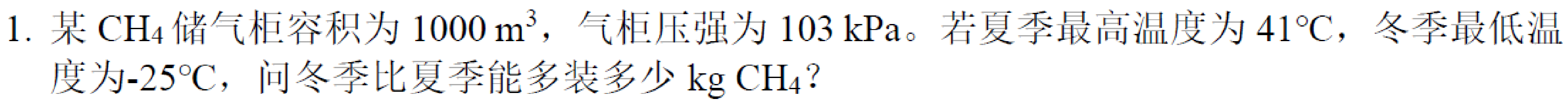
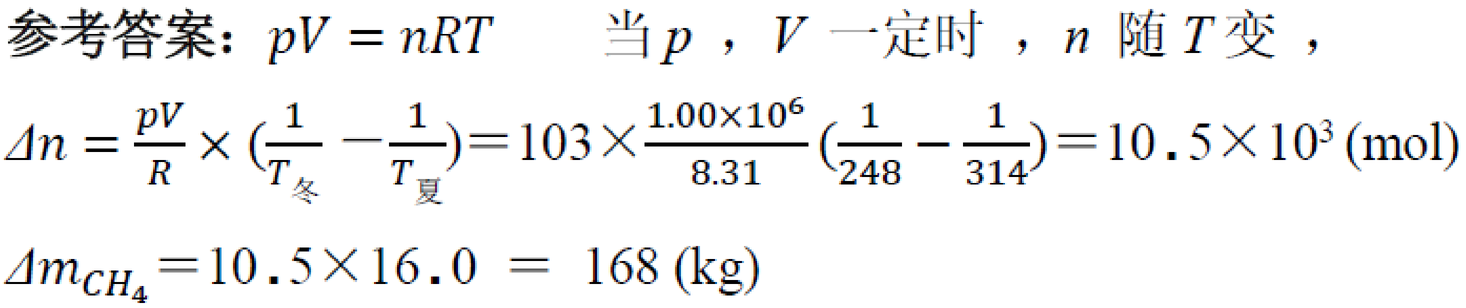
第一次习题课

钱培森 PB18000198

习题讲解



1. 某 CH_4 储气柜容积为 1000 m^3，气柜压强为 103 kPa。若夏季最高温度为 41°C，冬季最低温度为-25°C，问冬季比夏季能多装多少 kg CH_4?



参考答案：$pV = nRT$ 当 p，V 一定时，n 随 T 变，

$$\Delta n = \frac{pV}{R}\times\left(\frac{1}{T_{\text{冬}}}-\frac{1}{T_{\text{夏}}}\right)=103\times\frac{1.00\times10^{6}}{8.31}\left(\frac{1}{248}-\frac{1}{314}\right)=10.5\times10^{3}\ (\text{mol})$$

$$\Delta m_{CH_4}=10.5\times16.0 = 168\ (\text{kg})$$

$$pV = nRT$$ 分体积，分压？

$$\boxed{p_AV_A = n_ART}$$

在 25℃时，1.000 L 体积中含有 0.5000 mol N_2 。

② 用理想气体状态方程计算该气体的压力；

② 用范德华方程计算该气体的压力；（已知 $a=140.8\ \mathrm{kPa\cdot L^2\cdot mol^{-2}}$ ，$b = 0.03913\ \mathrm{L\cdot mol^{-1}}$ ）

③ 计算用理想气体状态方程求得该气体的压力的相对偏差 d_r 。

参考答案： ① **按理想气体状态方程计算该气体的压力：**

$$p_{N_2}=\frac{0.5000\times8.314\times298.15}{1.000\times10^{-3}}=\mathbf{1239\ (kPa)}$$

② **按范德华方程计算该气体的压力：**

$$\because\quad \boxed{\left(p+\frac{an^2}{V^2}\right)(V-n\mathrm{b})=nRT}$$

$$p_{N_2}=\frac{0.5000\times8.314\times298.15}{1.000\times10^{-3}-0.5000\times0.03913\times10^{-3}}-\frac{140.8\times10^{-3}\times(0.5000)^2}{(1.000\times10^{-3})^2}=\mathbf{1229\ (kPa)}$$

6. The correction of ideal gases is

$$\left(p+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

Try to illustrate the correction in detail.

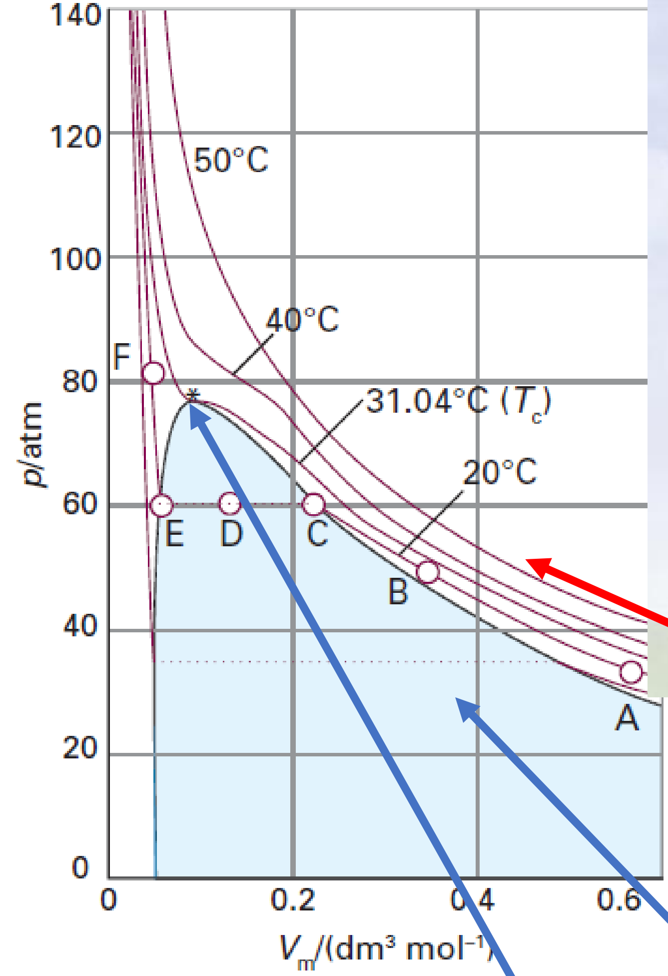
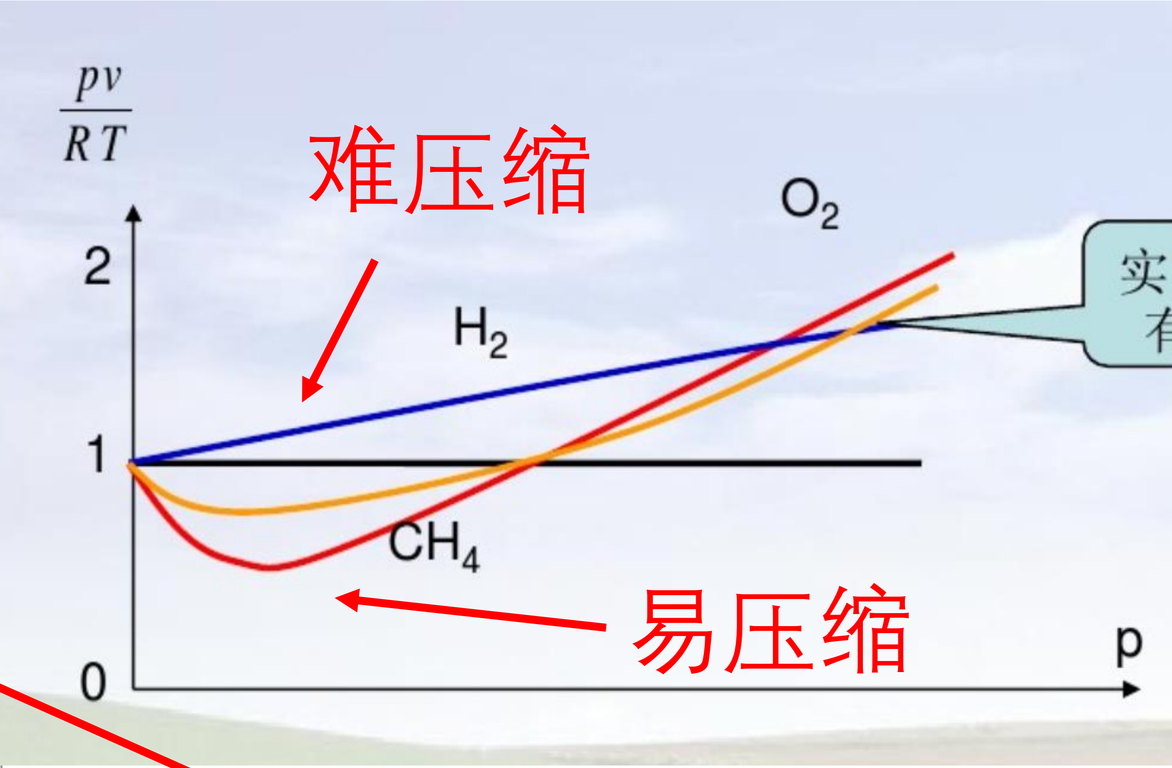


Fig. 1.15 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.04°C. The critical point is marked with a star.



难压缩

易压缩

同一条曲线上温度恒定

液态区

临界温度 T_c ,临界点 V_c, p_c

3、临界参数和范德瓦尔方程：

在临界点处：$(\frac{\partial p}{\partial v})_{T_c} = 0$ $(\frac{\partial^2 p}{\partial v^2})_{T_c} = 0$

$$\Rightarrow \begin{cases} -\frac{RT_c}{(v_c-b)^2}+\frac{2a}{v_c^{\ 3}}=0 \\ -\frac{2RT_c}{(v_c-b)^3}+\frac{6a}{v_c^{\ 4}}=0 \end{cases}$$

得：$p_c=a/27b^2$ $T_c=8a/27Rb$ $V_m=3b$

或

$$a=\frac{27R^2T_C^2}{64p_c} \qquad b=\frac{RT_C}{8p_C} \qquad R=\frac{8p_cv_c}{3T_c}$$

理想气体pV，$\langle v^2 \rangle$的关系的推导

Define

$$\mathcal{N} = \frac{total\ \ molecule\ \ number}{total\ \ volume}$$

The molecule rebounds elastically (without losing energy), the total momentum change is $2mv_x$. Therefore, for the total number of collisions,

$$F\Delta t = \left(\frac{1}{2}\mathcal{N}Av_x\Delta t\right)(2mv_x)$$

where A is the area of the collision wall and 1/2 is because half of the molecules move toward the wall. With

$$p = \frac{F}{A}$$

We obtain

$$p = \mathcal{N}mv_x^2$$

Of course, not all molecules will be travelling with the same velocity v_x. Now let us simply assume that the pressure will be proportional to the to the average of the square of the velocity in x direction, therefore

$$p = \mathcal{N} m \langle v_x^2 \rangle$$

Therefore

$$p = \frac{1}{3} \mathcal{N} m \langle v^2 \rangle$$

With

$$\mathcal{N} = \frac{n N_A}{V}$$

$$pV = \frac{1}{3} n N_A m \langle v^2 \rangle \tag{1}$$

With

$$\langle \varepsilon \rangle = \frac{1}{2} m \langle v^2 \rangle$$

Another way to write eqn (equation) (1) is

$$pV = \frac{2}{3} n N_A \langle \varepsilon \rangle \tag{2}$$

$$F(v_x) = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{mv_x^2}{2kT}} \qquad (5)$$

$$F(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} \qquad (6)$$

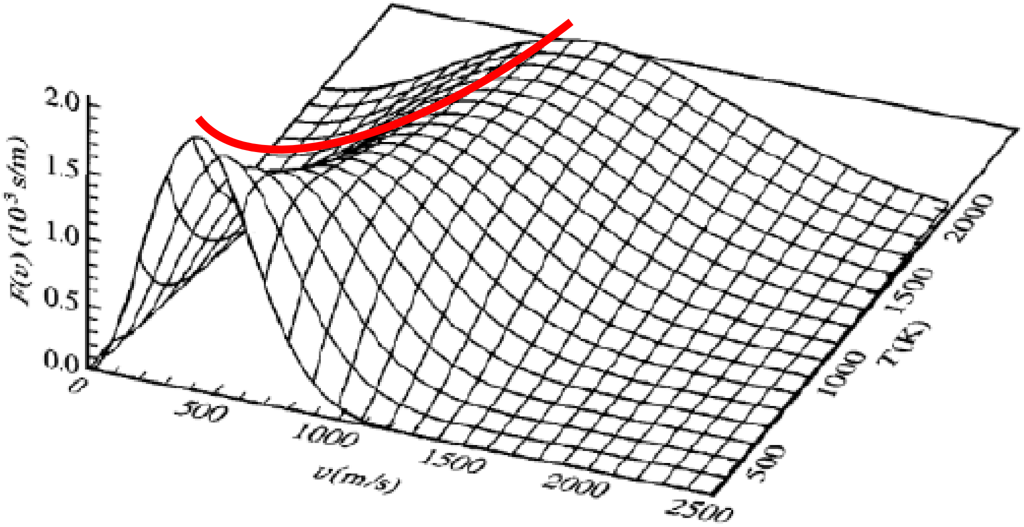


Figure 1 Maxwell distribution function related to T(temperature) and v(velocity, speed).

1. Try to derive Clausius-Clapeyron eqation

$$\boxed{\frac{d\ln p}{dT} = \frac{\Delta_{vap}H_m}{RT^2}}$$

$$\ln\frac{p_2}{p_1} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\boxed{\lg p} = A\left(\frac{1}{T}\right) + B$$

ln

气液共存⇒蒸气压等于饱和蒸气压

全部气化共存⇒蒸气压另行计算

写不出来的时候就列 $pV = nRT$

Bonus

1.设在一定的压力和温度下，某物质的两个相呈平衡。若温度改变 $\mathrm{d}T$，相应地压力改变 $\mathrm{d}p$ 后，两相仍呈平衡。根据在等温、等压下平衡时$\Delta G = 0$的条件。

因为$G_1 = G_2$，所以

$$\mathrm{d}G_1 = \mathrm{d}G_2$$

又根据热力学的基本公式，$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$，得

$$-S_1\mathrm{d}T + V_1\mathrm{d}P = -S_2\mathrm{d}T + V_2\mathrm{d}p$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta H}{T\Delta V}$$

（因为有$\Delta H = \Delta G - T\Delta S$）

上式称为 Clapeyron 方程式。这一公式可应用于任何纯物质的两相平衡系统。例如，对于气-液两相平衡，设有 1mol 物质发生了相的变化，则

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{T\Delta_{\mathrm{vap}}V_{\mathrm{m}}}$$

同理，对于液-固两相平衡为

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}}{T\Delta_{\mathrm{fus}}V_{\mathrm{m}}}$$

对于有气体参加的两相平衡，固体和液体的体积与气体相比，前者可以忽略不计，Clapeyron 方程式可进一步简化。以气-液两相平衡为例，若再假定蒸气是理想气体，则

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\mathrm{vap}}H}{TV_{(g)}}=\frac{\Delta_{\mathrm{vap}}H_m}{T\left(\frac{nRT}{p}\right)}$$

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T}=\frac{\Delta_{\mathrm{vap}}H_m}{RT^2}$$

假设液体摩尔蒸发焓与温度无关，或者因温度变化范围很小。

积分得

$$\ln p=-\frac{\Delta_{\mathrm{vap}}H_m}{R}\cdot\frac{1}{T}+C'$$

或做定积分

$$\int_{p_1}^{p_2}\mathrm{d}\ln p=\int_{T_1}^{T_2}\frac{\Delta_{\mathrm{vap}}H_m}{RT^2}\mathrm{d}T$$

$$\ln\frac{p_2}{p_1}=\frac{\Delta_{\mathrm{vap}}H_m}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

dG=-SdT+Vdp

固定温度，那么dG=Vdp

利用pV = nRT外推

$$\Delta G = nRTln\frac{p_2}{p_1}$$

规定标准值，就有

$$G = G^{\ominus} + nRTln\frac{p}{p^{\ominus}}$$

范特霍夫等温式：

$$\boxed{\Delta_r G_m = \Delta_r G_m^{\ominus} + RTln\prod_i \left(\frac{p_i}{p^{\ominus}}\right)^{\xi_i}}$$

!!!!!!!!!!!!!!!!!!很重要！！！即将学习!

2. **解 1：**

$$\Delta_r G_m = \Delta_r G_m^\theta + RT\ln Q$$

$$Q = \prod_B \left(\frac{p_B}{p^\theta}\right)^{\upsilon_B} = \frac{\left(\frac{p_G}{p^\theta}\right)^g \left(\frac{p_H}{p^\theta}\right)^h \cdots}{\left(\frac{p_D}{p^\theta}\right)^d \left(\frac{p_E}{p^\theta}\right)^e \cdots}$$

对于相变$A_{(l)} \Longleftrightarrow A_{(g,p_1)}$

$$\Delta_r G_m = \Delta_r G_m^\theta + RT_1\ln\frac{p_1}{p^\theta}$$

等温等压下平衡，故有$\Delta_r G_m = 0$。即

$$\Delta_r G_m^\theta = -RT_1\ln\frac{p_1}{p^\theta}$$

而又根据$\Delta H = \Delta G - T\Delta S$，有

$$-RT_1\ln\frac{p_1}{p^\theta} = \Delta_r H_m + T_1\Delta_r S_m$$

而又根据$\Delta H = \Delta G - T\Delta S$，有

$$-RT_1\ln\frac{p_1}{p^\theta} = \Delta_r H_m + T_1\Delta_r S_m$$

同理,对于相变$A_{(l)} \Longleftrightarrow A_{(g,p_2)}$，有

$$-RT_2\ln\frac{p_2}{p^\theta} = \Delta_r H_m + T_2\Delta_r S_m$$

即有

$$\Delta_r S_m = -R\ln\frac{p_1}{p^\theta} + \frac{\Delta_r H_m}{T_1}$$

$$\Delta_r S_m = -R\ln\frac{p_2}{p^\theta} + \frac{\Delta_r H_m}{T_2}$$

$$\ln\frac{p_2}{p_1} = \frac{\Delta_{\text{vap}} H_m}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Q&A