物理化學 (II) 第一次小考 (100%)  2007/11/05  姓名：KEY

R = 8.3145 J/K-mol; C_v(ideal gas) = 3R/2; C_p(ideal gas) = 5R/2; 1 atm = 1.01325 bar

一、推導題 40%
1. Show that the following functions have exact differentials:
   (a) \( x^2y + 3y^2 \), (b) \( x \cos xy \), (c) \( x^3y^2 \)

   Answer: A function has an exact differential if and only if its mixed partial derivatives are equal. That is, \( f(x, y) \) has an exact differential if and only if

\[
\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}
\]

(a) \[
\frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)_{xy} = \frac{\partial}{\partial y} (2xy) = 2x \quad \text{exact}
\]

(b) \[
\frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)_{xy} = \frac{\partial}{\partial y} (\cos xy - xy \sin xy) = -2x \sin xy - x^2y \cos xy
\]

(c) \[
\frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)_{xy} = 3x^2y^2 \quad \text{exact}
\]

2. (a) Write expressions for \( dV \) and \( dp \) given that \( V \) is a function of \( p \) and \( T \) and \( p \) is a function of \( V \) and \( T \). (b) Deduce expressions for \( d \ln V \) and \( d \ln p \) in terms of the expansion coefficient \( \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \) and the isothermal compressibility.

\[
\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T
\]

Answer: \( V = f(p, T) \); hence

\[
dV = \left( \frac{\partial V}{\partial p} \right)_V dp + \left( \frac{\partial V}{\partial T} \right)_p dT \quad \text{or}
\]

\[
d\ln V = \frac{dV}{V} = \left( \frac{\partial V}{\partial p} \right)_V dp + \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p dT = -\kappa_T dp + \alpha dT
\]
(b) \( p = f(V,T) \); hence
\[
\frac{dp}{p} = \left( \frac{\partial p}{\partial V} \right)_T dV + \left( \frac{\partial p}{\partial T} \right)_V dT
\]
or
\[
d \ln p = \frac{1}{p} \left( \frac{\partial p}{\partial V} \right)_T dV + \frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_V dT
\]
since
\[
\left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial p}{\partial V} \right)_T = -1 \quad \text{so} \quad \left( \frac{\partial p}{\partial T} \right)_V = -\left( \frac{\partial V}{\partial p} \right)_T \quad \frac{\partial T}{p_T} = \frac{\alpha}{\kappa_T}
\]
and
\[
d \ln p = \frac{1}{p} \left( -\frac{1}{\kappa_T} \right)_T dV + \frac{1}{p} \left( \frac{\alpha}{\kappa_T} \right)_T dT = \frac{1}{p} \left( \frac{\alpha dT - d\ln V} {\kappa_T} \right)
\]

3. The thermodynamic equation of state \( \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p \) was quoted in the chapter. Derive its partner \( \left( \frac{\partial H}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p + V \) from it and the general relations between partial differentials.

Answer:
\[
\left( \frac{\partial H}{\partial p} \right)_T = \left( \frac{\partial U}{\partial p} \right)_T + \left( \frac{\partial pV}{\partial p} \right)_T = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial p} \right)_T + \left[ V \left( \frac{\partial p}{\partial p} \right)_T + p \left( \frac{\partial V}{\partial p} \right)_T \right]
\]
\[
= T \left( \frac{\partial p}{\partial T} \right)_V - p \left( \frac{\partial V}{\partial p} \right)_T + V + p \left( \frac{\partial V}{\partial p} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial V}{\partial p} \right)_T - p \left( \frac{\partial V}{\partial p} \right)_T + V + p \left( \frac{\partial V}{\partial p} \right)_T
\]
\[
= T \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_V + V = -T \left( \frac{\partial V}{\partial T} \right)_p + V \quad \text{as} \quad \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_p = -1
\]

4. The barometric formula relates the pressure of a gas of molar mass \( M \) at an altitude \( h \) to its pressure \( p_0 \) at sea level. Derive this relation \( p = p_0 e^{-Mg h/RT} \) by showing that the change in pressure \( dp \) for an infinitesimal change in altitude \( dh \) where the density is \( \rho \) is \( dp = -\rho gdh \). Remember that \( \rho \) depends on the pressure.

Answer: 在忽略重力效應的等溫氣柱中,任一高度 \( h \) 的壓降等於質量,高度差與重力加速度的乘績. (\( h=0, p=p_0 \))
\[
\rho \frac{M}{V} = \frac{PM}{RT}
\]
\[
dP = -\rho g dh = -\frac{PM}{RT} g dh \quad \text{and} \quad \frac{dP}{P} = -\frac{Mg}{RT} dh \quad \text{so} \quad \frac{P}{p_0} \frac{dP}{P} = -\frac{Mg}{RT} dh
\]
\[
\ln \frac{P}{P_0} = -\frac{Mg}{RT} h \quad \frac{P}{P_0} = e^{-\frac{Mg h}{RT}} \quad P = p_0 e^{-\frac{Mg h}{RT}}
二、計算題 60%

1. Use the van der Waals parameters for hydrogen sulfide to calculate approximate values of (a) the Boyle temperature of the gas and (b) the radius of a H₂S molecule regarded as a sphere \((a = 4.484 \text{ dm}^6 \text{ atm mol}^{-2}, b = 0.0434 \text{ dm}^3 \text{ mol}^{-1})\).

Answer:

(a) The Boyle temperature is the temperature at which \(\lim_{v_n\to\infty} \frac{dZ}{d(1/V_m)}\) vanishes. According to the van der Waals equation

\[
Z = \frac{\rho V_m}{RT} = \left(\frac{RT}{V_n-b} - \frac{a}{V_n^2}\right) V_m = \frac{V_m}{V_m-b} - \frac{a}{V_m RT}
\]

so \(\frac{dZ}{d(1/V_m)} = \left(\frac{dZ}{dV_m}\right) \times \left(\frac{dV_m}{d(1/V_m)}\right)\)

\[
= -V_m^2 \frac{dZ}{dV_m} = -V_m^2 \left(\frac{-V_m}{(V_m-b)^2} + \frac{1}{V_m-b} + \frac{a}{V_m^2 RT}\right)
\]

\[
= \frac{V_m^2 b - a}{(V_m-b)^2 RT}
\]

In the limit of large molar volume, we have

\[
\lim_{v_n\to\infty} \frac{dZ}{d(1/V_m)} = b - \frac{a}{RT} = 0 \quad \text{so} \quad \frac{a}{RT} = b
\]

and \(T = \frac{a}{Rb} = \frac{(4.484 \text{ L}^2 \text{ atm mol}^{-2})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (0.0434 \text{ L mol}^{-1})} = 1259 \text{ K}\)

(b) By interpreting \(b\) as the excluded volume of a mole of spherical molecules, we can estimate the size of a molecule.

\[
b = \frac{1}{2 N_A} \left[\frac{4\pi(2r)^3}{3}\right] = 4 V_{molecule} N_A
\]

\[
r = \left(\frac{3b}{16\pi N_A}\right)^{1/3} = \left[\frac{3 \times 0.0434 \text{ dm}^3 \text{ mol}^{-1}}{16 \times 3.1416 \times 6.022 \times 10^{23}}\right]^{1/3} = 1.63 \times 10^{-9} \text{ dm} = 0.163 \text{ nm}
\]

2. A vessel of volume 22.4 dm³ contains 2.0 mol H₂ and 1.0 mol N₂ at 273.15 K initially. All the H₂ reacted with sufficient N₂ to form NH₃. Calculate the partial pressures and the total pressure of the final mixture.

Answer: \(3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3\)

<table>
<thead>
<tr>
<th></th>
<th>initial /mol</th>
<th>final /mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2)</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>1.0</td>
<td>1/3</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>0</td>
<td>4/3</td>
</tr>
</tbody>
</table>

(a) Mole fractions are \(x(\text{H}_2) = 0\) \(x(\text{N}_2) = 1/5 = 0.2\) \(x(\text{NH}_3) = 4/5 = 0.8\)
\[ p_i = x_i p = x_i \left( \frac{nRT}{V} \right) \]

(b) \[ p = \left( \frac{13/4}{3} \right) \text{mol} \times \left( \frac{0.08206 \text{ dm}^3 \text{ atm} \text{ K}^{-1} \text{ mol}^{-1}}{22.4 \text{ dm}^3} \right) x (273.15 \text{ K}) = 1.67 \text{ atm} \]

\[ p(\text{H}_2) = 0, \quad p(\text{N}_2) = 0.2p = 0.33 \text{ atm}, \quad p(\text{NH}_3) = 0.8p = 1.33 \text{ atm} \]

3. A gas at 250 K and 15 atm has a molar volume 12 per cent smaller than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

Answer: The compression factor \( Z \) is \( Z = \frac{pV_m}{RT} = \frac{V_m(\text{real})}{V_m(\text{ideal})} \)

(a) Because \( V_m(\text{real}) = (1-0.12) x V_m(\text{ideal}) \), we have \( Z = 0.88 \)

(b) The molar volume is \( V_m = 0.88 x V_m(\text{ideal}) = 0.88 \times (\text{RT/p}) = \)

\[ = 0.88 \times \left( \frac{0.08206 \text{ dm}^3 \text{ atm} \text{ K}^{-1} \text{ mol}^{-1}}{15 \text{ atm}} \right) x (250 \text{ K}) = 1.2 \text{ dm}^3 \text{ mol}^{-1} \]

4. A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm\(^3\) to 31.7 dm\(^3\) (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate \( q \), \( w \), \( \Delta U \), and \( \Delta H \).

Answer:

For a perfect gas at constant temperature

\[ \Delta U = 0 \] so \( q = -w \)

For a perfect gas at constant temperature, \( \Delta H \) is also zero

\[ dH = d(U + pV) \]

\( U \) does not change at constant temperature; nor does \( pV \) if the gas obeys Boyle’s law. These apply to all three cases below.

(a) Isothermal reversible expansion: \( w = -nRT \ln \left( \frac{V_f}{V_i} \right) \)

\[ w = -2.0 \times 8.3145 \times 295.15 \times \ln(31.7/22.8) = -1.62 \times 10^3 \text{ J} \]

(b) Expansion against a constant external pressure:

\[ w = -p_{ex}V = -nRT/V_i(V_f - V_i) \]

\[ w = -2.0 \times 8.3145 \times 295.15 \times (1 - (22.8/31.7)) = -1.38 \times 10^3 \text{ J} \]
Free expansion is expansion against no force, so \( w = 0 \) J, and \( q = -w = 0 \) J.

5. A sample consisting of 1.0 mol of perfect gas molecules with \( C_v = 20.8 \) J K\(^{-1}\) is initially at 3.25 atm and 310 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.

Answer: For reversible adiabatic expansion \( P_f V_f^\gamma = P_i V_i^\gamma \) so \( V_f = V_i (P_i / P_f)^{1/\gamma} \)

\[ V_f = \frac{V_i (P_i / P_f)^{1/\gamma}}{1.0 \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{mol}^{-1} \times 310 \text{ K}} \times (3.25 \text{ atm} / 2.50 \text{ atm})^{1/1.40} = 0.00944 \text{ m}^3 \]

\[ T_f = \frac{P_f V_f}{nR} = \frac{(2.50 \text{ atm}) \times (310 \text{ K} \times 101325 \text{ Pa} \times \text{atm}^{-1}) \times (0.00944 \text{ m}^3)}{1.0 \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{mol}^{-1}} = 288 \text{K} \]

\[ w = n C_v \Delta T = (1.0 \text{ mol}) \times (20.8 \text{ J K}^{-1} \text{mol}^{-1}) \times (288 \text{ K} - 310 \text{ K}) = -466 \text{ J} \]

6. The standard enthalpy of combustion of cyclopropane is \(-2091\) kJ mol\(^{-1}\) at 25°C. The enthalpy of formation for \( \Delta_f H^\circ (\text{CO}_2, \text{g}) = -393.51 \text{ kJ mol}^{-1} \) and \( \Delta_f H^\circ (\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ mol}^{-1} \), calculate the enthalpy of formation of cyclopropane. The enthalpy of formation of propene is \( \Delta_f H^\circ (\text{C}_3\text{H}_6, \text{g}) = +20.42 \text{ kJ mol}^{-1} \). Calculate the enthalpy of isomerization of cyclopropane to propene.

\[(1) \quad \text{(CH}_2\text{)}_3(\text{g}) + 9/2 \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 3 \text{ H}_2\text{O}(\text{l}) \quad \Delta_f H^\circ = -2091 \text{ kJ mol}^{-1} \]
\[(2) \quad \text{H}_2(\text{g}) + \frac{1}{2} \text{ O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{1}) \quad \Delta_f H^\circ = -285.83 \text{ kJ mol}^{-1} \]
\[(3) \quad \text{C(s, graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta_f H^\circ = -393.51 \text{ kJ mol}^{-1} \]
\[(4) \quad \text{(CH}_2\text{)}_3(\text{g}) \rightarrow \text{C}_3\text{H}_6 (\text{g}) \quad \Delta_f H^\circ = ? \text{ kJ mol}^{-1} \]

Answer: For reaction \((5)\) \( 3\text{C(s, graphite)} + 3\text{H}_2(\text{g}) \rightarrow (\text{CH}_2\text{)}_3(\text{g}) \quad \Delta_f H^\circ (\text{CH}_2\text{)}_3(\text{g}) \)

We have reaction \((5) = 3 \times \) reaction \((2) + 3 \times \) reaction \((3) - \) reaction \((1) \)

Thus, \( \Delta_f H^\circ (\text{CH}_2\text{)}_3(\text{g}) = -\Delta_f H^\circ (\text{CH}_2\text{)}_3(\text{g}) + 3 \times \Delta_f H^\circ (\text{H}_2\text{O}, \text{l}) + 3 \times \Delta_f H^\circ (\text{CO}_2, \text{g}) \)

\[= (2091) + 3 \times (-393.51) + 3 \times (-285.83) \text{ kJ mol}^{-1} = +53 \text{ kJ mol}^{-1} \]

For reaction \((4)\) \( \Delta_f H^\circ = \Delta_f H^\circ (\text{C}_3\text{H}_6, \text{g}) - \Delta_f H^\circ (\text{(CH}_2\text{)}_3(\text{g}) \)

\[= (20.42 - 53) \text{ kJ mol}^{-1} = -33 \text{ kJ mol}^{-1} \]