热力学与统计物理作业

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在 p-v 图上将范德瓦耳斯气体不同温度的等温线上的极大点与极小点连成一条曲线, 证明这条曲线的方程为

$$pv^3 = a(v-2b)$$

式中 v 为气体的摩尔体积, 并说明这条曲线分割的区域 I、II、III 的意义。

解: 对物质量为 n 的范德瓦耳斯方程为

$$\left(P+\frac{a}{v^2}\right)(v-b)=RT$$

即

$$P=\frac{RT}{v-b}-\frac{a}{v^2}$$

可得

$$\left(\frac{\partial P}{\partial v}\right)_T=-\frac{RT}{(v-b)^2}+\frac{2a}{v^3}$$

等温线的极大与极小值点满足

$$\left(\frac{\partial P}{\partial v}\right)_T=0$$

得

$$\frac{RT}{(v-b)^2}=\frac{2a}{v^3}$$

联立范德瓦耳斯方程, 可得

$$Pv^3=2a(v-b)-av=a(v-2b)$$

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证明处于两相平衡的单元系, 有下式成立:

$$\frac{C_V}{\kappa_S}=Tv\left(\frac{dp}{dT}\right)^2$$

其中, 等熵压缩率定义为 $\kappa_S=-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_S$.

解:

$$C_V=T\left(\frac{\partial S}{\partial T}\right)_V \quad \kappa_S=-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_S$$

故

$$\frac{C_V}{\kappa_S} = \frac{T(\partial S/\partial T)_V}{-(1/v)(\partial v/\partial p)_S} = -Tv\frac{(\partial S/\partial T)_V}{(\partial v/\partial p)_S}$$

利用关系 $\left(\frac{\partial v}{\partial p}\right)_S = \left(\frac{\partial v}{\partial T}\right)_S \left(\frac{\partial T}{\partial p}\right)_S$:

$$\frac{C_V}{\kappa_S} = -Tv\frac{(\partial S/\partial T)_V}{(\partial v/\partial T)_S(\partial T/\partial p)_S} = -Tv\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial v}\right)_S \left(\frac{\partial p}{\partial T}\right)_S$$

由麦克斯韦关系 $\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$:

$$\frac{C_V}{\kappa_S} = -Tv\left(\frac{\partial S}{\partial T}\right)_V \left(-\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial p}{\partial T}\right)_S = Tv\left[\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial p}{\partial S}\right)_V\right] \left(\frac{\partial p}{\partial T}\right)_S$$

利用链式法则 $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V$:

$$\frac{C_V}{\kappa_S} = Tv\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial p}{\partial T}\right)_S$$

$$= Tv\left(\frac{\partial p}{\partial T}\right)_V^2$$

两相平衡时, $p = p(T)$, 压力只是温度的函数, 偏导数等于全导数。故

$$\frac{C_V}{\kappa_S} = Tv\left(\frac{dp}{dT}\right)^2$$

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证明: 在用克拉珀龙方程描述相变过程中, 内能的变化为

$$u_2 - u_1 = L\left(1 - \frac{d\ln T}{d\ln p}\right)$$

解: 相变过程中, $\Delta U, \Delta H, \Delta V$ 满足关系 $\Delta U = \Delta H - P\Delta V$. 由克拉珀龙方程 $\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$. 得 $\Delta V = \frac{\Delta H}{T(dp/dT)}$. 故

$$\Delta U = \Delta H - P\Delta V = \Delta H - P\frac{\Delta H}{T(dp/dT)} = \Delta H\left(1 - \frac{P}{T}\frac{dT}{dp}\right)$$

注意到 $\frac{d\ln T}{d\ln p} = \frac{dT/T}{dp/p} = \frac{p}{T}\frac{dT}{dp}$.

$$\Delta U = \Delta H\left(1 - \frac{d\ln T}{d\ln p}\right)$$

考虑 $\Delta H = L$ (L 为相变潜热). 可得

$$u_2 - u_1 = L\left(1 - \frac{d\ln T}{d\ln p}\right)$$

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设气体的物态方程如下所示:

$$p(v-b)=RT\exp\left(-\frac{a}{RTv}\right)$$

试求出临界温度 T_c、临界压强 p_c 和临界体积 v_c.

解: 临界处要求 $\left(\frac{\partial p}{\partial v}\right)_T=0$, $\left(\frac{\partial^2 p}{\partial v^2}\right)_T=0$. 由物态方程 $p=\frac{RT}{v-b}\exp\left(-\frac{a}{RTv}\right)$ 可得

$$\begin{aligned}\left(\frac{\partial p}{\partial v}\right)_T&=\frac{\partial}{\partial v}\left[\frac{RT}{v-b}\exp\left(-\frac{a}{RTv}\right)\right]\\&=-\frac{RT}{(v-b)^2}\exp\left(-\frac{a}{RTv}\right)+\frac{RT}{v-b}\exp\left(-\frac{a}{RTv}\right)\left(\frac{a}{RTv^2}\right)\\&=\exp\left(-\frac{a}{RTv}\right)\left[-\frac{RT}{(v-b)^2}+\frac{a}{(v-b)v^2}\right]\end{aligned}$$

令 $\left(\frac{\partial p}{\partial v}\right)_T=0$, 由于 $\exp(...)\neq 0$, 则

$$-\frac{RT}{(v-b)^2}+\frac{a}{(v-b)v^2}=0$$

$$\frac{RT}{v-b}=\frac{a}{v^2}\quad(*).$$

得

$$a=\frac{RTv^2}{v-b}$$

对 $\left(\frac{\partial p}{\partial v}\right)_T$ 再求导:

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T=\frac{\partial}{\partial v}\left\{\exp\left(-\frac{a}{RTv}\right)\left[-\frac{RT}{(v-b)^2}+\frac{a}{(v-b)v^2}\right]\right\}$$

在临界点, $\left[-\frac{RT}{(v-b)^2}+\frac{a}{(v-b)v^2}\right]=0$, 故只需令中括号内项对 v 的导数为零:

$$\frac{\partial}{\partial v}\left[-\frac{RT}{(v-b)^2}+\frac{a}{(v-b)v^2}\right]=0$$

$$-RT(-2)(v-b)^{-3}+a\left[(-1)(v-b)^{-2}v^{-2}+(v-b)^{-1}(-2)v^{-3}\right]=0$$

$$\frac{2RT}{(v-b)^3}-a\left[\frac{1}{(v-b)^2v^2}+\frac{2}{(v-b)v^3}\right]=0$$

$$\frac{2RT}{(v-b)^3}=a\left[\frac{v+2(v-b)}{(v-b)^2v^3}\right]=a\frac{3v-2b}{(v-b)^2v^3}$$

$$\frac{2RT}{v-b}=\frac{a(3v-2b)}{v^3}$$

将 (*) 式 $\frac{RT}{v-b}=\frac{a}{v^2}$ 代入上式:

$$2\left(\frac{a}{v^2}\right)=\frac{a(3v-2b)}{v^3}$$

假设 $a\neq 0$:

$$\frac{2}{v^2}=\frac{3v-2b}{v^3}$$

$$2v=3v-2b$$

$$v=2b$$

得临界体积 $v_c = 2b$. 代回 (*) 式求 T_c:

$$\frac{RT_c}{v_c - b} = \frac{a}{v_c^2} \implies \frac{RT_c}{2b - b} = \frac{a}{(2b)^2}$$

$$\frac{RT_c}{b} = \frac{a}{4b^2} \implies RT_c = \frac{a}{4b}$$

得临界温度 $T_c = \frac{a}{4bR}$. 代回物态方程求 p_c:

$$\begin{aligned} p_c &= \frac{RT_c}{v_c - b} \exp\left(-\frac{a}{RT_c v_c}\right) \\ &= \frac{a/4b}{2b - b} \exp\left(-\frac{a}{(a/4b)(2b)}\right) \\ &= \frac{a/4b}{b} \exp\left(-\frac{a}{a/2}\right) \\ &= \frac{a}{4b^2} \exp(-2) = \frac{a}{4b^2 e^2} \end{aligned}$$

代回方程得 $p_c = \frac{a}{(2be)^2}$.

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