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Kinetics of reactive diffusion in a binary system with temperature dependence of solubility

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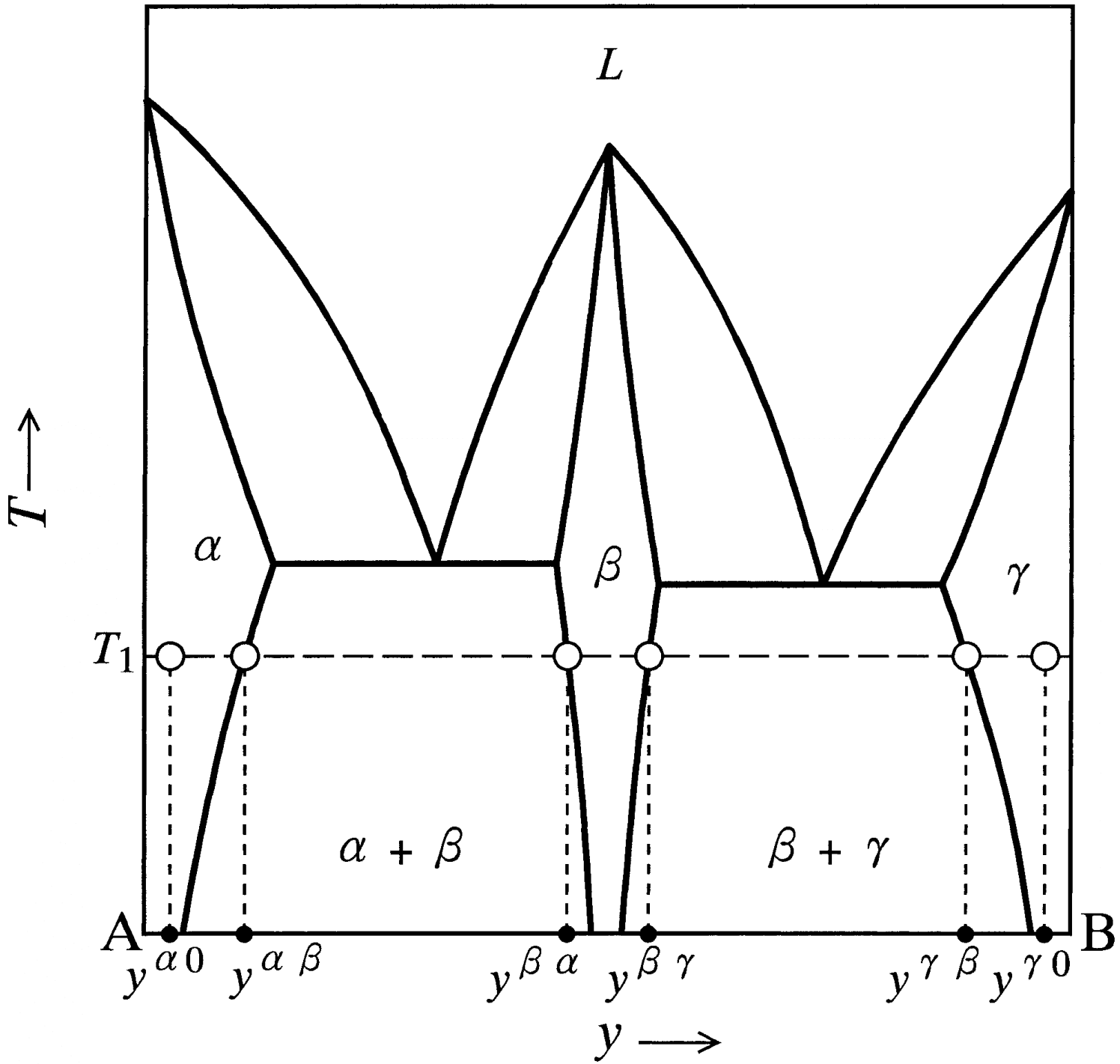
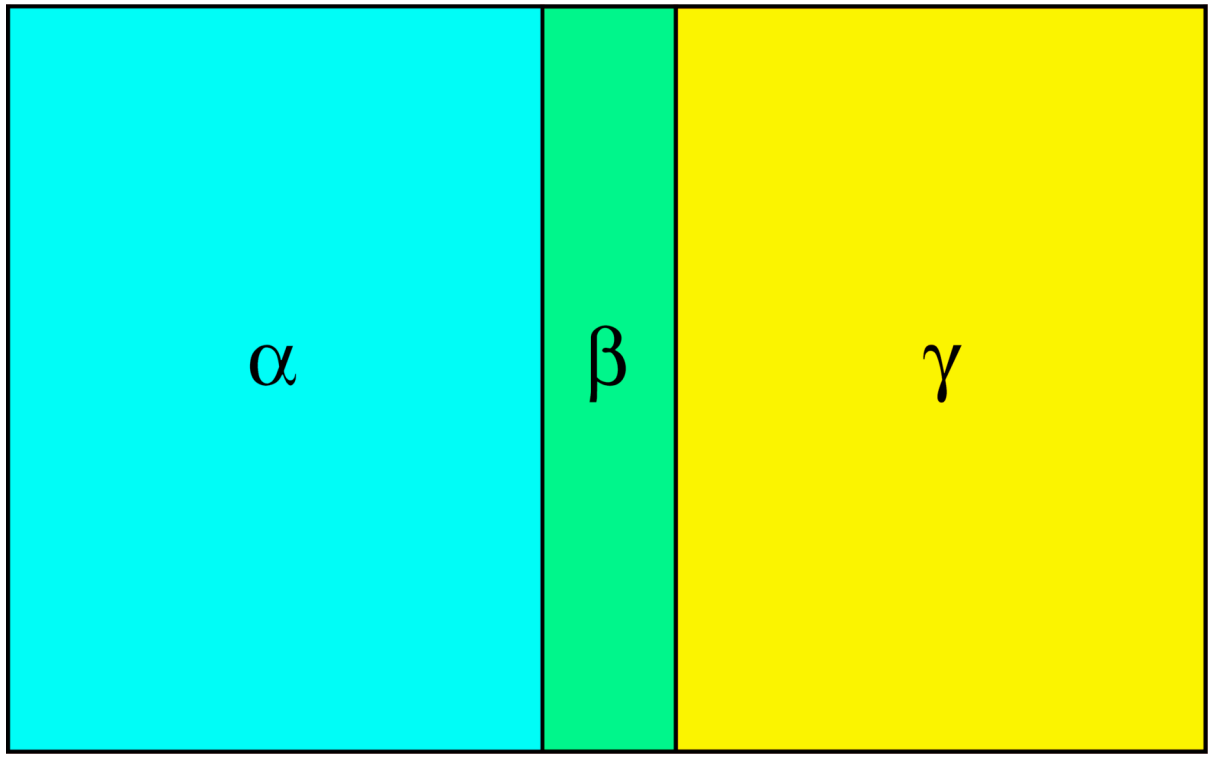

L
T
α
β
γ
T1
α + β
β + γ
A
B
y α 0
y α β
y β α
y β γ
y γ β
y γ 0
y

Reactive Diffusion between α and γ Phases

Annealing at $T = T_1$



Formation of β Phase

Reactive Diffusion

Production of Nb_3Sn superconductor by Bronze-method

Manufacturing of composite alloys

Soldering of Cu-base conductor with Sn-base solder

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Growth of β Phase in α/γ Diffusion Couple

$$l^2 = Kt$$

l: Thickness of β phase [m]

t: Annealing time [s]

K: Parabolic coefficient [m^2/s]

$$K = K_0 \exp(-Q_K/RT)$$

Growth of β Phase in α/γ Diffusion Couple

Interdiffusion coefficients: D^{α}, D^{β}, D^{γ}

Solubility ranges: Δy^{α}, Δy^{β}, Δy^{γ}

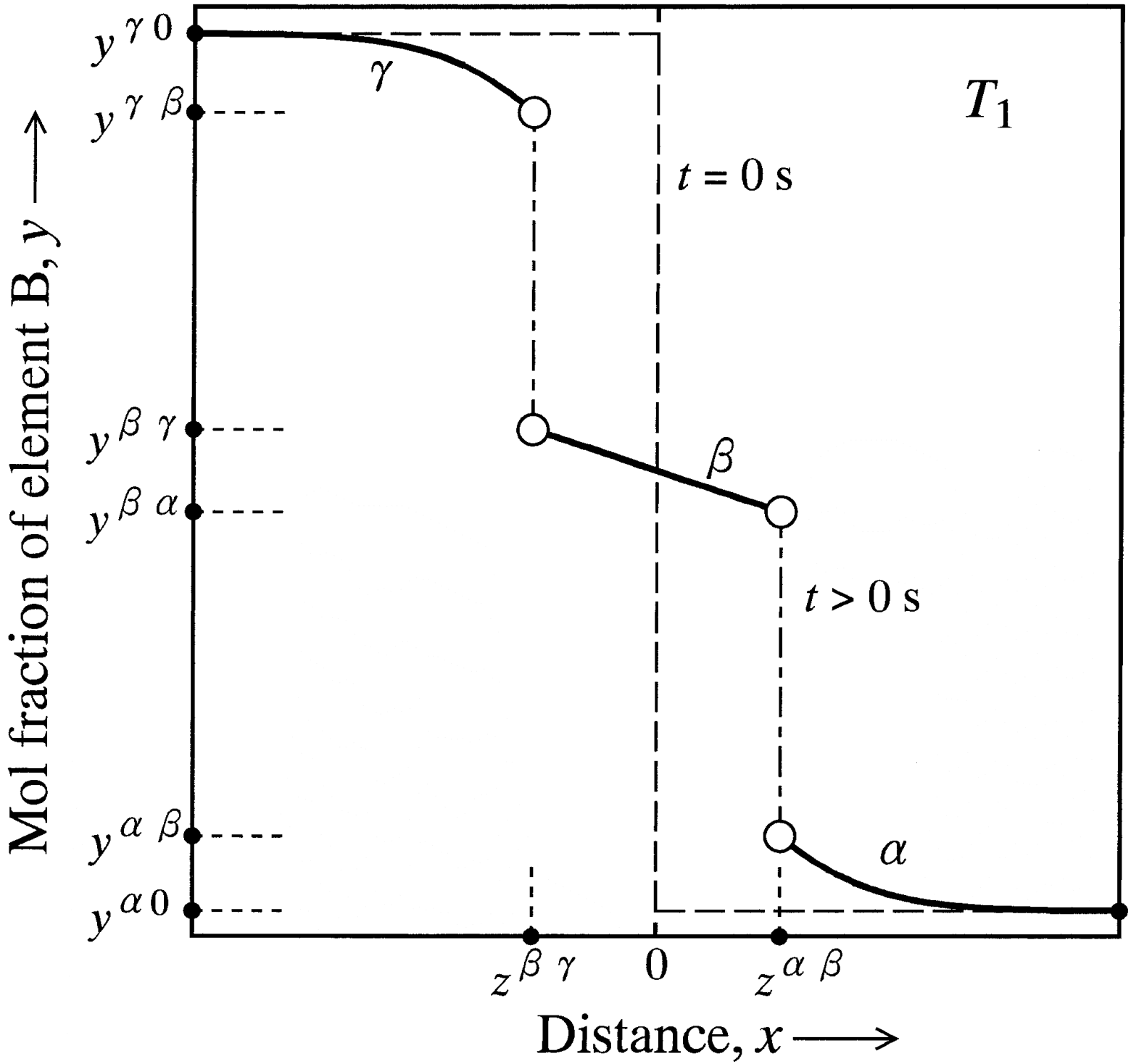
$$K = K_0 \exp(-Q_K/RT)$$

Growth of β Phase in α/γ Diffusion Couple

Effects of D^{α}, D^{β}, D^{γ} on K

Constant values of Δy^{α}, Δy^{β}, Δy^{γ}

$$K = K_0 \exp(-Q_K/RT)$$


$y^{\gamma}{}_{0}$
$y^{\gamma}{}_{\beta}$
$y^{\beta}{}_{\gamma}$
$y^{\beta}{}_{\alpha}$
$y^{\alpha}{}_{\beta}$
$y^{\alpha}{}_{0}$
γ
β
α
T_1
$t = 0$ s
$t > 0$ s
$z^{\beta}{}_{\gamma}$
0
$z^{\alpha}{}_{\beta}$
Mol fraction of element B, y ⟶
Distance, x ⟶

Migration of α/β Interface in A–B System

$$z = K^{\alpha\beta}\sqrt{4D^{\alpha}t} = K^{\beta\alpha}\sqrt{4D^{\beta}t}$$

z: Position of interface [m]

t: Annealing time [s]

D: Interdiffusion coefficient [m^2/s]

$K^{\theta_1\theta_2}$: Dimensionless coefficient

$$K^{\beta\alpha} = K^{\alpha\beta}\sqrt{D^{\alpha}/D^{\beta}}$$

Growth of β Phase in α/γ Diffusion Couple

$$l^2 = Kt$$

l: Thickness of β phase [m]

t: Annealing time [s]

K: Parabolic coefficient [m^2/s]

$$l^2 = \left(z^{\alpha\beta} - z^{\beta\gamma}\right)^2 = 4D^{\beta}\left(K^{\beta\alpha} - K^{\beta\gamma}\right)^2 t$$

$$K = 4D^{\beta}\left(K^{\beta\alpha} - K^{\beta\gamma}\right)^2$$

Growth of β Phase in α/γ Diffusion Couple

Assumption:

$$V_{\mathrm{m}}^{\alpha} = V_{\mathrm{m}}^{\beta} = V_{\mathrm{m}}^{\gamma} \quad \text{at } T = \text{constant}$$

V_{m}^{θ}: Molar volume [$\mathrm{m}^3/\mathrm{mol}$]

$$c^{\theta} = y^{\theta} / V_{\mathrm{m}}^{\theta} \ [\mathrm{mol}/\mathrm{m}^3]$$

$$y^{\beta\alpha} - y^{\alpha\beta} = \frac{y^{\alpha 0} - y^{\alpha\beta}}{K^{\alpha\beta}\sqrt{\pi}\left\{1 - \operatorname{erf}\left(K^{\alpha\beta}\right)\right\}} \exp\left\{-\left(K^{\alpha\beta}\right)^2\right\}$$

$$+ \frac{y^{\beta\gamma} - y^{\beta\alpha}}{K^{\beta\alpha}\sqrt{\pi}\left\{\operatorname{erf}\left(K^{\beta\alpha}\right) - \operatorname{erf}\left(K^{\beta\gamma}\right)\right\}} \exp\left\{-\left(K^{\beta\alpha}\right)^2\right\}$$

$$y^{\gamma\beta} - y^{\beta\gamma} = \frac{y^{\beta\alpha} - y^{\beta\gamma}}{K^{\beta\gamma}\sqrt{\pi}\left\{\operatorname{erf}\left(K^{\beta\alpha}\right) - \operatorname{erf}\left(K^{\beta\gamma}\right)\right\}} \exp\left\{-\left(K^{\beta\gamma}\right)^2\right\}$$

$$+ \frac{y^{\gamma 0} - y^{\gamma\beta}}{K^{\gamma\beta}\sqrt{\pi}\left\{1 + \operatorname{erf}\left(K^{\gamma\beta}\right)\right\}} \exp\left\{-\left(K^{\gamma\beta}\right)^2\right\}$$

$$K^{\beta\alpha} = K^{\alpha\beta}\sqrt{D^{\alpha}/D^{\beta}}, \quad K^{\beta\gamma} = K^{\gamma\beta}\sqrt{D^{\gamma}/D^{\beta}}$$

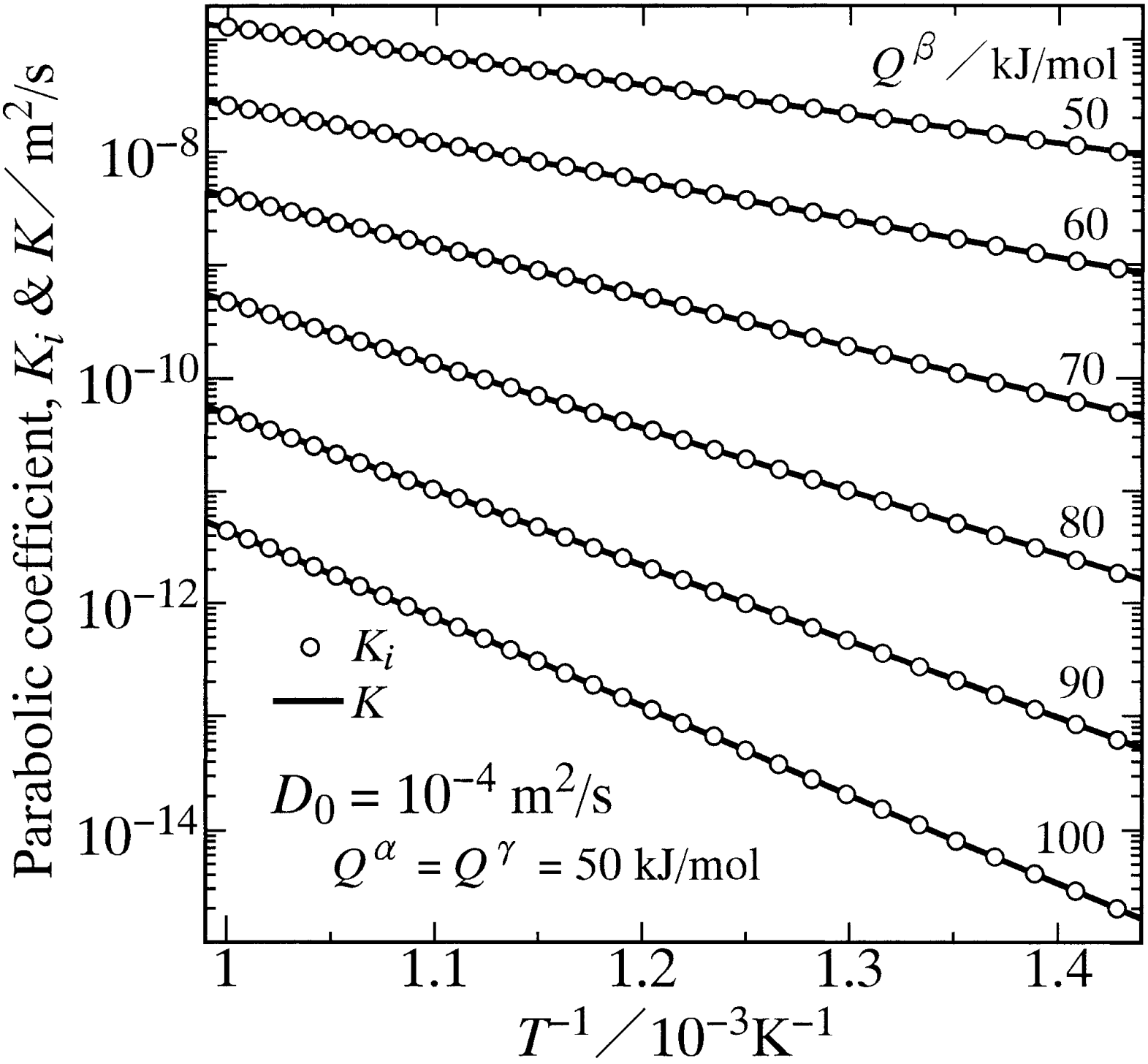
Growth of β Phase in α/γ Diffusion Couple

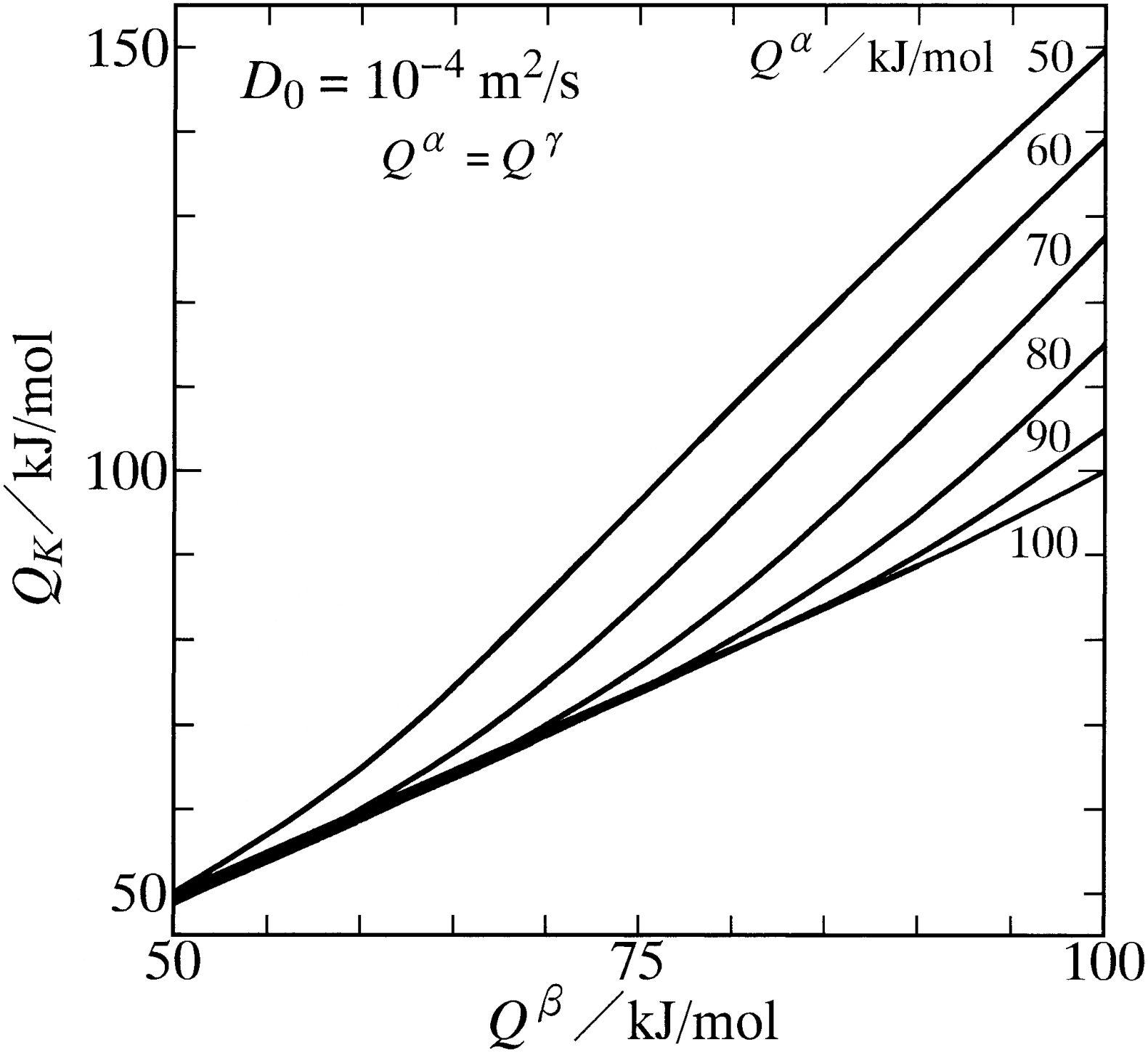
$$y^{\alpha 0} = 0, \quad y^{\alpha\beta} = 0.1$$
$$y^{\beta\alpha} = 0.45, \quad y^{\beta\gamma} = 0.55$$
$$y^{\gamma\beta} = 0.9, \quad y^{\gamma 0} = 1$$

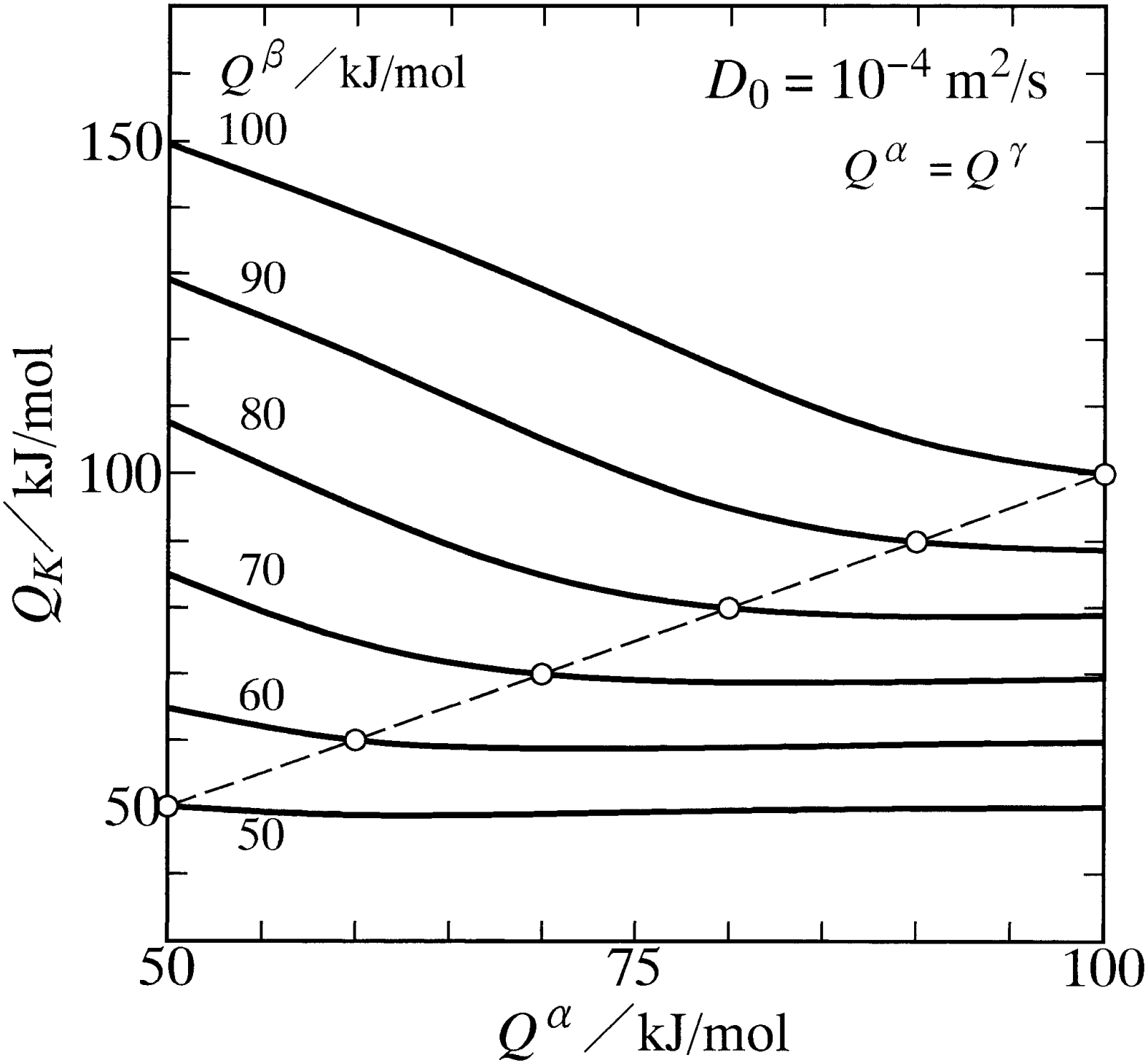
$$D^{\theta} = D_0{}^{\theta}\exp(-Q^{\theta}/RT) \quad (\theta = \alpha, \beta, \gamma)$$
$$D_0{}^{\theta} = 10^{-4}\ [\mathrm{m}^2/\mathrm{s}]$$
$$Q^{\theta} = 50\text{–}100\ [\mathrm{kJ/mol}]$$

↓

$$K = K_0\exp(-Q_K/RT)$$


Parabolic coefficient, K_i & K / m^2/s
10^{-8}
10^{-10}
10^{-12}
10^{-14}
Q^{β} / kJ/mol
50
60
70
80
90
100
K_i
K
$D_0 = 10^{-4}$ m^2/s
$Q^{\alpha} = Q^{\gamma} = 50$ kJ/mol
1
1.1
1.2
1.3
1.4
$T^{-1} / 10^{-3} K^{-1}$


$D_0 = 10^{-4}$ m^2/s
$Q^\alpha = Q^\gamma$
Q^α / kJ/mol
50
60
70
80
90
100
150
100
50
Q_K / kJ/mol
50
75
100
Q^β / kJ/mol


Q^{β} / kJ/mol
$D_0 = 10^{-4}$ m^2/s
$Q^{\alpha} = Q^{\gamma}$
100
90
80
70
60
50
150
100
50
Q_K / kJ/mol
50
75
100
Q^{α} / kJ/mol

Growth of β Phase in α/γ Diffusion Couple

Effects of D^{α}, D^{β}, D^{γ} on K

Constant values of Δy^{α}, Δy^{β}, Δy^{γ}

$$K = K_0 \exp(-Q_K/RT)$$

$$Q_K \cong Q_D^{\beta} \text{ at } Q_D^{\beta} \leq Q_D^{\alpha} \text{ and } Q_D^{\beta} \leq Q_D^{\gamma}$$

$$Q_K > Q_D^{\beta} \text{ at } Q_D^{\beta} > Q_D^{\alpha} \text{ or } Q_D^{\beta} > Q_D^{\gamma}$$

Growth of β Phase in α/γ Diffusion Couple

Effects of Δy^{α}, Δy^{β}, Δy^{γ} on K

Same value of D^{α}, D^{β}, D^{γ}

$$K = K_0 \exp(-Q_K/RT)$$

Growth of β Phase in α/γ Diffusion Couple

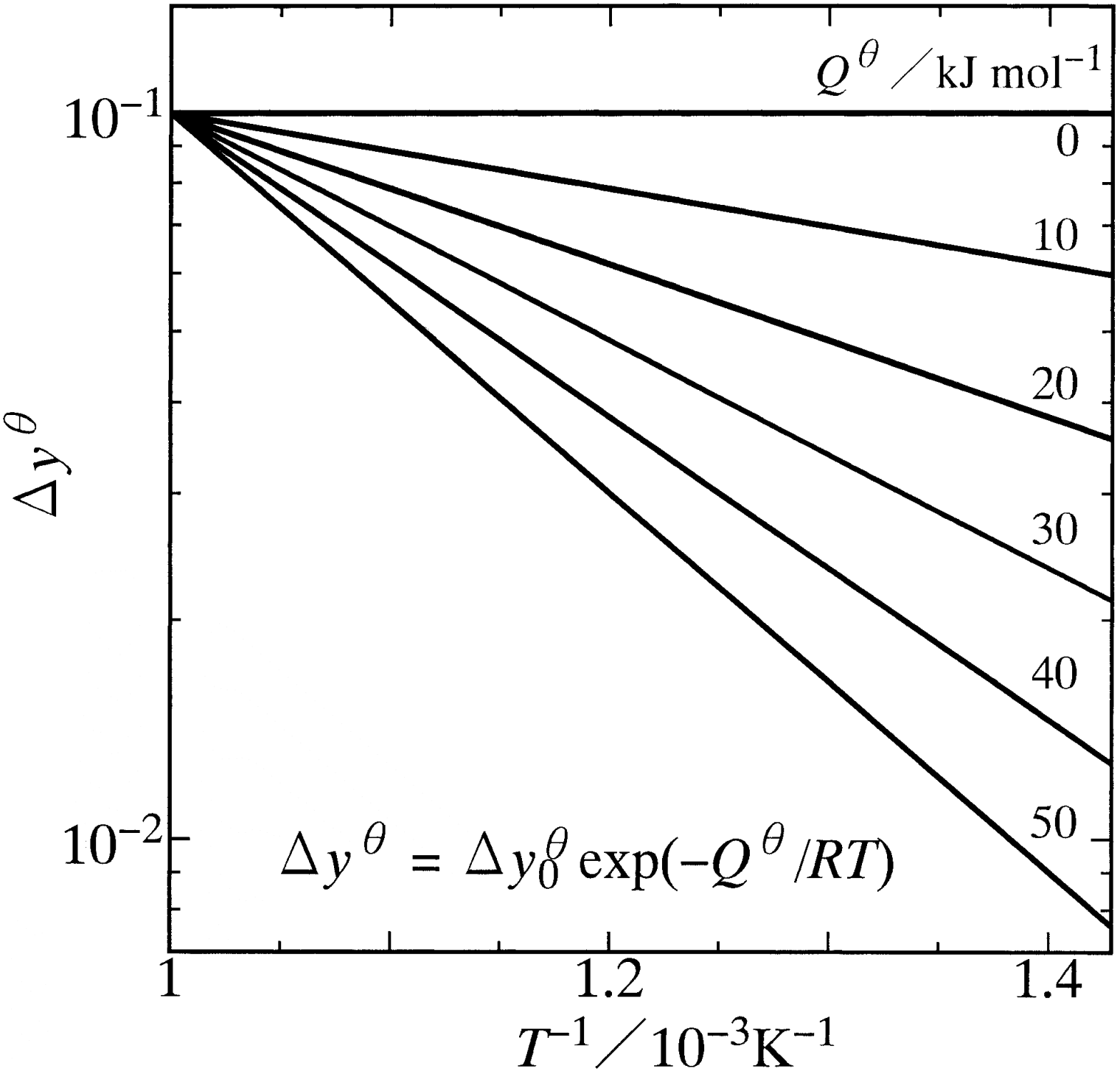
$$D = D_0 \exp(-Q/RT)$$

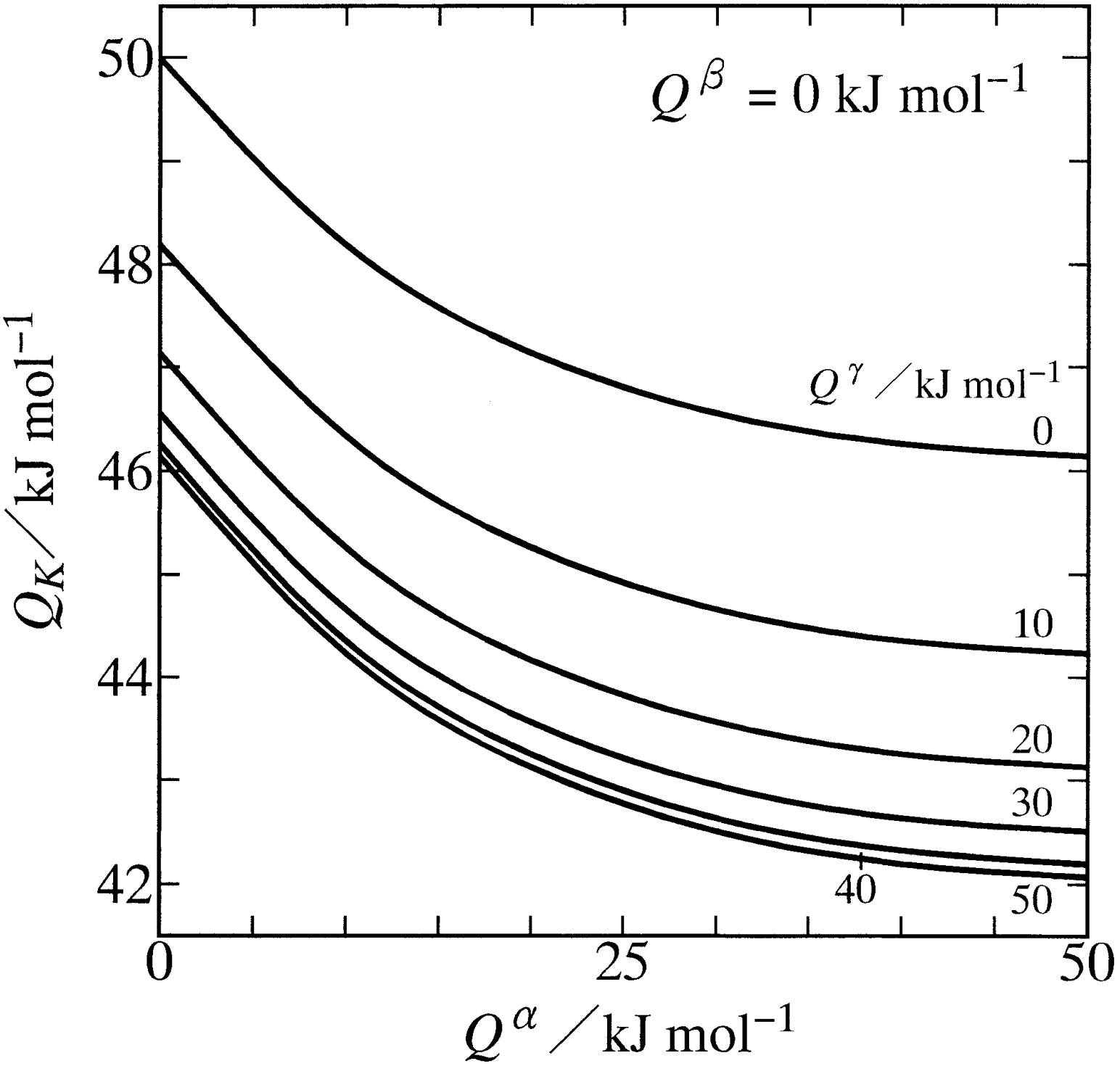
$$D_0 = 10^{-4}\ [\mathrm{m^2/s}]$$

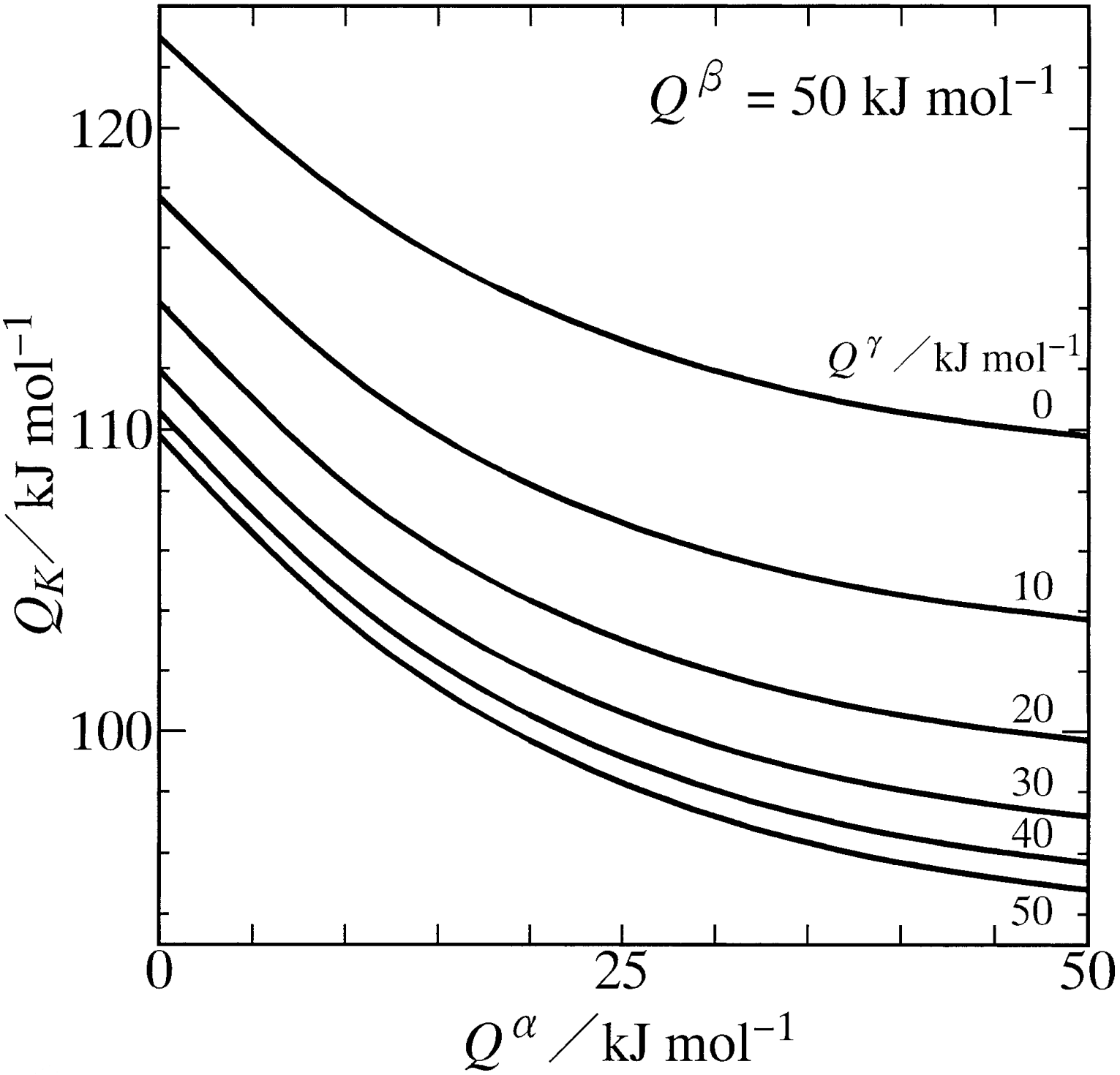
$$Q = 50\ [\mathrm{kJ/mol}]$$

$$y^{\alpha 0} = 0,\ y^{\beta 0} = 0.5,\ y^{\gamma 0} = 1$$

$$\Delta y^{\theta} = \Delta y_0{}^{\theta} \exp(-Q^{\theta}/RT)$$


Q^θ / kJ mol^{-1}
0
10
20
30
40
50
10^{-1}
10^{-2}
Δy^θ
$\Delta y^\theta = \Delta y_0^\theta \exp(-Q^\theta/RT)$
1
1.2
1.4
T^{-1} / 10^{-3}K^{-1}


$Q^{\beta} = 0$ kJ mol^{-1}
Q^{γ} / kJ mol^{-1}
0
10
20
30
40
50
Q_K / kJ mol^{-1}
50
48
46
44
42
0
25
50
Q^{α} / kJ mol^{-1}


Q^{β} = 50 kJ mol^{-1}
Q^{γ} / kJ mol^{-1}
0
10
20
30
40
50
120
110
100
Q_K / kJ mol^{-1}
0
25
50
Q^{α} / kJ mol^{-1}

Growth of β Phase in α/γ Diffusion Couple

Effects of D^{α}, D^{β}, D^{γ}, Δy^{α}, Δy^{β}, Δy^{γ} on K

$$K = K_0 \exp(-Q_K/RT)$$

$$Q_K \cong Q_D^{\beta} + Q^{\beta} \text{ at } Q_D^{\beta} \leq Q_D^{\alpha} \text{ and } Q_D^{\beta} \leq Q_D^{\gamma}$$

$$Q_K > Q_D^{\beta} + Q^{\beta} \text{ at } Q_D^{\beta} > Q_D^{\alpha} \text{ or } Q_D^{\beta} > Q_D^{\gamma}$$