{const}}{V^\gamma}\right)_S = -\gamma \times \left(\frac{\text{const}}{V^{\gamma+1}}\right) = \frac{-\gamma p}{V}$$

$$\text{Therefore, } \kappa_S = \frac{-1}{V\left(\frac{-\gamma p}{V}\right)} = \frac{+1}{\gamma p}$$

Hence, $p\gamma\kappa_S = +1$

P3.34

The starting point for the calculation is eqn 3.60. To evaluate the integral, we need an analytical expression for Z , which can be obtained from the equation of state.

- (a) We saw in Section 1.4 that the van der Waals coefficient a represents the attractions between molecules, so it may be set equal to zero in this calculation. When we neglect a in the van der Waals equation, that equation becomes

$$p = \frac{RT}{V_m - b}$$

and hence

$$Z = 1 + \frac{bp}{RT}$$

The integral in eqn 3.60 that we require is therefore

$$\ln \phi = \int_0^p \left(\frac{Z-1}{p}\right) dp = \int_0^p \left(\frac{b}{RT}\right) dp = \frac{bp}{RT}$$

Consequently, from eqns 3.60 and 3.59, the fugacity at the pressure p is

$$f = pe^{bp/RT}$$

From Table 1.6, $b = 3.71 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$, so $pb/RT = 1.516 \times 10^{-2}$, giving

$$f = (10.00 \text{ atm}) \times e^{0.01515} = 10.2 \text{ atm}$$

COMMENT. The effect of the repulsive term (as represented by the coefficient b in the van der Waals equation) is to increase the fugacity above the pressure, and so the effective pressure of the gas—its “escaping tendency”—is greater than if it were perfect.

(b) When we neglect b in the van der Waals equation we have

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

and hence

$$Z = 1 - \frac{a}{RTV_m}$$

Then substituting into eqn 3.60 we get

$$\ln \phi = \int_0^p \left(\frac{Z-1}{p} \right) dp = \int_0^p \frac{-a}{pRTV_m} dp$$

In order to perform this integration we must eliminate the variable V_m by solving for it in terms of p . Rewriting the expression for p in the form of a quadratic we have

$$V_m^2 - \frac{RT}{p} V_m + \frac{a}{p} = 0$$

The solution is

$$V_m = \frac{1}{2} \left(\frac{RT}{p} \pm \frac{1}{p} \sqrt{(RT)^2 - 4ap} \right)$$

Applying the approximation $(RT)^2 \gg 4ap$ we obtain

$$V_m = \frac{1}{2} \left(\frac{RT}{p} \pm \frac{RT}{p} \right)$$

Choosing the + sign we get

$$V_m = \frac{RT}{p} \text{ which is the perfect-gas volume.}$$

Then

$$\ln \phi = \int_0^p -\frac{a}{(RT)^2} dp = \boxed{-\frac{ap}{(RT)^2}}$$

For ammonia $a = 4.169 \text{ atm dm}^6 \text{ mol}^{-2}$

$$\ln \phi = -\frac{4.169 \text{ atm dm}^3 \text{ mol}^{-1} \times 10.00 \text{ atm}}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})^2} = -0.06965$$

$$\phi = 0.9237 = \frac{f}{p}$$

$$f = \phi p = 0.9237 \times 10.00 \text{ atm} = \boxed{9.237 \text{ atm}}$$

Solutions to applications

P3.36 Taking the hint, we have

$$\Delta_{\text{trs}} S^{\ominus}(25^{\circ}\text{C}) = \Delta S_i + \Delta S_{\text{ii}} + \Delta S_{\text{iii}}$$